

MASS SPECTROMETRIC APPROACH FOR IDENTIFICATION OF MERCURY COMPOUNDS IN SOLID SAMPLES

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Doctoral Dissertation
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IDENTIFIKACIJA ŽIVOSREBROVIH SPOJIN V
TRDNIH VZORCIH S POMOČJO MASNE
SPEKTROMETRIJE
Doktorska disertacija

Supervisor: Prof. Dr. Milena Horvat

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...in memory of my father...

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Abstract

Mercury is present as a trace pollutant in coal. During coal burning, it is volatilized and emitted through the stack gases into the atmosphere, where it becomes a subject of long-range transport. With respect to Minamata convention, it is necessary to reduce those emissions by the installation of different air pollution control devices (APCD), such as electrostatic precipitators (ESP), selective catalytic reduction (SCR) and wet flue gas desulphurization (WFGD). WFGD system with forced oxidation is very efficient in SO_2 removal and therefore the most commonly used technology in modern coal-fired power plants. It is known that in these systems elemental mercury, $\text{Hg}(0)$, is not retained due to its low solubility in water, whereas the oxidized mercury is almost completely dissolved and accumulates in the WFGD scrubber. The biggest power plant in Slovenia, Šoštanj thermal power plant (Šoštanj TPP), burns lignite which is extracted from the nearby Velenje Coal Mine. In WFGD scrubber of Šoštanj TPP all forms of mercury effectively retain, with an average of 89% (99% for oxidized mercury, 98% for particulate mercury and 76% for $\text{Hg}(0)$). The removal of mercury from the solution by the reactions with the solids produced during desulfurization process represents a significant part of the chemistry. As a result, mercury concentration is elevated in the resulting gypsum.

Flue gas containing volatile elements, fine fly ash particulates not retained by particle control devices, and limestone are the most important sources of trace and major elements (TMEs) in WFGD gypsum. In this study, samples of gypsum slurry from block 4, 5 and 6 of Šoštanj TPP were separated into fine and coarse fractions. Since the separation procedure may significantly change the concentration of Hg in the samples, in the present doctoral dissertation, the differences in particle size distribution and the concentrations of TMEs in gypsum fractions after separation were studied. Multi-elemental analysis of 45 elements in the different size fractions of gypsum, slurry waters and lignite were performed by k_0 -INAA (instrumental neutron activation analyses). The study found that the volatile elements (Hg, Se and halogens) in the flue gas accumulate in the fine fractions of gypsum. Moreover, the concentrations of most TMEs are considerably higher in the fine fractions compared to the coarse fractions. The exceptions are Ca and Sr that primarily originate from the limestone. Variations of TMEs in the fine fractions are dependent on the presence of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ that is the main constituent of the coarse fraction. Consequently, the content of TMEs in the fine fraction is highly dependent on the efficiency of separating the fine fraction from the coarse fraction.

In addition to characterization of the gypsum samples, the main aim of this study was the identification of mercury compounds in gypsum samples. Temperature-programmed desorption/decomposition (TPD) technique with an atomic absorption spectrometric (AAS) detection is frequently used for determination of stability of mercury compounds present in solid substrates and different solid samples. Because the sensitivity of TPD method with AAS detection was not sufficient to detect low concentrations of Hg in coarse solid gypsum fractions, we turned to mass spectrometry. We developed a new method using mass spectrometer for studying mercury decomposition reaction and stability of mercury species in the solid sample at higher temperatures. In particular, the method was calibrated

by using self-prepared mercury compounds. Identification of mercury compounds was performed by using actual gypsum samples. We hypothesise that better sensitivity and the ability to measure other volatile species and their fractions would allow us to identify the Hg species present in the gypsum samples.

Two different mass spectrometers were used, a magnetic sector and quadrupole mass spectrometer (QMS). Samples were heated and ions were produced by electron ionization. Results were recorded as thermograms (TPD spectra), representing the relative intensity/count per second of Hg concentration versus temperature. Two mercury isotopes were simultaneously measured, ^{200}Hg and ^{202}Hg . Important advantage compared to AAS is the ability to observe other volatile compounds (gases), not only Hg. However, we were not able to study the decomposition of mercury compounds in all gypsum samples, and predict the exact desorption/decomposition reactions for Hg-species present. This was possible only in case of pure mercury species such as HgS mixed with SiO_2 or $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and in the samples with an elevated concentration of mercury. However, in actual samples high uncertainty exists since volatile compounds are present in much higher concentrations compared to Hg. Big advantage of QMS is also the possibility for continuous detection of evaporated Hg(0) at very small concentration, even at room temperature. Due to the differences in peak positions, we can distinct between weakly adsorbed mercury (Hg(0) adsorbed to the surface) and mercury adsorbed (bounded) within the sample matrix.

TPD method using mass spectrometer has been applied on gypsum samples from block 4, 5 and 6 from the lignite burning Šoštanj TPP. We examined the effect of particle size on mercury accumulation in WFGD gypsum. The mercury concentration in different gypsum samples varies from 0.22 mg kg^{-1} (coarse particles) to 20.6 mg kg^{-1} (fine particles). For comparison, samples from ten Chinese TPPs were analysed as well. Since the gypsum represents the mixture of finer and coarse fraction, so-called bulk gypsum, the concentration is significantly lower ($0.04 - 1.66 \text{ mg kg}^{-1}$). All the samples from block 6 have a similar, symmetrical, single-peak in the TPD spectra. On the contrary, gypsum fractions from block 5 show at least two peaks that differ from those from block 6. Block 4 has similar TPD spectra to samples from block 6, but the concentrations are much lower and do not exceed 4.05 mg kg^{-1} in a fine fraction. Chinese TPD spectra are similar to samples from block 4 and 6, and normally contain one peak. However, due to the presence of a lower Hg concentration in the sample, few TPD mass spectra have a high background that distorted the peaks. Decreasing the background and better sensitivity were also important issues in the present work.

Different mercury standards were prepared to identify mercury species present in various gypsum samples. The use of ‘wet’ methods for preparing mercury compounds is introduced in addition to the mercury standards prepared using the ‘dry’ method, as commonly found in the TPD approach. The study showed that selected metals, such as Fe enriched in gypsum samples, could significantly influence the shape and the maximum temperature of the Hg TPD curves and that during mercury compound preparation and the TPD process, Hg species undergo transformations that prevent the identification of their original identity. Moreover, the sample might change over time and part of Hg-compounds can be changed into other less stable mercury species or Hg(0). Literature data suggest HgCl_2 and HgS as the most common mercury compounds present in the gypsum. In the present doctoral dissertation, the inability to detect directly low concentrations of HgCl_2 in gypsum by mass spectrometry is discussed in detail. The hydrolysis of HgCl_2 vapours under specific experimental conditions in the mass spectrometer was considered theoretically and proved experimentally. Also HgS has not been proved in gypsum samples of Šoštanj TPP when dry mercury standards were used for comparison. However, H_2S and SO_2 were found as a volatile species released simultaneously with Hg (as found with pure HgS mixed with $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and thus we proposed the presence of HgS in the samples.

Finally, X-ray Absorption Spectroscopy (XAS) method indicates the presence of Hg-S and Hg-O as a species present in the gypsum samples RECY from block 6.

Povzetek

Živo srebro je v premogu prisotno v majhnih količinah. Ker je hlapno, se tekom kurjenja premoga sprošča in gre skupaj z dimnimi plini v okolje. Minamata konvencija, ki je bila sprejeta leta 2013, teži k zmanjšanju le-teh emisij z uvedbo različnih naprav za čiščenje dimnih plinov (elektrostatični filtri, katalizatorji za selektivno redukcijo, mokre razžvepljevalne naprave). Mokri kalcitni postopek za razžvepljevanje dimnih plinov (RDP) z dodatnim vpihom kisika je zelo učinkovit pri odstranjevanju SO_2 in je najbolj razširjena oblika čistilne naprave v sodobnih termoelektrarnah. Zaradi slabe topnosti se elementarno živo srebro v teh sistemih slabo zadrži, medtem ko se oksidirano živo srebro skoraj v celoti akumulira. Največja termoelektrarna v Sloveniji je Termoelektrarna Šoštanj (TEŠ), ki za proizvodnjo energije porablja lignit iz velenjskega premogovnika. Prejšnje študije so pokazale, da se v TEŠ-u vse oblike živega srebra, vključno z elementarnim, zelo učinkovito zadržijo v sistemu RDP (v povprečju 89 %, pri čemer se zadrži 99 % oksidiranega, 98 % vezanega na delce in 76 % elementarnega živega srebra). Pri RDP pomemben del predstavlja odstranjevanje živega srebra v netopni del, tako imenovano sadro, ki se kot stranski produkt odstrani iz sistema. Koncentracije živega srebra so v sadri lahko precej visoke.

Dimni plini, ki vstopajo v razžvepljevalno napravo vsebujejo hlapne komponente in fine delce pepela, ki se ne zadržijo v napravah za odstranjevanje delcev. Skupaj z apnenčevo moko predstavljajo najpomembnejši vir elementov. V tej študiji smo vzeli vzorce raztopin sadre iz treh različnih blokov v termoelektrarni Šoštanj in netopni del ločili na fine in grobe delce. V vzorcih sadre, vodnega preostanka in v lignitu je bila narejena tudi multielementna analiza za 45 različnih elementov. Na podlagi prejšnjih študij vemo, da ločevanje frakcij lahko bistveno vpliva na vsebnost živega srebra v vzorcih, zato smo v tem delu preučevali razliko v porazdelitvi delcev in vpliv na koncentracijo ostalih elementov v frakcijah sadre. Rezultati kažejo, da se hlapni elementi, kot so živo srebro, selen in halogeni elementi, bolje zadržijo na finih delcih sadre. Ne samo hlapni elementi, ampak tudi večina ostalih elementov, ki smo jih preučevali, kažejo zadrževanje v fini fazi v primerjavi z grobo. Izjemi sta kalcij in stroncij, ki prvenstveno v sadro vstopata preko apnenčeve moke in sta tako sestavna elementa v grobi fazi, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. Iz tega sledi, da je vsebnost elementov v fini fazi v največji meri odvisna od deleža grobe faze ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), ki pa zavisi od natančnosti in izbire postopka ločevanja.

Glavni cilj doktorske disertacije je bila identifikacija živosrebrovih spojin v zgoraj omenjenih vzorcih sadre. Za določanje stabilnosti živosrebrovih spojin v različnih trdnih vzorcih se pogosto uporablja metoda temperaturne desorpcije/razpada z atomskim absorpcijskim spektrometrom (AAS). V tem delu smo želeli določiti stabilnost živosrebrovih spojin tudi v grobi frakciji sadre, ki v primerjavi s fino fazo vsebuje nizke koncentracije živega srebra. Ker s pomočjo AAS nismo zaznali živega srebra, smo kot alternativo izbrali masni spektrometer (MS). Občutljivost MS je v primerjavi z AAS veliko boljša, zato smo to s pridom uporabili za določevanje stabilnosti živosrebrovih spojin v vzorcih sadre, ki so vsebovale različne koncentracije, in tudi za študijo določitve reakcij razpada živosrebrovih spojin pri višjih temperaturah. Običajno je metoda temperaturne

desorpcije/razpada kalibrirana s pomočjo predhodno pripravljenih živosrebrovih standardov (mešanica čiste živosrebrove spojine in substrata). Termogrami (desorpcijski spektri), dobljeni s pomočjo standardov, se potem primerjajo s termogramom, ki ga dobimo v realnih vzorcih. Za uporabo masnega spektrometra smo se odločili, ker smo predpostavili, da bomo zaradi boljše občutljivosti lahko opazovali tudi druge hlapne spojine, ki nastanejo pri temperaturnem razpadu živosrebrovih spojin v vzorcu. To bi olajšalo identifikacijo živosrebrovih spojin v vzorcih sadre in drugih trdnih vzorcih.

Pri delu smo uporabili dva različna masna spektrometra, masni spektrometer na magnetni razklon in kvadrupolni masni spektrometer. Rezultati, pridobljeni z linearnim segrevanjem od sobne temperature do temperature največ 700 °C, so prikazani v obliki termogramov (desorpcijskih spektrov), pri čemer graf predstavlja odvisnost intenzitete signala od temperature. Sočasno sta bila merjena dva različna živosrebrova izotopa, m/z 200 in 202. Prednost MS je tudi v tem, da poleg živega srebra lahko opazujemo katero koli hlapno spojino (do m/z 512). Na žalost opazovanje razpadnih komponent živosrebrovih spojin ni bilo možno v vseh vzorcih. To je bilo možno v vzorcih z večjo vsebnostjo živega srebra in pa ko smo uporabili živosrebrove standarde (npr. HgS primešan substratu SiO_2 ali $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). S kvadrupolnim masnim spektrometrom lahko opazujemo izhajanje zelo nizkih koncentracij elementarnega živega srebra ($\text{Hg}(0)$) tudi pri sobni temperaturi. Metoda nam omogoča opazovanje $\text{Hg}(0)$, ki konstantno izhaja iz vzorca, pri povišanih temperaturah pa zaradi različnih temperatur nastalih vrhov v spektru lahko razlikujemo med slabo vezanim (živim srebrom adsorbiranim na površje) in živim srebrom vezanim v matrico (močnejše, kemijsko vezanje).

Metodo temperaturne desorpcije/razpada z masno-spektrometrično detekcijo smo uporabili na vzorcih sadre iz termoelektrarne Šoštanj. Kot že omenjeno, ima velikost delcev bistveno vlogo pri zadrževanju živega srebra v vzorcih sadre. Koncentracije tako variirajo od 0.22 mg kg⁻¹ v grobi fazi, pa vse do 20.6 mg kg⁻¹ v najfinejši fazi. Analizirali smo tudi deset vzorcev kitajskih sader, ki pa niso bile ločene na fino in grobo fazo in so posledično vsebovale bistveno nižje koncentracije (0.04 – 1.66 mg kg⁻¹). Intenziteta in oblika vrhov se je med vzorci sadre, vzeti iz različnih blokov (4, 5 ali 6), nekoliko razlikovala med seboj. Vsi vzorci, vzeti iz bloka 6, kažejo en simetričen vrh, medtem ko termogrami vzorcev iz bloka 5 kažejo vsaj dva vrhova. Blok 4 prikazuje podobne termograme kot blok 6, razlika je le v vsebnosti živega srebra (najvišja vsebnost je bila 4.05 mg kg⁻¹). Kitajske sadre kažejo podobne spektre kot vzorci blokov 4 in 6. Ker le-ti vzorci vsebujejo precej nižje koncentracije v primerjavi z ločenimi fazami iz termoelektrarne Šoštanj, je opazen vpliv ozadja, ki spektre včasih popači.

V naslednji fazi smo za identifikacijo živosrebrovih spojin uporabili živosrebrove standarde. Primerjali smo mokro in suho pripravo standardov. Literaturni podatki navajajo vpliv določenih kovin (npr. železo) na spremembo desorpcijskih spektrov. V ta namen je bilo narejenih nekaj poskusov, ki so potrdili, da se oblika in temperatura, pri kateri se živo srebro sprosti iz vzorca, lahko bistveno razlikujeta v prisotnosti/odsotnosti Fe. Poleg tega lahko prisotnost različnih spojin v vzorcih lahko vpliva na redukcijo živega srebra, ki se tako sčasoma pretvori v drugo (manj stabilno) obliko in/ali reducira v $\text{Hg}(0)$. V splošnem to otežuje identifikacijo živosrebrovih spojin in potrjuje vpliv matrice na sproščanje živega srebra iz vzorca. HgCl_2 in HgS sta spojini, ki se v literaturi največkrat pojavljata kot spojini, ki naj bi bili prisotni v sadri. V tej doktorski disertaciji smo želeli identificirati hlapno spojino HgCl_2 s pomočjo MS, saj bi nam identifikacija bistveno olajšala določanje spojin v vzorcih. Na podlagi eksperimentalnih poskusov in teoretičnih izračunov smo pokazali, da hidroliza in eksperimentalni pogoji onemogočajo dokaz HgCl_2 v realnih vzorcih. Prav tako nismo uspeli dokazati prisotnosti HgS v sadri na podlagi živosrebrovih standardov, saj so se termogrami sproščenega živega srebra v realnih vzorcih (npr. iz bloka 6) in HgS standarda razlikovali za 100 °C. Kljub razliki v temperaturah se je pokazalo ujemanje

spektrov s sproščanjem H_2S in SO_2 , ki smo jih kot razpadna produkta dobili pri segrevanju čiste spojine HgS . Prisotnost HgS je bila z gotovostjo potrjena šele z metodo rentgenske absorpcijske spektroskopije (XAS). Poleg Hg-S pa je bil v vzorcu RECY dokazan tudi majhen delež Hg-O .

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Abbreviations

AAS	... Atomic absorption spectrometry; a technique for measuring the concentrations of elements (Hg) in the samples
APCI	... Atmospheric pressure chemical ionisation is an ionisation method used in mass spectrometry which utilises gas-phase ion-molecule reactions at atmospheric pressure (10^5 Pa)
BA	... Bottom ash
CF	... Coarse fraction of industrial gypsum samples
CV AAS	... Cold vapour atomic absorption spectrometry; a technique for Hg detection, based on absorption of UV light by Hg atoms
CV AFS	... Cold vapour atomic fluorescence spectrometry; a technique for Hg detection, based on fluorescence of Hg atoms
DMA-80	... Direct mercury analyser; an automatic Hg analyser based on cold vapour atomic absorption spectrometry technique
Eh	... Reduction potential of chemical substance
EPA	... Environmental protection agency
Eq.	... Equation
ESP	... Electrostatic precipitator; a filtration device for removing fine particles
FA	... Fly ash
FF	... Fine fraction of industrial gypsum samples
FGD	... Flue gas desulphurization; either a process or a unit for removing sulphur from the flue gas
GC	... Gas chromatography; a technique for Hg separation most commonly used for environmental and biological samples based on differences of vapour pressures
GEM	... Gaseous elemental mercury
GOM	... Gaseous oxidized mercury
Hg(0)	... Elemental mercury; the uncharged mercury atom
Hg(I)	... Mercurous ion (Hg_2^{2+}); a monovalent form of mercury
Hg(II)	... Mercuric ion (Hg^{2+}); a divalent form of mercury
Hg(P)	... Particulate mercury
HPGe	... Detector High-purity germanium detector; a device used as a total absorption detector for gamma rays
INAA	... Instrumental neutron activation analyses; a technique for determining the concentrations of elements, based on neutron activation conducted directly on irradiated samples.
LOD	... Limits of detection
LOQ	... Limit of quantification
LSFO	... Limestone with forced oxidation process
MS	... Mass spectrometry; a technique for identifying the amount and type of chemicals in a sample by measuring the mass-to-charge ratio and the abundance of ions

m/z	... Mass to charge ratio
ORP	... Oxidation/reduction potential
PBM	... Particulate bound mercury
pH	... A measure of the acidity or basicity of an aqueous solution with a scale from 0 to 14
PM	... Particulate matter
RM	... Reactive mercury
SCR	... Selective catalytic reduction; a process or unit used for removing nitrogen oxides from flue gases with catalysts
SEM	... Scanning electron microscopy
SEP	... Sequential extraction procedure; a type of wet sample decomposition methods, at which different reagents are used to separate different fractions of the sample
TEM	... Transmission electron microscopy
TGA	... Thermal gravimetric analysis
THg	... Total mercury; the sum of all mercury species present
TPD	... Temperature programmed desorption
TPP	... Thermal power plant
TRIGA	... A class of small nuclear pool-type reactors
UNEP	... United nations environment programme
US EPA	... United states environmental protection agency
UV	... Ultraviolet light; an electromagnetic radiation with a wavelength from 400 nm to 10 nm
WFGD	... Wet flue gas desulphurization; either a process or a unit for removing sulphur from the flue gas, where gypsum slurry is used
XANES	... X-ray Absorption Near-Edge Structure
XAS	... X-ray absorption spectroscopy
XRD	... X-ray Powder Diffraction

Chapter 1

Introduction

1.1 Mercury: General Properties

Elemental mercury, Hg(0), is the only metal that is liquid at ordinary temperature and has a shiny silvery-white colour. Molecular orbital theory, the electronic configuration, relativistic effects, and lanthanide contraction, can explain why Hg(0) is liquid at room temperature. Hg boils below 650 °C, and it is quite inert chemically, having a higher ionisation potential than any other electropositive element with the sole exception of hydrogen. The only type of interaction between mercury atoms is through weak Van der Waals interactions (Keeler & Wothers, 2013; Norrby, 1991). Mercury has a high vapour pressure. The reason is weak inter-atomic bonding, which is due to the nucleus having a tight hold on its valence electrons. It is relatively insoluble in water and therefore will readily avoid liquids (high surface tension) (Drasch, Horvat, & Stoeppler, 2004). Au, Ag, Cu, Zn and alkali metals dissolve readily in mercury and consequently form a liquid, pastry or solid amalgams (Cain, Disch, Twaroski, Reindl, & Case, 2007; Jasinski, 1995). The interaction between Hg(0) and these metals is not very strong (explained by molecular bonding theory), suggesting Van der Waals interaction (Cremer, Kraka, & Filatov, 2008; Kraka & Cremer, 2008). Mercury is a rather poor conductor of heat but a fair conductor of electricity (Jasinski, 1995). Hg(0) could be used in various applications such as barometers, thermometers, electrical switches, fluorescent bulbs, ballast for submarines. (Enghag, 2004).

Due to the electronic configuration ($[\text{Xe}]4f^{14}5d^{10}6s^2$) it is qualified as a non-transition metal and has valence states of +1 and +2. In any higher oxidation state of this group, the d-orbitals would have to be involved in bonding, thus changing the classification of this element in the Periodic Table from a post-transition element to a transition metal. Hg was also found in +4 oxidation state as HgF_4 (Kaupp & von Schnering, 1993; Riedel & Kaupp, 2009; X. Wang, Andrews, Riedel, & Kaupp, 2007). Mercury consists of seven stable isotopes and more than 40 synthetic and radioactive isotopes (mass number 171-210) (Buleev, Grudinkina, & Pevzner, 1968; Lide, 2009). Because of its large size and stable electronic configuration, Hg(II) is easily polarised by interacting atoms. The strong covalent character of the C–Hg bond is the reason for the high stability of the organic-mercury molecule (MeHg). Similarly, the Hg(II) ion forms very strong covalent bonds with soft Lewis bases (ligands) such as halides and sulphur compounds, but relatively weak bonds with hard Lewis bases such as fluorine. These exceptional properties make Hg the “softest” of all metals, a so-called “Type B metal” (Skylberg, 2012). Typical for Hg(II) complexes is a low coordination number (2, 3, or 4). The linear two-coordination of Hg(II) is caused by relativistic effects (Tossell & Vaughan, 1981) and is a very unusual structure for metal.

Table 1.1: Summary of chemical and physical properties of mercury are provided (Bank, 2012; Enghag, 2004; King, 2006; Kozin & Hansen, 2013).

Element	Mercury (Hg)
Atomic number	80
Atomic mass	200.59
Density	13.55 g cm ⁻³
Atomic volume	14.26 · 10 ⁻⁶ m ³ mol ⁻¹ at 25 °C
Melting point	-38.829 °C
Boiling point	357.3 °C
Main isotopes	202, 200, 199, 201, 198, 204, 196
Oxidation states	0, +1, +2, (+4)
Vapour pressure	14 mg m ⁻³ at 20°C; 31 mg m ⁻³ at 30°C
Ionization energies (kJ mol ⁻¹ , *eV)	1 st ...1007 (*10.4375); 2 nd ...1809; 3 rd ...3300
Henry's law coefficient	729 at 20°C
Solubility in water	~49 µg L ⁻¹ at 20 °C

Mercury is a naturally occurring element which can never be destroyed, but it can recycle through the environment. In the Earth's crust elemental mercury (Hg(0)) is found only in a limited number of regions. More than 90 minerals of Hg are known (International Mineralogical Association, 2014). The most abundant Hg compound is HgS, which occurs in three polymorphs: cinnabar, metacinnabar, and extremely rare hypercinnabar (Hazen et al., 2012; IMA, 2014). Several less abundant minerals exist including calomel (Hg₂Cl₂), Livingstonite (HgSb₄S₈) and Tiemannite (HgSe), corderoite (Hg₃S₂Cl₂) (Bank, 2012; Hazen et al., 2012; Jasinski, 1995; Kim, Brown, & Rytuba, 2000).

Since a wide range of mercury species exists within our environment, the chemical form of mercury controls its bioavailability, transport, persistence and impact on the human body, with methylmercury being the most toxic species (Leopold, Foulkes, & Worsfold, 2010). Mercury that is deposited in soils, lakes, wetlands, or oceans and may later be released to the atmosphere (Drasch et al., 2004; UNEP, 2013a). The biogeochemical transformations and high mobility of mercury species make it a global pollutant that can be transported thousands of kilometres through the atmosphere. Therefore, an understanding of mercury species transformations and accurate monitoring of mercury and its species in the environment are essential for reliable risk assessment (Bank, 2012).

1.2 Chemical Species of Mercury

A series of complex chemical transformations allows the three-oxidation states of Hg (Hg(0) – metallic; Hg(II) – mercuric; Hg(I) – mercurous) to cycle in the environment and biological systems (Bank, 2012; Gonzalez-Raymat et al., 2017; Kozin & Hansen, 2013).

- Elemental mercury, Hg(0): In the natural environment, it can exist in the gaseous or liquid state where Hg(0) is the dominant form in the atmosphere. It could also be trapped in the crystalline lattice in the solid samples such as coal.
- Monovalent mercury, Hg(I) or Hg₂²⁺: It is mostly found in dimeric salts (e.g., Hg₂Cl₂, calomel, Hg₂SO₄) that are sparingly soluble in water and much less toxic than Hg(II) (e.g., HgCl₂) (Horvat, 2005).

- Divalent mercury, Hg(II) or Hg²⁺: Inorganic and organic divalent mercury compounds exist in gaseous, dissolved, and solid states. Toxicity, solubility, vapour pressure, and reactivity of Hg(II) species differ significantly. Hg(II) species prevails in waters rather than in the atmosphere.
 - o Organic mercury compounds (R-Hg-X or R-Hg-R) form one or two covalent bonds with carbon. Organic compounds are limited to alkylmercurials (monomethylmercury (CH₃Hg⁺, MeHg), monoethylmercury (CH₃CH₂Hg⁺, EtHg) and dimethylmercury (CH₃-Hg-CH₃, DMHg)), alkoxymercury and the arylmercurials compounds (Horvat, 2005).

1.2.1 Mercury species in air

Most of Hg in the atmosphere is elemental mercury, Hg(0) (also gaseous elemental mercury, GEM), which is relatively stable with the net average atmospheric residence time around one year (Ariya et al., 2015; Fitzgerald, Lamborg, Heinrich, & Karl, 2007; W. H. Schroeder & Munthe, 1998). This is sufficient time for atmospheric mercury being distributed over the entire planet before returning to the land, lakes, sea, and ice. In addition to Hg(0), two other atmospheric Hg fractions have been operationally defined based on physicochemical properties – the reactive gaseous Hg/gaseous oxidized Hg (GOM), and particulate-bound Hg (PBM) (Mason, 2005). The residence time for oxidised species is much shorter (hours to days, weeks) (Bullock & Brehme, 2002; Gustin, Lindberg, & Weisberg, 2008). GOM, usually Hg(II) species (e.g., HgBr₂, HgCl₂, HgBrOH), are highly surface-reactive and substantially more water soluble than Hg(0). These species can deposit faster than PBM. PBM consists mainly of Hg(II) species adsorbed to surfaces or incorporated into particles during high-level combustion and other processes. PBM resides predominantly in the fine particulate fraction (<2.5 µm) (Bullock & Brehme, 2002).

1.2.2 Mercury species in water

In the natural aquatic environment, mercury may be present in various physical and chemical forms. The nature and reactions of these species determine the solubility, mobility, and toxicity of Hg in the aquatic ecosystem, as well as the potential for methylation (Ullrich, Tanton, & Abdrashitova, 2001). Mercury in surface waters exists in two oxidation states, Hg(0), as a dissolved gas (DGHg), and Hg(II). The ionic mercury exists both in dissolved, attached to particulate matter and in most surface water a small fraction of the total Hg is methylmercury (MeHg), which can also be dissolved or particulate-associated. Hg(II) and MeHg in the dissolved phase make complexes with inorganic or organic ligands where only a small fraction of each exists as a free metal ion (Mason, 2005). Hg(I) is only stable as a dimer (Hg₂²⁺) in aqueous solution and readily disproportionate into Hg(0) and Hg(II), which is the most stable form in water (Ullrich et al., 2001). The mercury species occurring in the water environment divide into volatile (Hg(0), (CH₃)₂Hg), easily water-soluble Hg(II) (e.g., HgCl₂, Hg(NO₃)₂) and hardly soluble organic complexes (CH₃Hg⁺, CH₃HgS) (Boszke, Głosińska, & Siepak, 2002; Ullrich et al., 2001). In the Mediterranean sea high Hg(0) concentrations are also found in bottom waters, probably due to intense tectonic activity (Kotnik et al., 2007). The chemical form of Hg in an aquatic system is firmly influenced by redox and pH conditions, and the concentrations of inorganic and organic complexing agents (Horvat et al., 2003).

1.2.3 Mercury species in soil and sediment

Soils and sediments are important because they are primary sinks of anthropogenic Hg that can accumulate in the food chain (bioaccumulation) resulting in perturbation of ecosystem and unfavourable health effects (Issaro, Abi-Ghanem, & Bermond, 2009). Mercury cycling in soils is critical to our understanding of Hg accumulation and loss in the environment mostly attributed to: (a) the typically larger areal extent of the watershed as compared with the water body, (b) the role of a vegetative canopy in expanding the active surface area, and (c) soil's high capacity to store Hg (Bank, 2012). The biogeochemistry of mercury in soils and sediments dominates by inorganic and organic Hg(II) complexes (Skylberg, 2012). Under environmentally relevant concentrations, Hg and MeHg have a higher binding strength with organic matter than with soil minerals (Amirbahman, Reid, Haines, Kahl, & Arnold, 2002; Drexel, Haitzer, Ryan, Aiken, & Nagy, 2002; Haitzer, Aiken, & Ryan, 2002; Hintelmann, Welbourn, & Evans, 1995; Karlsson & Skylberg, 2003). Physical-chemical soil parameters such as the pH, cation exchange capacity, particle size, organic matter content, types of clay minerals present, redox condition, sulphide concentration, and other geochemical factors of the system play important roles in the variation of the oxidation state and the type of interaction with Hg soil components and, therefore, their mobility and availability (Bransford, Hilbert, & Roulet, 1998; Chakraborty, Raghunadh Babu, Vudamala, Ramteke, & Chennuri, 2014; Gilmour, Henry, & Mitchell, 1992).

Hg speciation in solution influences its adsorption, which is in turn controlled by pH and the presence of dissolved ligands. The most critical ligands for mercury binding are OH⁻, Cl⁻, and S-containing functional groups in addition to nitrogen- and oxygen-containing functional group (Skylberg, 2012). With higher solubility of mercury species, such as HgCl₂ and Hg(OH)₂, the affinity of Hg to these ligands leads to increased mobility. In the presence of organic matter, the primary forms of ionic mercury, Hg(II) and MeHg⁺, are strongly complexed by humic acids, fulvic acids and other organic molecules present in natural ecosystems (Xia et al., 1998). Mercury has a high affinity to sulphur which explains the strong binding of Hg to soft organic matter and also the high stability of HgS. These chemically stable species are considerably less mobile than alkyl and inorganic soluble Hg species (MeHg⁺, EtHg⁺, HgCl₂) and less toxic to organisms. Organo-mercury complexes can be adsorbed onto the surface of clays and iron, aluminium and manganese oxides (Reis et al., 2012).

1.3 Mercury Cycling in the Environment

Mercury releases into the environment from natural sources and processes, and as a result of human activities. Once it has entered the environment, mercury cycles between air, land, and water until it is eventually removed from the system through burial in deep ocean sediments or lake sediments and entrapment in stable mineral compounds. MeHg, the most toxic and bioaccumulative form of mercury, which presents the highest health risk to humans and wildlife, is mainly formed in aquatic environments through natural microbial processes.

1.3.1 Sources of mercury (anthropogenic, natural)

Mercury is a naturally occurring element which is found throughout the world. Natural sources of mercury create background environmental levels that have been present since long before humans appeared (UNEP, 2013a). The global mercury emissions consist of three group of Hg sources into the environment (Gustin et al., 2016; E. G. Pacyna et al., 2010; Pirrone & Mason, 2009; UNEP, 2013a); **natural processes** including natural

emissions such as volcanos, geothermal events, soils with naturally enriched mercury, forest fires, and ocean emissions. The next group representing **anthropogenic sources of mercury in the air** where it is divided into three subgroups: releases from the mobilisation of mercury impurities (coal combustion, cement production, mining and other metallurgic activities such as production of iron and steel, ferromanganese, zinc, gold, and other non-ferrous metals), releases from intentional extraction and use of mercury: mercury mining, small-scale gold and silver mining (amalgamation process), chlor-alkali production, use of fluorescent lamps, various instruments and dental amalgam fillings, manufacturing of products containing mercury (e.g., thermometers, manometers and other instruments, electrical and electronic switches), and the third subgroup represents Hg releases originating from both impurities and intentional uses of mercury from waste incineration (municipal, medical and hazardous wastes), landfills, cremation and cemeteries (release to soil). The last group of the main Hg sources represents **re-emission of previously deposited mercury back into the atmosphere**. Quantifying the total fraction of current emissions that is natural or anthropogenic is not an easy task. The ice-core and the lake-sediment cores that are indicating historical deposition trends are the best evidence for large-scale changes in global mercury cycling (Bank, 2012).

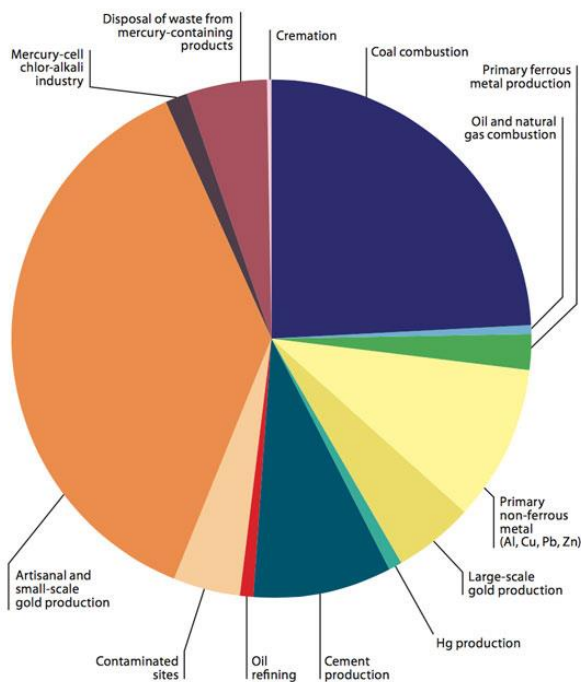


Figure 1.1: Relative contributions to estimated emissions to air from anthropogenic sources in 2010. Uncertainty arises from each of the factors used to estimate the emissions: the correctness of the activity data, the validity of the emission factors applied, and the validity of assumptions regarding the effectiveness and use of emission-control technologies (UNEP, 2013a).

1.3.2 The global cycle of mercury

The atmosphere is the major transport pathway for distribution of Hg globally. Once released it actively cycles in the environment for hundreds-to-thousands of years before being buried in sediment (Selin, 2009). Atmospheric deposition represents the main pathway of Hg input aquatic and terrestrial ecosystem outside areas of direct

contamination (Gustin et al., 2016). Natural sources of Hg in the atmosphere are mainly in the form of GEM (>95%) although PBM also occurs, while emissions of anthropogenic sources contribute all forms of Hg to the atmosphere (Ebinghaus et al., 1999). In remote locations, where particulate mercury concentrations are usually low, total gas mercury makes up the predominant part (>99%) of the total concentration in air. Contribution of natural sources varies in time and space depending on a number of factors including the presence of volcanic belts or geothermal activities, geological formations with high mercury concentration like cinnabar deposits, exchange processes between water and atmosphere, re-emission of previously deposited mercury from top soils, plants and forest fires (Holmes, Jacob, Mason, & Jaffe, 2009; Pirrone, Costa, Pacyna, & Ferrara, 2001; Pirrone & Mason, 2009). The ratio between the relative contributions of anthropogenic and natural source categories may vary from a region and time of the year (Elisabeth G. Pacyna, Pacyna, Steenhuisen, & Wilson, 2006; J. M. Pacyna, Pacyna, Steenhuisen, & Wilson, 2003; Pirrone, Keeler, & Nriagu, 1996).

GEM vapour in the atmosphere is subject to long-range transport. Due to low solubility, only a small fraction of GEM vapour can wash out of the atmosphere during precipitation events. Hg(0) in the gas can be oxidized by different oxidizers (H_2O_2 , NO_3 , O_3 , $\text{OH}^\cdot$, Cl , Br , Br_2 , Cl_2 , BrCl , $\text{BrO}^\cdot$) (Ariya, Khalizov, & Gidas, 2002; Khalizov, Viswanathan, Larregaray, & Ariya, 2003; Lin & Pehkonen, 1999; W. H. Schroeder & Munthe, 1998; Simpson et al., 2007; Subir, Ariya, & Dastoor, 2012). GOM is much more soluble and therefore a subject to washout from the atmosphere with precipitation. This is called wet deposition and is a major source of mercury input to the environment. A small amount of the Hg may adhere to fine particles in the atmosphere and may fall out without rainfall as dry deposition (Fitzgerald, 1995). Understanding the cycling of Hg between the ocean and atmosphere is complicated, mainly because of the enhanced oxidation of Hg(0), and the formation of GOM in the marine boundary layer (Mason & Sheu, 2002).

Aquatic ecosystems are an essential component of the biogeochemical cycle of mercury (Hg), as inorganic Hg can be converted to toxic MeHg (Hsu-Kim, Kucharzyk, Zhang, & Deshusses, 2013) in these environments and reemissions of Hg(0) rival anthropogenic Hg releases on a global scale (Kocman et al., 2017). However, there is a lack of inventories of direct releases of Hg to aquatic systems compared to global atmospheric emission inventories (Kocman et al., 2017). Mercury is released to freshwater systems from a variety of sources and subjected to complex transport pathways (Driscoll, Mason, Chan, Jacob, & Pirrone, 2013). It can enter rivers and lakes directly via atmospheric deposition. Rivers and lakes further receive Hg as a result of releases from industrial sources within their drainage area, as well as indirectly from terrestrial environments via surface runoff, and through soil leaching and erosion. Depending on the soil characteristics, part of this Hg reservoir can be leached to groundwater. Riverine loads are enhanced by river bank erosion as well as remobilization of previously deposited Hg with bed sediments during high water flow, especially in contaminated systems (Carroll, Warwick, James, & Miller, 2004; Horvat et al., 1999). On the contrary, transport of Hg from rivers to coastal environments is diminished by its sedimentation behind various impoundments during transport to the ocean. Artisanal and small-scale gold mining (ASGM) represents the single largest source, followed by disposal of Hg-containing products and domestic waste water, metal production, and releases from industrial installations such as chlor-alkali plants and oil refineries. In addition to these direct anthropogenic inputs, diffuse inputs from land management activities and remobilization of Hg previously accumulated in terrestrial ecosystems are likely comparable in magnitude (Kocman et al., 2017).

MeHg is only present at low pg m^{-3} concentration levels in ambient air; it is not an important species for the overall atmospheric cycling of Hg, but mainly due to its toxicity and capacity for bioaccumulation (W. H. Schroeder & Munthe, 1998). MeHg enters the

aquatic food chain (mainly by aquatic bacteria) (Gochfeld, 2003). Species high in the trophic web tend to have higher concentrations of mercury (e.g. $>10 \mu\text{g/g}$ in whales and $>1 \mu\text{g/g}$ in sharks, pike, swordfish, and tuna) (UNEP, 2002). MeHg levels in freshwater fish vary with the level of deposition of mercury from the air, though other factors such as inputs from the watershed and the number of trophic levels within the lake's food web are also important. Methylation predominantly occurred in lake sediments, wetlands and floodplain soils, where sulphate reducing bacteria are believed to be primarily responsible. MeHg is de-methylated in sediments and also taken away in the outlet river from each lake. However, owing to the bioaccumulation of methylmercury, methylation is more prevalent in the aquatic environment than demethylation (Horvat, 2005). In contrast to the methylation process, which is principally most active under sub- and anoxic conditions, demethylation reactions are usually promoted by toxic conditions (Skylberg, 2010). In aqueous systems contaminated with oxidized Hg, Hg(II) may reduce, and a portion of the Hg(0) may volatilize back into the atmosphere.

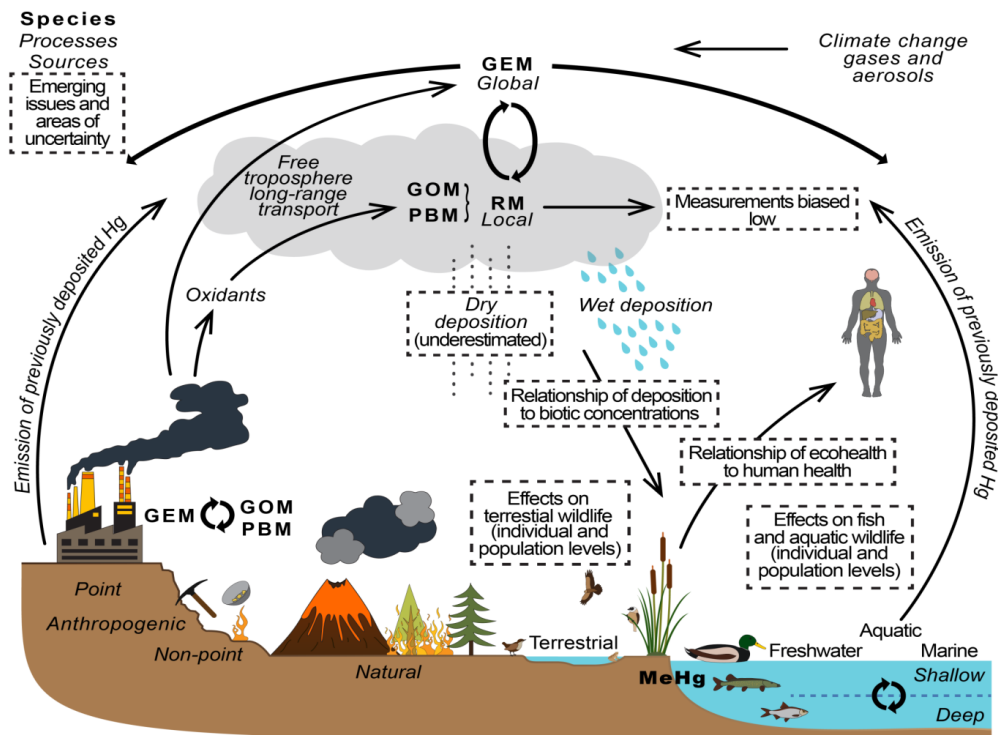


Figure 1.2: Mercury cycling in the environment (Adopted from Gustin et al., 2016).

1.3.3 Modelling approach

The accuracy of model projections depends on the scientific knowledge of processes and mechanisms that affect transport, transformations, and fate of Hg (Gustin et al., 2016). The number of models that have been developed to simulate atmospheric Hg has multiplied in the last decade (Amos et al., 2014; Horowitz, Jacob, Amos, Streets, & Sunderland, 2014; E. G. Pacyna et al., 2010; J. M. Pacyna et al., 2016; Pirrone et al., 2010; Streets et al., 2017). However, uncertainties in the measurements exist, especially with reactive mercury ($\text{RM} = \text{GOM} + \text{PBM}$). Different GOM compounds were derived from different primary sources, sources producing different oxidants, and variation across the season. There are no calibration standards for GOM, a breakthrough can result in the collection on the PBM filter, and collection efficiencies for GOM and PBM are uncertain (Gustin & Jaffe, 2010;

Huang, Miller, Weiss-Penzias, & Gustin, 2013; Talbot et al., 2011). Better measurement techniques should be developed for oxidized and particulate mercury to improve the global mercury emission models. Chemistry of emissions from different sources needs to be considered and will influence the scale and range of Hg transport (local, regional, and global). Without accurate measurements, modellers cannot develop and test robust models, and, by extension, policy makers cannot develop effective regulations.

Current models: i) Are evaluated based on limited data for atmospheric GOM and dry deposition; ii) Do not consider the presence of different compounds of Hg in the atmosphere; and iii) Apply reaction rate constants that are either highly uncertain or unknown. However, the present models are based on emission inventories with high uncertainties or simply do not exist. Not all emissions are considered or are not considered adequately (e.g. biomass burning), such as nonpoint sources and unquantified coal-burning processes (Gustin et al., 2016). ASGM is not well understood, and ASGM activities may be greater than coal-fired power plants (Kocman et al., 2017; UNEP, 2013a). Anthropogenic emissions due to the historical deposition and therefore Hg releases into the air, water and to the land are important to obtain a complete and consistent quantification of total Hg releases (Streets et al., 2011, 2017). High uncertainty also exists in models using abiotic compartment (e.g. air, sediment and water) to predict biomagnification and bioaccumulation of MeHg, especially for high trophic level biota (Gustin et al., 2016).

The new Hg mass balance reported in 2017 by Streets et al. indicates that between the period 1850-2010 73% of mercury (1060-2800 Gg) was released as a consequence of human activities. 470 Gg was emitted directly into the atmosphere where 74% of the air emissions represent Hg(0). About 1070 Gg were released to land and water bodies. However, annual Hg releases have been relatively stable since 1880 (8 ± 2 Gg). During the wartime, the distribution of those releases among source types, world regions, and environmental media have changed dramatically. Hg production accounts for 27%, followed by silver production (24%) and chemicals manufacturing (12%). The largest release is caused by North America (30%), Europe (27%), and Asia (16%). About 40% (390 Gg) of the Hg discarded to land and water must be sequestered at contaminated sites to maintain the consistency with recent declines in atmospheric Hg concentrations. Biogeochemical modelling shows a 3.2 fold increase in the atmospheric burden compared to 1850 that is consistent with observational constraints. 18 source types and 17 world regions were involved in the model calculations. Emissions to land and water for coal combustion and metals smelting has been estimated for the first time.

1.3.4 Mercury exposure and health effects

The majority of human exposure and health risk associated with mercury comes from the consumption of marine and freshwater foods (Cusack, Smit, Kile, & Harding, 2017; Mahaffey, Clickner, & Bodurow, 2004). However, there are three primary categories of mercury and its compounds to be aware: elemental mercury (Hg(0)), inorganic mercury compounds, Hg(I, II) (e.g. HgCl₂, Hg₂Cl₂, HgO, etc.) and organic mercury compounds (e.g. MeHg). Human absorption of liquid Hg(0) is minimal, and acute toxicity does not occur even when the liquid mercury used in thermometers is accidentally ingested. Exposure to Hg(0) by the general population and in occupational settings is primarily through inhaling mercury vapours/fumes (e.g., dental amalgams) where 80% of inhaled mercury retains. Intestinal absorption varies widely among the various forms of mercury, with Hg(0) being the least absorbed form (<0.01%) and only about 10% of Hg(I, II) is absorbed. Hg(I, II) may absorb through the skin in toxicologically relevant quantity. Hg(0) is lipid soluble and easily penetrates biological membranes, including the blood-brain barrier. After exposure to Hg(0) or Hg(I, II), the principal route of excretion is via the urine. Determination of

concentrations in urine and blood has extensively been used in the biological monitoring of exposure to inorganic forms of mercury. However, hair mercury levels do not reflect exposure to Hg(0) or Hg(I, II) reliably, but rather to organic mercury (MeHg). MeHg easily crosses the blood-placenta barrier, accumulating more in the fetus than in the mother (Choi, 1991; M. Sakamoto et al., 2004; M. Sakamoto, Kubota, Matsumoto, Nakano, & Akagi, 2002; Stern & Smith, 2003; WHO, 1990).

Association between prenatal exposure to Hg and neurodevelopment of the child, taking into account genetic polymorphism of apolipoprotein E (*ApoE*) and other relevant confounders (Snoj Tratnik et al., 2017). An evidence exists that gene polymorphisms for enzymes involved in glutathione and metallothionein metabolism can affect retention of MeHg in the human body (Barcelos et al., 2013; Engström et al., 2008; Gundacker, Gencik, & Hengstschläger, 2010) and that polymorphisms of ABC transporter genes can modify the transport of MeHg across the placenta and the accumulation of MeHg during early development (Llop et al., 2014). Apart from the genes involved in the absorption-distribution-metabolism-elimination pathways, there are certain other genotypes that can increase susceptibility to toxic effects.

1.3.5 Minamata convention: Control of Hg emissions

Under the UNEP, countries negotiated the Minamata Convention on Mercury, a legally binding agreement intended “to protect human health and the environment from anthropogenic emissions and releases of mercury and mercury compounds” (UNEP, 2013b). The convention was adopted on 10 October 2013. It has 128 signatories until February 2018. With the Minamata Convention, global society has a regulatory mechanism to decrease environmental Hg loadings. Now the convention is ratified by 87 nations. Major highlights of the Minamata Convention include a ban on new mercury mines, the phase-out of existing ones, the phase-out and phase down of mercury use in a number of products and processes, control measures on emissions to air and on releases to land and water, and the regulation of the informal sector of artisanal and small-scale gold mining. The Convention also addresses interim storage of mercury and its disposal once it becomes waste, sites contaminated by mercury as well as health issues (UNEP, 2013b).

This dissertation is mainly devoted to emissions coming from the thermal power plant (TPP), in particular, emission of Hg that is accumulated in the solid wastes. These wastes are thought to be stable, however, after disposing and during the re-processing of the raw material Hg may release. Therefore it is important to mention **Article 8 of the Minamata convention** which addresses *emissions* of mercury and mercury compounds in the atmosphere (relevant sources, new sources, substantial modification of relevant source, and existing source) and calls for a reduction in the emissions of Hg and its compounds in particular from point sources addressed in Annex D (coal-fired power plants, smelting and roasting processes, waste incineration and cement clinker production facilities). It also calls for comparable measurements and harmonised methodologies for Hg and its compounds in emission sources (Article 19) and information on environmental cycling including long-range transport and deposition, transformation and fate of Hg and its compounds in different environmental compartments, taking appropriate account of the distinction between anthropogenic and natural emissions (UNEP, 2013b). However, for the successful implementation of Minamata convention different critical and emerging areas such as uncertainty in atmospheric and biological Hg measurements and impact on the understanding of the Hg biogeochemical cycle are fundamental (Gustin et al., 2016).

1.4 Coal Combustion

Coal burning, and to a lesser extent the use of other fossil fuels, is one of the most significant anthropogenic sources of mercury emissions to the atmosphere. Coal does not contain high concentrations of mercury, but due to the large volume of coal burned and the fact that a significant portion of the mercury present in coal emits to the atmosphere yields substantial overall emissions from this sector. However, the mercury content in coal varies widely, introducing a high degree of uncertainty in estimating mercury emissions from coal burning (UNEP, 2013a).

In the present doctoral dissertation, we studied the accumulation of mercury and other trace and major elements (TMEs) in various by-products of coal combustion. We were mainly interested in Hg and mercury compounds present in the gypsum. Previous work showed high accumulation of mercury and other TMEs in the gypsum (Sedlar et al., 2015; Stergaršek et al., 2008). A lot of work has been done already, however, identification of mercury compounds in the gypsum is not an easy task due to the different sample composition that affects the determination of Hg-species. Therefore, it is important to understand the whole combustion process and the presence of other elements in the flue gas that may interact with Hg after combustion and enter in the wet flue gas desulphurization system (WFGD) where gypsum is formed. For that purpose, a brief description of the combustion process and cleaning of the flue gas is described in this chapter. Theoretical background is divided into four main parts; first part is more related to coal properties and partitioning TMEs according to their volatility; mercury behaviour during coal combustion is described in the second part, in the third part flue gas removal technologies are presented and the last part is mainly devoted to Hg reaction present in WFGD scrubber. Short description of the Slovenian biggest thermal power plant, Šoštanj (Šoštanj TPP) is provided at the end of this chapter.

1.4.1 Distribution of trace and major elements during coal combustion

The occurrence and concentration of trace elements in coal have been studied by several researchers (Clarke & Sloss, 1992; Finkelman, 1994, 1995; Swaine, 1990; Yudovich & Ketris, 2005a). Coal combustion is a major source of toxic metals in the environment and is probably the primary source of As, Cd, Cr, Cu, Hg, Mn, Mo, Pb, Sb, Tl and Zn (Nalbandian, 2012; Nriagu, 1986). Not only trace elements, but also SO₂, NO_x, CO₂, N₂O, particulate matter, and other gases are released into the environment by coal combustion. In general, the elements present in coal occur over a wide concentration range that varies according to the geochemical evolution of the coal deposits (Querol, Fernández-Turiel, & López-Soler, 1995; Querol, Juan, Lopez-Soler, Fernandez-Turiel, & Ruiz, 1996). They can have organic or mineral affinities (elements associated with sulphides (Pires, Fiedler, & Teixeira, 1997), aluminosilicates, carbonates and other minerals in coal) (Finkelman, 1994, 1995; Huggins & Huffman, 1996; Querol et al., 1996; Swaine, 1990).

Different processes are taking place during combustion including **char formation**, **agglomeration** of melted minerals, and **vaporisation of volatile elements**. Most trace elements are removed by solids while some of them are released as aerosols or as vaporised elements in the gas phase. Coarse residues (combustor bottom or flying ash/slag; 1-100 µm), heterogeneous condensation onto the existing fine fly ash due to the evaporation (coal-mineral, mineral-mineral association), and sub-micron ash caused by homogeneous condensation of trace elements itself (0.01-1 µm). Fragmentation is very important in the distribution of trace elements in ash particles where a higher rate of fragmentation results in the formation of fine ash particles. Residence time in the high-temperature zone is significant because short residence time caused that some larger mineral particles might be

only partly melted or mineral particles with higher melting point may never achieve this temperature. Three modes of fine ash exist (fine, intermediate and coarse) and usually, emissions are categorised into three groups PM_{10} , $PM_{2.5}$ and PM_1 (PM, particulate matter less than $1\ \mu m$) (Vejahati, Xu, & Gupta, 2010).

The volatility of elements is the result of several factors: their affinity to other elements, their physical properties, chemical reactions and transformations (Meij, 1994a) and it also depends on the combustion setup (e.g., combustion temperature, time of exposure, ash generation) (Galbreath & Zygarlicke, 2000; Meij, 1994a; Querol et al., 1995, 1996; M. Xu et al., 2004). Volatile elements are preferentially concentrated on the smallest particles due to condensation (Meij, 1994a) whereas the non-volatile ones deposit on the largest ash particles (Helble & Sarofim, 1993). As a result, the finest fly ash particles contain larger amounts of trace and major elements (TMEs) due to their higher surface to volume ratio (Clarke & Sloss, 1992; Klein et al., 1975; Meij, 1992, 1994a; Querol et al., 1995; M. Xu et al., 2004), and are a significant source of TMEs in gypsum (Y. K. Liu, Zhuo, Zhu, & Chen, 2013).

Based on their concentrations, chemical elements in coal are classified into three groups (M. Xu et al., 2004):

1. Major elements in concentrations above $1000\ \mu g\ g^{-1}$ (C, H, O, N, S);
2. Elements in concentrations between 100 and $1000\ \mu g\ g^{-1}$ (Si, Al, Ca, Mg, K, Na, Fe, Mn, Ti, F, Cl, Br, I);
3. Trace elements with a concentration less than $100\ \mu g\ g^{-1}$.

Trace elements are further divided into three groups according to their **volatility** as shown in Figure 1.3 (Clarke & Sloss, 1992; Klein et al., 1975; Meij, 1994a; M. Xu et al., 2004):

- The first group are the least volatile elements that are concentrated in coarse residues (bottom ash) or are equally distributed between the bottom and fly ash. These elements are not volatilized in combustion zone but form a melt of a rather uniform composition that becomes both fly ash and slag. The slag is removed directly and quickly from the combustion zone while the fly ash remains in contact with the cooling flue gas. Elements in the class one stay condensed, and therefore show minimal partitioning between slag, inlet and outlet fly ash. According to Klein et al. twenty elements are in the first group, as follows Al, Ba, Ca, Ce, Co, Eu, Fe, Hf, K, La, Mg, Mn, Rb, Sc, Si, Sm, Sr, Ta, Th and Ti.
- Elements in the second group are those that volatilize during coal combustion and condense afterwards onto the particles in the flue gas stream. These are more concentrated in fly ash than in bottom ash (As, Cd, Cu, Ga, Pb, Sb, Se and Zn (Klein et al., 1975)). Since the slag is removed from combustion zone, they have no opportunity to condense on the slag, so they condense or become adsorbed on the fly ash when the flue gas cools. These elements are depleted from the slag due to the volatility effect, and due to the particle size effect and are preferentially concentrated onto outlet fly ash compared to the inlet.
- The most volatile elements are in the third group, and they have little or no tendency to condense from the vapour phase and therefore emit from the stack. In class three Hg, Cl and Br are entirely in the vapour phase. According to the Meij, class three divides into three subclasses; elements almost entirely in the vaporisation phase (Cl, F, I), those with vaporisation of about 50% (B, Br, Hg), and one with low vaporisation (As and Se) (Meij, 1994a).
- Elements such as Cr, Cs, Na, Ni, U and V appeared as intermediate between class one and two.

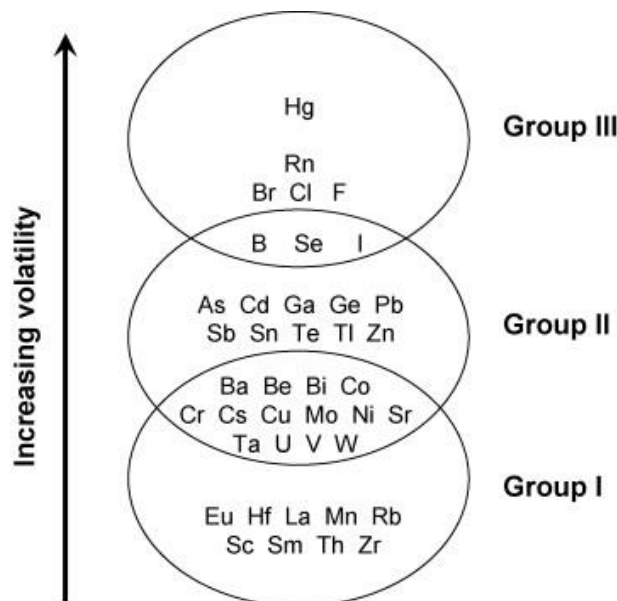


Figure 1.3: Classification of trace elements during combustion (Clarke & Sloss, 1992).

In principle, the elements released from feed coal are partitioned between the fly ash, bottom ash, gypsum and flue gas discharged into the environment (Helble & Sarofirm, 1993). However, the final distribution of (trace) elements in waste products depends on modes of occurrence, mineral content and their distribution in coal, coal particle size (Helble & Sarofirm, 1993), and factors related to the physical process (emission control devices (J. M. Pacyna, 1982), temperature profile (Yan, Gauthier, & Flamant, 2001), turbulence (Helble & Sarofirm, 1993; Juda-Rezler & Kowalczyk, 2013; Nriagu, 1986; Vejehati et al., 2010). Improvement of the technologies used to control emissions can lead to changes in their distribution (López-Antón, Díaz-Somoano, Ochoa-González, & Martínez-Tarazona, 2011). There are numerous literature sources describing TMEs partitioning during the coal combustion process (Álvarez-Ayuso, Querol, & Tomás, 2006; Bhangare, Ajmal, Sahu, Pandit, & Puranik, 2011; Córdoba, Ochoa-Gonzalez, et al., 2012; Esenlik et al., 2006; J. Li et al., 2012; Z. Li et al., 2005; López-Antón et al., 2011; Otero-Rey et al., 2003; Spears & Martinez-Tarrazona, 2004; Swanson, Engle, Ruppert, Affolter, & Jones, 2013; Q. Tang, Liu, Yan, & Sun, 2012; Q. Tang, Liu, Zhou, & Sun, 2013; C. Zheng et al., 2017). However, partitioning differs among different sorts of coal and power plants, so each thermal power plant has to be studied separately.

According to the Council Decision 2003/33/EC on waste disposal, the leaching behaviour of all the solid combustion by-products arising from the coal combustion-desulphurization plant (slag, fly ash and WFGD gypsum) allowed to classify them as wastes admissible at landfills for non-hazardous wastes (Council Decision 2003/33/EC, 2002).

1.4.2 Mercury in coal

Coal is classified into four ranks: anthracite, bituminous, sub-bituminous, and lignite. The coal rank is defined by properties such as carbon content, heat value, volatility, and ash. In general, mercury is among the least abundant elements in coal. Different data for Hg concentrations in coal are reported to be in the average range between 0.01–1.5 mg kg⁻¹ and are somewhat lower in lignite than in bituminous and sub-bituminous coals (Dajnak, Clark, Lockwood, & Reed, 2003; Davidson & Clarke, 1996; S. H. Lee, Rhim, Cho, & Baek,

2006; Mukherjee, Zevenhoven, Bhattacharya, Sajwan, & Kikuchi, 2008; Park, Seo, Lee, & Lee, 2008; Schoefield, 2004; C. L. Senior, Sarofim, Zeng, Helble, & Mamani-Paco, 2000; Swaine, 1990; Vejehati et al., 2010; S. X. Wang et al., 2010; Yudovich & Ketris, 2005a). Lower heating values of lignite than bituminous and sub-bituminous coals may increase its consumption to generate an equivalent amount of energy and may thus release more mercury into the atmosphere (Tewalt, Bragg, & Finkelman, 2001). However, the concentrations of mercury within the same mining field may vary by one order of magnitude or more (Mukherjee et al., 2008). Use of indigenous mercury-enriched coal in the coking by-product industry, metallurgical plants, coal-fired electric-generating stations, and other types of industries, as well as use in households, has led to widespread pollution of the environment by mercury, arsenic, lead, and other toxic substances. Understanding the nature of Hg in coals used for power generation, and the partitioning of Hg in the combustion system is a fundamental part of an emission-control strategy. (Yudovich & Ketris, 2005b).

Depending on the origin of Hg, three forms may be present in coals; as clays (Hg_{clay}), organic matter (Hg_{org}) and sulphides (Hg_{sulf}). Within coals, mercury exists in several components, including biogenic (from coal-forming plants, Hg_{bio}), sorption (Hg_{sorp}), terrigenous or volcanogenic clastics (Hg_{clast}), and diagenetic or epigenetic (infiltration) mineral fractions (Hg_{inf}). In coal cleaning, as much as 50-60% of the Hg remains in the cleaned coal product, and the rest disseminates in tails, sludges, and middlings. Hg_{org} and Hg_{sulf} are the dominant forms of Hg in coal, and their occurrence controls Hg distribution in coal. In low-sulphur coals, which are poor in Hg, only two Hg sites dominate, Hg_{org} and Hg_{sulf} (commonly pyritic mercury, Hg_{pyr}). In more sulphur-rich coals, the Hg content is usually higher, and the Hg_{pyr} contribution also increases (Yudovich & Ketris, 2005b).

A promising technique for the determination of Hg(0) and other mercury species in the coal (Gao, Wang, Huang, & Guo, 2017; Mashyanov, Pogarev, Panova, Panichev, & Ryzhov, 2017; P. Xu et al., 2017), coal gangue and slime (Gao et al., 2017; Niu, Guo, Gao, Cao, & Wei, 2017) is the so-called thermal decomposition (thermal scanning or temperature programmed desorption). More details about this methodology are described in Chapter 1.5. Here some literature data regarding mercury speciation/fractionation in coal samples are provided. In the study of Mashyanov et al. (2017) the portions of mercury releasing at the low-, mid-, and high-temperature intervals (between room temperature and 900 °C) depend on mercury chemical forms and their binding to matrix constituents: organics, sulphides, silicates, and other mineral impurities. Mercury in pyrite exists as a Hg(0) (adsorbed) that releases at lower temperatures and species releasing with the destruction of FeS_2 lattice releasing at higher temperatures. (Mashyanov et al., 2017). By using the extraction procedure, pyrite-bound Hg is the dominant form of Hg followed by organic-bound Hg (Gao et al., 2017). These results are similar as reported by Yudovich and Ketris (2005). The results provided by using coal gangue or slime showed an increased amount of Hg regarding raw coal but similar releasing profile as in clean or raw coal which indicates the presence of similar Hg-species in all those samples (Gao et al., 2017).

1.4.2.1 Mercury transformations during coal combustion processes

During the coal combustion process at high-temperature mercury is released mainly as Hg(0) because the thermodynamic equilibrium favours this state at coal combustion temperatures. As combustion gases cool, Hg(0)(g) interacts with oxygen and other combustion by-products, including halogens and fly ash, leading to oxidation of mercury to form GOM (Hg(I, II)).

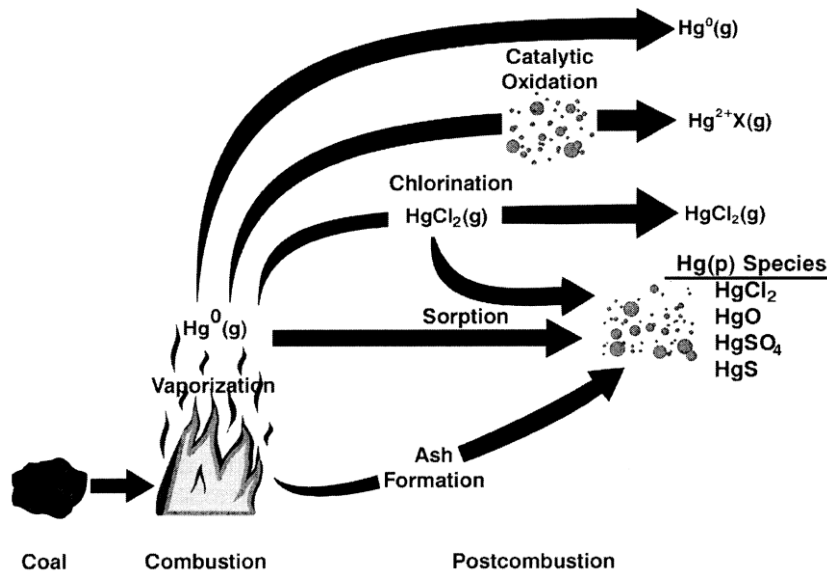


Figure 1.4: Potential mercury transformations during coal combustion and in the resulting flue gas (C. L. Senior et al., 2000).

Total mercury concentration in coal combustion flue gas is in range $5\text{--}10\ \mu\text{g m}^{-3}$, where many parameters can potentially affect the formation of various mercury species (GEM, GOM and PBM) throughout a combustion system, including boiler design, coal type, coal composition, combustion environment (gas composition and reducing/oxidizing conditions), heat transfer/cooling rate, residence time at lower temperatures during convective cooling, air pollution control devices (APCDs), and operating practices (e.g., boiler load, excess air, soot blowing, etc.) (Galbreath, Zygarlicke, Tibbetts, Schulz, & Dunham, 2005; Pavlish et al., 2003). Identification of the fundamental mechanisms involved in mercury–flue gas interactions that transform $\text{Hg}(0)$ to $\text{Hg}(\text{II})$ and PBM improved mercury emission control efficiencies and transport deposition models for coal-fired boilers (Galbreath & Zygarlicke, 2000; Hall, Schager, & Lindqvist, 1991).

1.4.2.2 Homogenous and heterogeneous oxidation

$\text{Hg}(0)$ may be oxidized to $\text{Hg}(\text{II})$ via homogenous (gas phase) or heterogeneous (gas-solid) reactions. The homogeneous reaction mechanism usually underestimates the oxidation rate because heterogeneous reactions on fly ash play a more important role under low temperatures (between $100\text{--}300\ ^\circ\text{C}$) (L. Zhang et al., 2016). Specific surface area, loss on ignition (LOI) and average particle size are correlated positively with both the $\text{Hg}(0)$ oxidation and the $\text{Hg}(\text{II})$ adsorption (Bhardwaj, Chen, & Vidic, 2009).

During coal combustion, mercury starts to volatilize at temperatures below $200\ ^\circ\text{C}$, regardless of its form. $\text{Hg}(0)$ is partially oxidized at low temperatures (35–95%). Since the temperature of coal combustion process is above $1000\ ^\circ\text{C}$, all mercury is released. The most stable form of Hg in the coal is attributed to silicate-bound Hg which released around $1100\ ^\circ\text{C}$ with respect to the thermal decomposition method (Gao et al., 2017). When Hg released, the only stable form above $600\text{--}700\ ^\circ\text{C}$ is $\text{Hg}(0)$ (Galbreath, Toman, Zygarlicke, & Pavlish, 2000). Mercury oxidation in boiler systems is kinetically controlled; chlorine, bromine and SO_2 promote **homogeneous oxidation** reactions and are considered to be very important in mercury transformations (Pavlish et al., 2003). Other potential homogenous reaction pathways involve HCl , O_2 , NO_2 , NO , CO but are less important because of kinetic limitations (Galbreath & Zygarlicke, 2000; Hall, 1995; Hall et al., 1991; Niksa, Helble, &

Fujiwara, 2001; C. L. Senior et al., 2000). After mercury chlorination, the resulting HgCl_2 may remain in the flue gas or adsorb onto inorganic and carbonaceous ash particles entrained in the flue gas stream. The porous morphology and surface area of particles are dominant factors controlling HgCl_2 adsorption (Krishnan, Gullett, & Jozewicz, 1997).

Heterogeneous oxidation of $\text{Hg}(0)$ is promoted by fly ash and sorbents (Pavlish et al., 2003). They accelerate the oxidation and contribute to the adsorption of $\text{Hg}(\text{II})$ onto fly ash or activated carbon to form PBM (Hall et al., 1991; Pavlish et al., 2003). Mercury sorption by fly ash can occur via physical adsorption, chemisorption, chemical reaction, or a combination of these processes (Galbreath et al., 2000). It is necessary to consider how both the properties of solid surfaces and the composition of the flue gas together affect the oxidation and capture of mercury. Many studies have been performed to evaluate mercury adsorption properties of actual and simulated fly ashes, activated carbons (including iodine-, sulphur-, and other impregnated carbon), various mineral compounds, and noble metals (Pavlish et al., 2003).

The mercury adsorption capacity of the inorganic fraction is typically low (Hassett & Eylands, 1999), although certain fly ashes with low carbon content may still exhibit significant mercury capture. When the temperature of the flue gas decreases below 400 °C, the capture of mercury on fly ash is progressively increased (Ghorishi & Gullett, 1999; Gibb, Clarke, & Mehta, 2000) as well as by extending the effective contact time between flue gas and fly ash. Mercury capture is often but not always enhanced by high levels of unburned carbon (UBC) in the fly ash (high LOI) (Abad-Valle, Lopez-Anton, Diaz-Somoano, & Martinez-Tarazona, 2011; Bhardwaj et al., 2009; Hower et al., 2005; S. Li et al., 2007; López-Antón, Abad-Valle, Díaz-Somoano, Suárez-Ruiz, & Martínez-Tarazona, 2009; Y. Lu, Rostam-Abadi, Chang, Richardson, & Paradis, 2007; Suárez-Ruiz & Parra, 2007). Mercury tends to concentrate in the finer fly ash fractions for both low- and high-rank coals (Hassett & Eylands, 1999).

1.4.2.3 Thermodynamic models for mercury speciation in coal combustion flue gas

The modelling results predict that in conventional coal combustion systems at low temperature in the absence of chlorine, $\text{HgSO}_4(\text{s})$ is the stable form of mercury. $\text{HgO}(\text{s})$ is the most stable form at low temperatures when $\text{HgSO}_4(\text{s})$ is excluded from the modelling prediction. Temperatures stability for these solid phases ranges from 110 to 320 °C because of the effects of chlorine in the system. At higher temperatures, mercury is predicted to react with flue gases, producing three forms: $\text{HgCl}_2(\text{g})$, $\text{HgO}(\text{g})$, and $\text{Hg}(0)(\text{g})$.

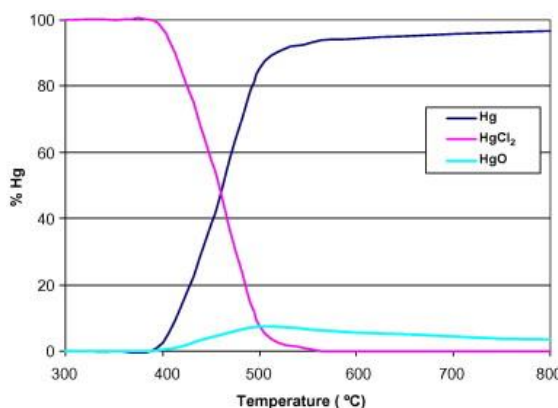


Figure 1.5: Thermodynamic equilibrium calculation of Hg-species for burning coal; an example of $\text{Hg}(0)$, HgCl_2 and HgO proportion in flue gas at different temperatures (D. Lu et al., 2007).

Table 1.2: Equilibrium reactions (Frandsen, Dam-Johansen, & Rasmussen, 1994).

	Reaction	Temperature (°C)
a)	$\text{HgO(g)} \leftrightarrow \text{Hg(0)(g)} + 2\text{O}_2\text{(g)}$	320**; 680***
b)	$\text{HgCl}_2\text{(g)} + \text{H}_2\text{O(g)} \leftrightarrow \text{HgO(g)} + 2\text{HCl(g)}$	430***
c)	$\text{HgSO}_4\text{(s)} \leftrightarrow \text{HgO(g)} + \text{SO}_2\text{(g)} + \frac{1}{2}\text{O}_2\text{(g)}$	320
d)	$\text{HgO(s)} \leftrightarrow \text{HgO(g)}$	170****
e)	$\text{HgSO}_4\text{(s)} + \text{Cl}_2\text{(g)} \leftrightarrow \text{HgCl}_2\text{(g)} + \text{SO}_2\text{(g)} + \text{O}_2\text{(g)}$	110***

*Reactions proceed to the right at temperatures higher than, but to the left at temperatures lower than, the stated temperature.

** In the absence of chlorine.

*** In the presence of chlorine.

**** $\text{HgSO}_4\text{(s)}$ not included in the model.

$\text{HgCl}_2\text{(g)}$ is dominant in a chlorine-bearing flue gas below 430 °C (Figure 1.5, Table 1.2). Hg(0)(g) and minor proportions of HgO(g) are predicted to coexist at higher temperatures; however, Hg(0)(g) is the only thermodynamically stable species above 750 °C (Frandsen et al., 1994). According to the Yudovich and Ketris (2005) Hg(0) is the only stable species at $T > 527$ °C. HgO is an important intermediate form of oxidised Hg that arises in the temperature transition range (400–600 °C), before conversion to the final stable Hg products as HgSO_4 or HgCl_2 (C. L. Senior et al., 2000). As the temperatures decline to 140 °C, HgCl_2 can condense on fly ash particles. In general the higher the chlorine content of the coal (and correspondingly, more HCl in the gases phase), the more mercury is captured by the fly ash. In oxidizing conditions at low temperatures, gaseous Hg-halogenides are stable: HgCl_2 (<427 °C), HgBr_2 (327–527 °C). In reducing conditions, Hg(0) is a dominant species in the wide temperature range; only at ambient temperature can solid HgSe be a stable species (Yudovich & Ketris, 2005b).

1.4.3 Removal technologies

Some possible technical approaches exist to control mercury emissions, but no single best technology can be applied broadly. Mercury is captured as a co-benefit of existing PM, NO_x , and SO_2 controls, however, the degree of this co-benefit will vary significantly depending on the type of coal burnt and the specific control-technology configuration (Srivastava, Hutson, Martin, Princiotta, & Staudt, 2006). Plants that burn coal and emit mainly Hg(0) will face a more difficult challenge in achieving a high level of control at acceptable cost (Pavlish et al., 2003). Moreover, relative proportions of GOM, PBM and GEM can vary widely, and the corresponding decreases in total mercury achieved by APCD may also differ (Pavlish et al., 2003; Srivastava et al., 2006; S. X. Wang et al., 2010). Volatile Hg(0) is likely to be emitted in the flue gas. Examination of mercury speciation in flue gases showed that Hg existed as GOM and/or particulate PBM, depending on the flue gas conditions. Moreover, Hg is known to associate with fine particulate fly ash (Guo, Zheng, & Xu, 2004; Otero-Rey et al., 2003; Taerakul, Sun, Golightly, Walker, & Weavers, 2006).

There are some techniques to remove mercury where GOM and PBM are easy to capture through conventional air pollution control devices (APCDs), such as electrostatic precipitator (ESPs) or fabric filter (FF), selective catalytic reduction (SCR), wet flue gas desulfurization (WFGD) and other scrubbers (Figure 1.6). Depending on the approach used, APCDs can remove up to 90% of the mercury released during the combustion. But

usually, mercury removal is much lower than 90%. Therefore, the conversion of mercury forms from one to another is an important key for selecting the appropriate mercury removal technology. Many studies have been conducted to develop sorbent and techniques that can efficiently remove mercury in the gaseous phase (Pavlish et al., 2003).

Hazardous trace elements tend to be adsorbed on PMs and subsequently captured by the ESP and FF with the decreasing flue gas temperature. Therefore, new ultra-low-emission technology for coal-fired power plants was proposed and has been widely applied in China to satisfy the strict environmental regulations (C. Zheng et al., 2017). In some TPP, wet ESP (WESP) is installed downstream of the WFGD to capture ultrafine particulates and other pollutants. With the ultra-low-emission system, PM, NO_x, and SO₂ emissions can be limited. Ultra-low-emission reformation has significant effects on trace element emission control (Y. Zhang et al., 2017; Zhao et al., 2016).

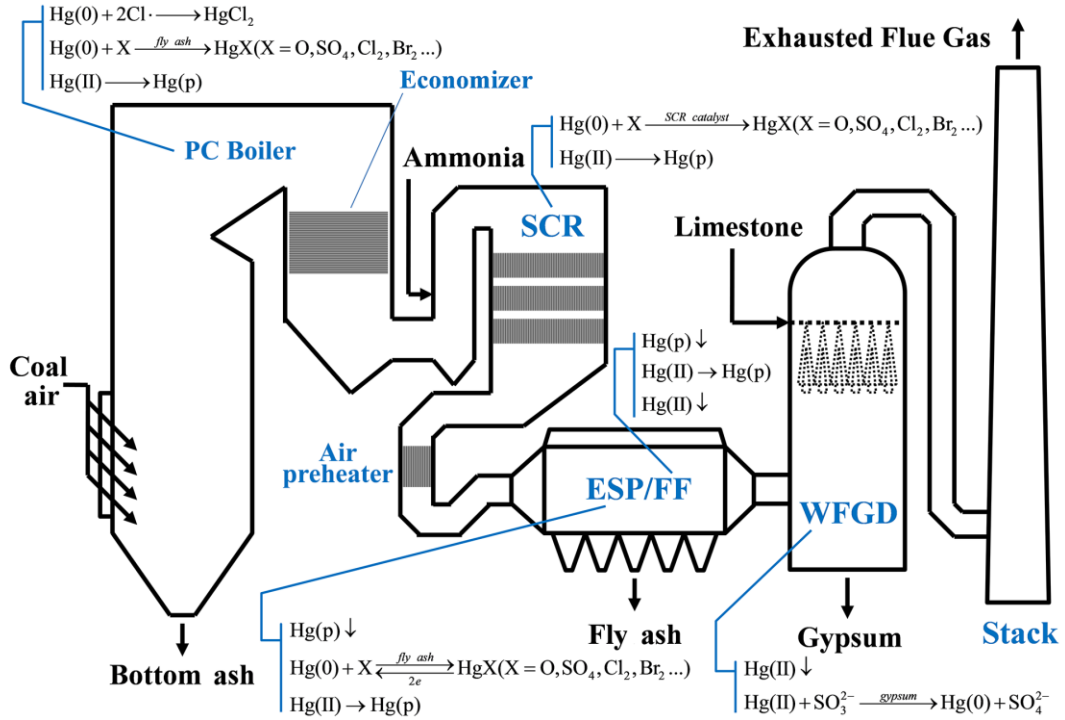


Figure 1.6: Mercury transformation and removal across typically APCDs in coal-fired power plants (L. Zhang et al., 2016).

1.4.3.1 Selective catalytic reduction

SCR catalysts are used to decrease NO_x concentration in flue gas. The catalyst is typically made of vanadium pentoxide (V₂O₅)/tungsten trioxide (WO₃) supported on titanium dioxide (TiO₂). NO_x is reduced by NH₃, which is injected upstream of the SCR catalyst bed (Monterroso, Argyle, & Fan, 2011). SCRs also increase the amount of oxidised mercury downstream. Since scrubbers capture more oxidised mercury, the combination of these flue gas controls may efficiently capture a significant amount of mercury (Blythe, 2003). Increasing the NH₃ concentration reduces the extent of mercury oxidation and appears to deactivate the catalyst (Benson, Laumb, Crocker, & Pavlish, 2005). Typically operation temperature in the SCR is 300–400 °C (L. Zhang et al., 2016).

The efficiency of SCR for oxidising mercury has also been tested for different flue gas conditions and coal types (Blythe, 2003; Laudal et al., 2000). Field tests in coal-fired power plants showed an average Hg(0) oxidation rate of 71% with a range of 34–85% (J. Chen et

al., 2008; L. Zhang et al., 2013). SCR catalysts are capable of enhancing the reaction kinetics of mercury oxidation, especially when HCl is present (Presto & Granite, 2006). Atomic chlorine is also responsible for Hg(0) oxidation inside SCR (C. W. Lee, Srivastava, Ghorishi, Hastings, & Stevens, 2003). The extent of mercury oxidation decreased when the NH_3/NO ratio increased, and it also decreased when the HCl concentration decreased (Presto & Granite, 2006; C. Senior, 2004). The ability to oxidise mercury is mainly dependent on the composition of the coal (Laudal, 2002). Under certain conditions, SCRs can promote the oxidation of Hg(0) to Hg(II), e.g., for bituminous coals but not for sub-bituminous coals; unfortunately, no data are available for lignite (Srivastava et al., 2006).

1.4.3.2 Electrostatic precipitator

Most coal-fired power plants are equipped with dust-cleaning equipment such as ESP or FF where PBM can be removed along with fly ash particles. ESPs are devices that precipitate particles in a gas stream by inducing an electrostatic charge. The most commonly applied operation temperature is 150 °C (Noda & Makino, 2010).

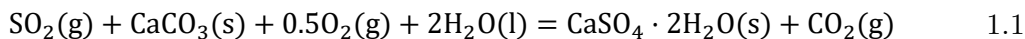
Over 99% of PBM is removed inside ESP (S. X. Wang et al., 2010). A small portion of Hg(II) can also be adsorbed onto fly ash and removed by ESP. The Hg(II) capture rate is determined by the UBC on fly ash (C. L. Senior & Johnson, 2005) as well as the surface property, size, porous structure, and mineral composition of fly ash affect the mercury capture rate of ESP as well (Y. Lu et al., 2007). When coal with high chlorine content is burned, more UBC is generated on fly ash and more Hg(II) and PBM are formed in the flue gas, which in turn increase the mercury capture rate inside ESP. Improvement of ESP for capturing fine particles (e.g., adding electric fields inside ESP) will also increase mercury removal efficiency (L. Zhang et al., 2016). Although it has a low operating costs capacity for mercury removal, it is limited because Hg is not generally adsorbed in the fly ash at combustion temperatures (Pavlish et al., 2003).

1.4.3.3 Wet flue gas desulphurization technology

WFGD technology, which based on using limestone or lime as a reagent, is a wet scrubbing process and has been the FGD technology most frequently selected for sulphur dioxide (SO_2) reduction from coal-fired utility boilers. The WFGD flue gas treatment system typically located after removal of PM from flue gas by a particulate removal system such as ESP. The cleaned gas discharges to the stack. This type of FGD system removes SO_2 by scrubbing the flue gas with either limestone or lime (reagent) slurry (Sargent & Lundy, 2003). In Slovenia, WFGD system is used in the Šoštanj thermal power plant (Šoštanj TPP). A lot of studies have been done already to improve the desulphurization process in Šoštanj TPP (Frkal, n.d., 2013; Gerbec, Stergaršek, & Kocjančič, 1995; Stergaršek et al., 2008; Stergaršek, Kocjančič, & Gerbec, 1996).

Flue gases in an absorber pass the flue gas stream through a limestone or lime slurry spray. In a typical absorber design, the gas flows upward through the absorber to the spray liquor flowing downward through the absorber. The slurry is normally pumped through banks of spray nozzles to atomise it to fine droplets and uniformly contact the gas. The droplets absorb SO_2 from the gas, facilitating the reaction of the SO_2 with a reagent in the slurry. Hydrogen chloride and other acid gases present in the flue gas are also absorbed and neutralised with a reagent, causing an accumulation of ions in the process liquid. Some of the water in the spray droplets evaporates, cooling the gas at the inlet from approximately 149 °C to 52–54 °C, and saturating the flue gas with water. The desulfurised flue gas passes through mist eliminators to remove entrained droplets before the flue gas goes to the stack. The slurry is collected in the bottom of the absorber in a reaction tank (BREFs, 2006; Srivastava, 2002).

Limestone or lime consumed in the process is replenished by adding fresh limestone or lime slurry to the reaction tank. In the limestone with forced oxidation (LSFO) process, the slurry is also aerated in the reaction tank to oxidise calcium sulphite hemihydrate ($\text{CaSO}_3 \cdot 0.5\text{H}_2\text{O}$) to calcium sulphate dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), or gypsum, which precipitates as follows (Sargent & Lundy, 2003):



The oxidised slurry is then recirculated to the spray headers. A portion of the slurry is withdrawn to remove the precipitated gypsum. Typically, this slurry is dewatered in a two-stage process involving a hydrocyclone and vacuum filter system to produce a gypsum cake for disposal or sale. Water removed from the gypsum slurry is returned to the process. A portion of this water is removed from the system as wastewater to limit the accumulation of corrosive chloride salts in the process liquid (U.S. EPA, 2003).

1.4.4 Mercury in wet flue gas desulphurization system

1.4.4.1 Retention of mercury in the scrubber

WFGD is important in the co-benefit mercury control technologies in coal-fired power plants. Its primary purpose is for SO_2 control but also acts as a precursor to acid deposition and aerosol formation (Brimblecombe, 2005). Additionally, $\text{Hg}(\text{II})$ is removed there as well. Hg could be partitioned between the solid (gypsum, unconsumed limestone, insoluble constituents of limestone and solids washed out of the flue gas) and aqueous phases, and show the affinity for retention in the fine fractions. A portion of the captured $\text{Hg}(\text{I}, \text{II})(\text{l})$ species in the scrubbing liquor reacts with other species and functions as the precursor of $\text{Hg}(0)(\text{g})$ re-emissions. Another portion is relatively stable, and it retains in the grained fraction of gypsum as $\text{Hg}(\text{I}, \text{II})(\text{s})$ precipitation. The left portion remained in the aqueous phase and recirculated through the system. The particle size and porosity of gypsum are critical in partitioning Hg between phases. Thermal and dissolution stability can vary between Hg compounds and other species present in the gypsum. Knowledge about the conditions and interactions of Hg with ligands, metals, and particles present in WFGD slurry is essential to predict the possible Hg species present in the gypsum.

The average $\text{Hg}(\text{II})$ removal efficiency of WFGD is 64% ranging from 56 to 99% (L. Chen et al., 2007; J.-H. Kim, Pudasainee, Yoon, Son, & Seo, 2010; S. J. Lee et al., 2006; Stergaršek et al., 2008; S. X. Wang et al., 2010). $\text{Hg}(0)$ due to poor solubility in water passes through WFGD without being captured (Chang & Zhao, 2008). In principle, PBM does not contribute to any water-phase mercury species. When PBM entrained in the flue gas enters the WFGD, it is transferred from the gas phase into the scrubber liquor and subsequently removed from the WFGD. On the other hand, GOM is absorbed by the scrubber liquor to form various hydrated ionic mercury salts. The overall mercury removal efficiency of WFGD is on average 45% with a range of 10–85% (L. Chen et al., 2007; Ito, Yokoyama, & Asakura, 2006; J.-H. Kim et al., 2010; S. J. Lee et al., 2006; Meij & te Winkel, 2006; Srivastava et al., 2006; S. X. Wang et al., 2010; Yokoyama, Asakura, Matsuda, Ito, & Noda, 2000).

The applications of high-chlorine coal, SCR and halogen addition can increase the $\text{Hg}(\text{II})$ proportion in flue gas before WFGD, and therefore enhance the overall mercury capture efficiency of WFGD. Also, the addition of metals such as Fe favour Hg oxidation. Consequently, the optimised strategy for WFGD is to stabilise the $\text{Hg}(\text{II})$ in the WFGD slurry to prevent mercury re-volatilisation.

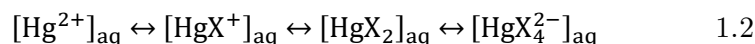
1.4.4.2 Mercury oxidation/reduction processes

In general Hg(II) may follow one of the three pathways in WFGD systems:

- It may react with other species (e.g., SO_3^{2-} , HSO_3^-) to form Hg(0) which is then re-emitted from the scrubber (Chang & Ghorishi, 2003);
- It may be retained in the sludge and recirculated through the system, and therefore high concentrations of mercury may accumulate (Córdoba et al., 2011);
- Alternatively, it may be captured in the grained fraction of solid by-products or gypsum and disposed of to the landfill sites (e.g., with additives added for better retention).

Chemical reduction of the dissolved Hg(II) reduces total mercury removal efficiency in WFGD due to re-volatilisation of Hg(0) (Chang & Ghorishi, 2003; Ochoa-González, Díaz-Somoano, & Rosa Martínez-Tarazona, 2013; Wo et al., 2009). Flue gas and slurry composition, operating temperature, limestone injection rate, and slurry pH, the oxidation-reduction potential (ORP) are the key factors affecting the re-volatilization of Hg(0) (Acuña-Caro, Brechtel, Scheffknecht, & Braß, 2009; Cheng et al., 2009; Díaz-Somoano, Unterberger, & Hein, 2007; Heidel, Rogge, & Scheffknecht, 2016; Ochoa-González, Díaz-Somoano, & Rosa Martínez-Tarazona, 2013; Shuetze, Kunth, Weissbach, & Koeser, 2012; Van Loon, Mader, & Scott, 2000).

However, excess concentrations of SO_3^{2-} would promote the formation of stable mercuric-sulphite complex $\text{Hg}(\text{SO}_3)_2^{2-}$, which prevents re-emission of Hg(0) (Blythe, Currie, DeBerry, & Miller, 2008). It has been established that if Cl^- is present, Hg(II) will form mercury chloride complexes, inhibiting the reduction of Hg by sulphite (Heidel et al., 2016). Stable Hg-halogenated complexes form in the presence of excessive concentration either of Cl^- or Br^- ions (Blythe, DeBerry, Marsh, Paradis, & Range, 2004). One simplified aqueous phase equilibrium involving halide ions (X^- ; such as Cl^- and Br^-) as in the following equation:



Additionally, the existence of Hg(0) and the SO_2 complex was observed, and it is predicted that this complex should have three orders of magnitude higher solubility in water than Hg(0) (Van Loon et al., 2000).

1.4.4.3 Influence of additives

Addition of various FGD oxidation additives, e.g., aluminium sulphates might oxidise Hg(0) and prevent reduction of Hg(I, II) in the slurry solution (Ochoa González, Díaz-Somoano, López Antón, & Martínez-Tarazona, 2012). Fenton additives (FeCl_3 and $\text{Fe}(\text{SO}_4)_3$ (Y. Liu et al., 2015; D. Lu et al., 2007) act together with H_2O_2 as a catalyst in WFGD scrubber and show an increase in mercury retention in the solid by-products by formation of HgSO_4 which might decompose into $\text{HgO}(\text{s})$ or exists in solution as HgCl_2 (Ochoa-González, Díaz-Somoano, & Rosa Martínez-Tarazona, 2013). Other catalysts could be added such as Fe, Mn and Cu (Stergaršek, Horvat, Frkal, Ribeiro Guevara, & Kocjančič, 2013; Stergaršek, Horvat, Frkal, & Stergaršek, 2010).

Among various techniques employed to remove aqueous Hg(II), the chelation/precipitation is widely applied owing to its convenience and high efficiency. In general, scrubber additives collect "soluble ionic mercury". The resulting Hg-containing complex ion prevents Hg(I, II) reduction to Hg(0). Commonly used chelating agents are TMT (2,4,6-trimercaptotriazine, trisodium salt monohydrate $\text{Na}_3\text{S}_3\text{C}_3\text{N}_3 \cdot 9\text{H}_2\text{O}$), thiosulfate ions ($\text{S}_2\text{O}_3^{2-}$), NaHS, Na_2S , Na_2S_4 , sodium dithiocarbamate (DTCR) (Blythe et al., 2008; Ochoa-González, Díaz-Somoano, & Rosa Martínez-Tarazona, 2013; Sun et al.,

2015; T. Tang, Xu, Lu, Wo, & Xu, 2010; Q. Wang, Liu, & Wu, 2018). Insoluble Hg species (e.g., HgS, $\text{Hg}_3(\text{TMT})_2$, $\text{Hg}(\text{DTCR})_2$) may precipitate onto the gypsum (see Figure 1.7). However, the addition of an elevated amount of additives may decrease the thermal stability of Hg compounds (Q. Wang et al., 2018).

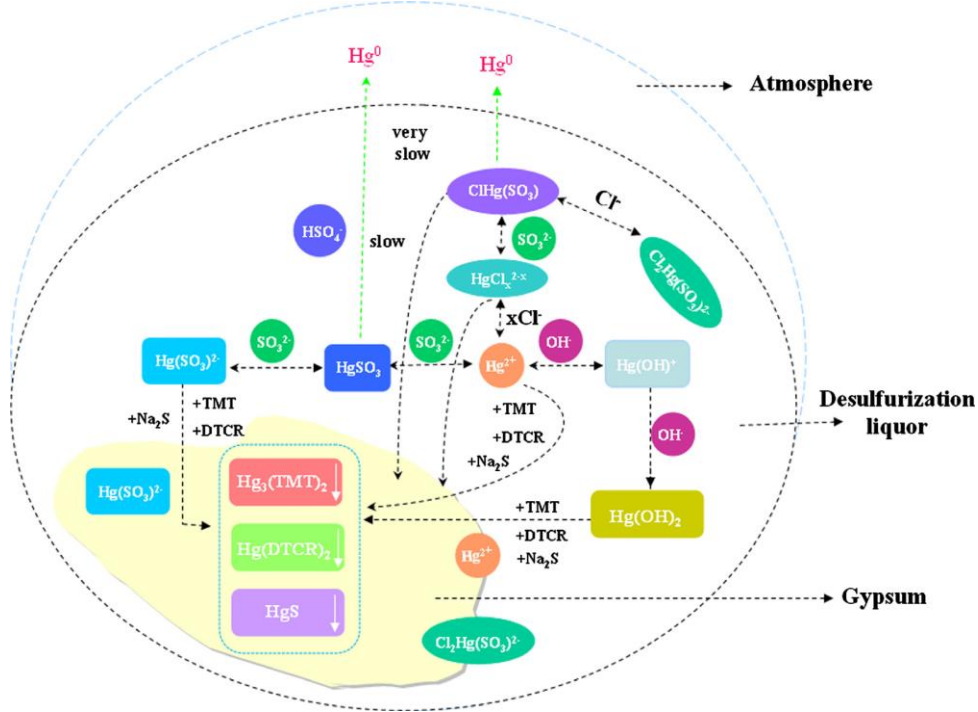


Figure 1.7: Schematic mechanism of main reaction pathways of Hg(II) reduction and absorption in desulfurization solutions (Sun et al., 2015) including the role of various slurry additives.

1.4.5 Šoštanj thermal power plant

In the present study, Šoštanj TPP was studied. It consists six power blocks, with a combined power of 1304 MW. It uses lignite as a fuel, from a local mine, with a heating value of 9.5 MJ kg^{-1} and with a consumption rate between 3.5 and 4.2 million tons per year. Šoštanj TPP has installed 3 WFGD units for SO_2 removal; the first covering blocks 1 to 4 while the other two are installed separately in block 5 and 6. All WFGD units using the wet limestone process with forced oxidation (Official technical information, 2016). Also, it is equipped with SCR DeNOx systems for controlling nitrogen oxide emissions (NO_x) from combustion sources and ESP to eliminate particles.

The effect of the WFGD system on Hg accumulation was observed. The retention efficiency of total Hg in the WFGD is as high as 89%; 99% for GOM, 98% for PBM and 76% for GEM (Stergaršek et al., 2008). Gypsum slurry and gypsum afterwards are very important in accumulating of Hg, especially in a fine fraction. For example, 12% of total gypsum mass contains 62% of its Hg bound to small particles (Stergaršek et al., 2008). Moreover, the results reported in the study of Sedlar et al. (2015) show that the majority of Hg is retained in the slow-settling, the fine particulate phase of the WFGD, with concentrations exceeding values of $10 \text{ mg} \cdot \text{kg}^{-1}$ of Hg (Sedlar, Pavlin, Jaćimović, et al., 2015).

Study of Stergaršek et al. (2010, 2013) showed that the complex chemistry in WFGD solution could be modified in so that dissolved Hg(0) is oxidized by air introduced for the

oxidation of S(IV) to S(VI) compounds. Oxidation is enhanced by catalytic reactions with transition metals like Fe and Mn, which, when combined, show a positive synergistic effect. It seems that the radicals involved in the chain reactions of autoxidation of S(IV) are also responsible for the oxidation of Hg(0). In slurry solutions manganese is more soluble than iron at the pH values that are typically encountered in the FGD process, i.e., pH = 4–6, usually close to 5.6. The catalysts such as iron and manganese could precipitate. The reddish precipitate of Fe(hydro)oxides accumulate on the equipment walls with time, and the black precipitates of MnO_2 occasionally occur when the oxygen supply was too high.

The formation of Hg(II) complexes with ligands like Cl^- , HSO_3^- , HSO_4^- , HCO_3^- , OH^- and many others is very important. The formation of Hg(I) seems to be involved as well and could play an important role in the elimination of insoluble compounds from the solution, shifting the equilibrium and enhancing the retention of mercury in wet FGD. The schematic chemical model which includes the conclusions derived from experimental results and published chemical mechanisms is proposed in Figure 1.8 (Stergaršek et al., 2013, 2010).

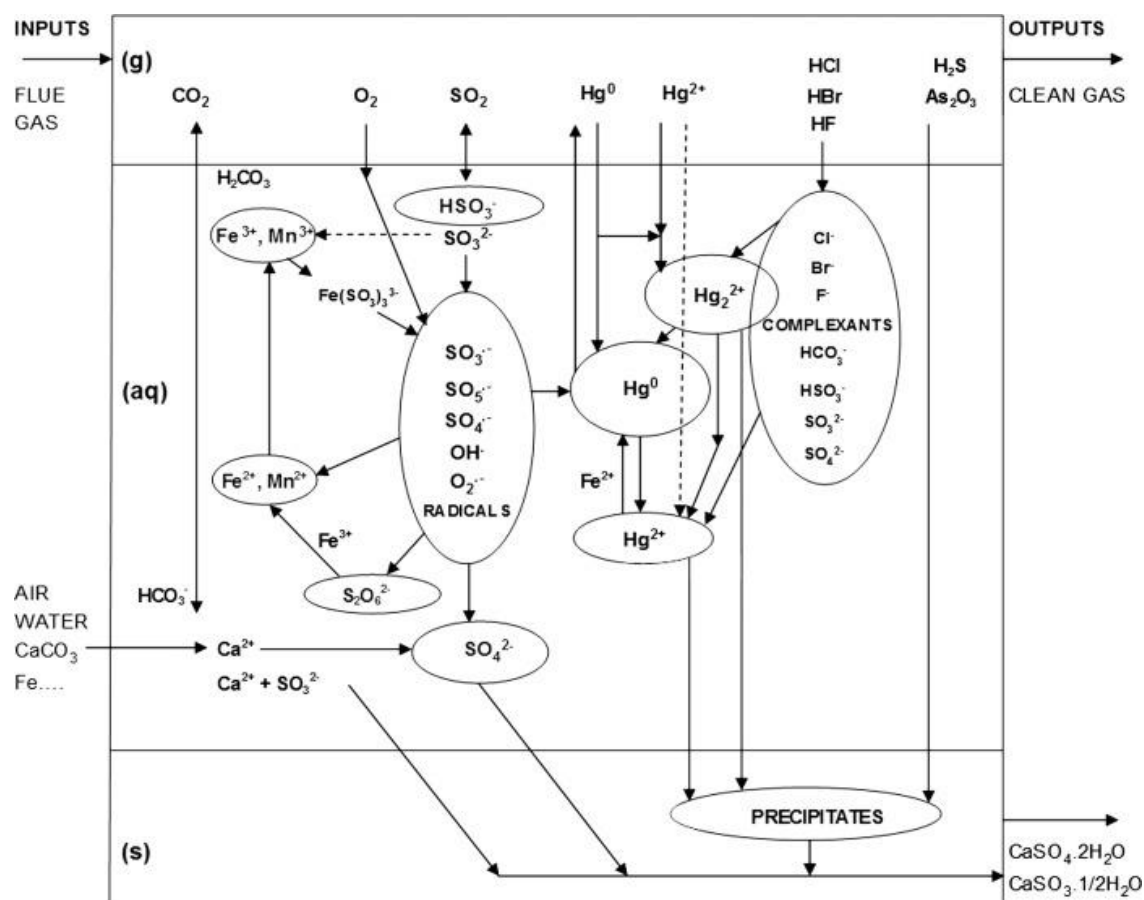


Figure 1.8: A schematic chemical model of catalytic oxidation of Hg(0) with air in wet FGD (Stergaršek et al., 2013).

1.5 Characterization of Mercury Compounds in Solid Samples

Measurements of total mercury concentrations in different solid samples are not enough. This information does not provide any information about mercury species present in the solid sample. The identification and quantification of different chemical species are necessary to determine mercury toxicity, bioaccumulation, emission control, and atmospheric fate and transport, due to the physical, chemical, and biological properties. The analytical measurement (the final steps of the analytical procedure) typically receives the greatest attention, although the first steps of analysis including sampling, sample storage and sample preparation are the most problematic ones. The main problem is to maintain the original distribution of species (speciation) through all the steps until the final step of determination and quantitation. Therefore, the best sample preparation for speciation analysis is no preparation at all.

Before starting to describe the appropriate sampling procedure and methods for determination of mercury in solid environmental samples and industrial by-products, it is important to define some terms in analytical chemistry (Templeton et al., 2000):

- ✓ ***SPECIATION** is a distribution of an element amongst defined chemical species in a system.*
- ✓ ***CHEMICAL SPECIES OF AN ELEMENT** are a specific form of an element defined as to isotopic composition, electronic or oxidation state, and complex or molecular structure.*
- ✓ ***CHEMICAL SPECIES** is an ensemble of chemically identical molecular entities that can explore the same set of molecular energy levels on the time scale of the experiment. The term is applied equally to a set of chemically identical atomic or molecular structural units in a solid array.*
- ✓ ***FRACTIONATION OF ANALYTES** is a process of classification of an analyte or a group of analytes from a sample according to physical (e.g., size, solubility) or chemical (e.g., bonding, reactivity) properties.*

Mercury emissions appear from various stationary combustion sources such as coal-fired power plants, oil-fired power plants, industrial utility oil boilers, iron manufacturing plants, municipal waste incinerators, and other Hg emitters. In coal-fired plants, different mercury forms (GEM, GOM and PBM) are partly or mostly removed by APCDs. Then, it is quantified by collecting and analysing gaseous, solid and liquid samples, such as fuel (coal), fly ash from the hopper, bottom ash, gypsum, lime or limestone, and effluents.

Different analytical techniques become available to contribute a better understanding of mercury chemistry in different systems. Some of the methods are very sensitive, with special analytical equipment and contamination-free methods. All these improvements allow the determination of total mercury as well as mercury species to be formed in water, sediments, soils, and biota.

1.5.1 Analytical methods for mercury speciation/fractionation in solid samples

The speciation and the way how the different species interact with the solid matrix cause changes in solubility, toxicity and bioavailability of the metal (Biester, Müller, & Schöler,

2002). Based on their properties, Hg species classify into volatile compounds, reactive and non-reactive species. Reactive species are the most challenging group, corresponding to the bioavailable and toxic chemical forms, in contrast with the non-reactive species group. Determination of a total mercury concentration is insufficient for understanding the biogeochemical cycle of the metal and for establishing an appropriate remediation method. (Issaro et al., 2009).

The study of mercury speciation/fractionation can be used to predict and explain the behaviour of mercury in soil. Several approaches such as sequential extraction procedures (SEP), temperature programmed desorption (TPD; pyrolysis, thermal desorption methodology), X-ray absorption spectroscopy (XAS), as well as nuclear magnetic resonance (NMR), electron paramagnetic resonance (EPR) and XPS (X-ray photoelectron spectroscopy or electron spectroscopy for chemical analysis (ESCA)), have been used to study mercury speciation in soil (Biester, Gosar, & Müller, 1999; Delnomdedieu, Boudou, Georgescauld, & Dufourc, 1992; C. S. Kim et al., 2000; E.-A. Kim, Seyfferth, Fendorf, & Luthy, 2011; Laumb, Benson, & Olson, 2004; Piskunov, Aivaz'yan, Cherkasov, & Abakumov, 2006; Jianxu Wang et al., 2011). Among these methods, sequential extraction procedure (SEP), TPD, and XAS are most frequently used in mercury speciation analysis and are briefly described in the following sections.

1.5.1.1 X-ray absorption spectroscopy

Synchrotron radiation-based X-ray absorption spectroscopy (XAS) has been shown to provide direct, in situ information on heavy metal speciation (Huggins & Huffman, 1996). The method is suitable for determining Hg in different contaminant samples such as ore, slag, soil from Hg mines, mine tailings, mine waste and chloro-alkali plants to identify multiple mercury phases in a heterogeneous sample (e.g., HgS, HgSO₄, HgO, HgCl₂). This method is also applicable for studying Hg accumulation and processes in the plants (Kodre et al., 2017). The technique is non-destructive, element-specific, relatively sensitive at lower concentrations, and requires minimal sample preparation, thus allowing the analysis of samples in conditions similar to those observed in their natural state (C. S. Kim et al., 2000).

The principle of operation: XAS data is obtained by tuning the photon energy using a crystalline monochromator to a range where core electrons can be excited (0.1–100 keV photon energy). The generation of photoelectrons induces specific electronic scattering interactions between the central absorbing atom and neighbouring atoms (Brown & Parks, 1989). The incident X-ray energy at that point corresponds to the absorption edge of the element for a given electron shell (K, L_{III}), while the electron scattering interactions result in the X-ray absorption near-edge structure (XANES) and the extended X-ray absorption fine structure (EXAFS) regions (C. S. Kim et al., 2000). EXAFS yields information about the interatomic distances, near neighbour coordination numbers, and lattice dynamics. XANES gives information about the valence state, energy bandwidth and bond angles (Alp, Mini, & Ramanathan, 1990).

Disadvantages: However, this technique has some drawbacks; it is expensive and requires samples with Hg concentration higher than 100 mg kg⁻¹. The sensitivity improves by pre-separation and pre-concentration of Hg (Huggins & Huffman, 1996). Specific Hg species must be in the XANES spectral database for correct identification, and quantitative accuracy of the proportions of individual species present may vary by ±15%, making identification of minor phases difficult. Sample weigh is also limited to 200 mg and must be homogenised (Sladek, Gustin, Kim, & Biester, 2002). EXAFS is based on mathematical modelling of local atom environment, with average ±10% accuracy of identification of the first shell neighbouring atoms and interatomic distances (Kodre et al., 2017).

1.5.1.2 Sequential extraction methods

The analysis of Hg species in soil or sediment can be accomplished by the using of sequential extraction procedure (SEP) (Bloom & Preus, 2003; Fernández-Martínez & Rucandio, 2003; Han et al., 2003; Kocman, Horvat, & Kotnik, 2004; Revis, Osborne, Holdsworth, & Hadden, 1989; H. Sakamoto, Tomiyasu, & Yonehara, 1992). Extraction procedures are used to subdivide the Hg content of solid samples into several operational defined groups of more or less soluble species (Rubio & Rauret, 1996). The chemical speciation/fractionation method may involve several steps; extraction, derivatization, purification, and final analysis. A comprehensive review of the different procedures available for Hg speciation is provided by Issaro et al. (Issaro et al., 2009).

The fractions extracted early in the process are most weakly bound to the solid phase and have a higher potential for mobility and toxicity. The use of the remaining soil matrix for the next step may influence further steps of chemical extraction since substrate composition may alter. In most of these procedures, the different fractions are defined as the following (Issaro et al., 2009):

- The exchangeable fraction means the mobile and bioavailable parts;
- The acid soluble or carbonate associated fraction means the metals precipitated or co-precipitated with carbonate constituent;
- The fraction bound to metal oxides such as Fe, Al, and Mn oxide, which can trap the metals. These oxide compounds are thermodynamically unstable in anoxic conditions induced by the decreasing of redox potential;
- The organic fraction means the part of Hg bound to organic matter;
- The residual fraction means the part of Hg bound to the elements that cannot be extracted by the previous reagents.

As seen above, typical techniques for Hg speciation comprise numerous steps with one or more reagents as extractants, resulting in complex, time-consuming processes with poor reproducibility, lack of selectivity, and non-specificity. Re-adsorption, background contamination or procedural losses of the volatile mercury species have also been observed as problems associated with Hg sequential extraction procedures (Bacon & Davidson, 2008; Reis, Rodrigues, Davidson, Pereira, & Duarte, 2010). It has to be emphasised that a limitation of these procedures is the lack of validation and reference materials for checking the performance both of method and the laboratory (Bacon & Davidson, 2008). If the environmental mobility of Hg in a substrate is the most crucial information needed, SEP or similar extraction methods should be applied. Data obtained provide insight as to whether Hg is in a stable form (such as HgS) or in a soluble form (e.g., HgCl₂).

1.5.1.3 Temperature programmed desorption/decomposition method

Temperature programmed desorption/decomposition (TPD) method for Hg studies is based on the thermal decomposition/desorption of Hg(0) and Hg-compounds from solids at different temperatures and continuous determination of the released volatile Hg. According to the definition of "*speciation analysis*" by IUPAC, *thermal programmed desorption analysis* is not a method for speciation analysis but a fractionation technique because it cannot differentiate between distinct species but can only separate more volatile fractions from less volatile fractions.

Sequential leaching procedures used for the determination of inorganic Hg-compounds often suffer from insufficient selectivity to distinguish Hg-binding forms and from poor reproducibility of the results. Therefore, TPD method such as solid phase Hg-pyrolysis, have been applied to start specifying and quantifying Hg-binding forms in soils and

sediments (Azzaria & Aftabi, 1991; Bombach, Bombach, & Klemm, 1994; Windmüller, Wilken, & Jardim, 1996). The method is simple, usually without sample preparation, cheap and relatively fast for identification of Hg species in the solid matrix, and represents an alternative to chemical extraction. However, sampling and sample manipulation influence the final results. In the last decades TPD method has been widely applied to identify the mercury compounds (e.g., Hg-halogenides, HgSO_4 , Hg_2SO_4 , HgO and HgS) in a variety of solid samples, such as silica, coal, fly ash, gypsum, contaminated soil, sediments, fluorescent lamps, charcoal and iron-based sorbents (Biester & Scholz, 1997; Coufalík, Pavel, Marek, & Josef, 2012; Feng et al., 2004; Hojdová, Navrátil, Rohovec, Pen'izek, & Grygar, 2009; X. Liu et al., 2013; Lopez-Anton, Yuan, Perry, & Maroto-Valer, 2010; Luo, Yao, Xu, Gupta, & Xu, 2011; Mashyanov et al., 2017; Milobowski, Amrhein, Kudlac, & Yurchhison, 2001; Ozaki, Uddin, Sasaoka, & Wu, 2008; Rallo, Lopez-Anton, Perry, & Maroto-Valer, 2010; Raposo, Windmüller, & Durão Júnior, 2003; Sedlar et al., 2015; Shuvaeva, Gustaytis, & Anoshin, 2008; Windmüller et al., 1996).

The principle of operation: TPD approach for determining mercury speciation in solid samples is basically a transpiration method (Kubaschewski, Alcock, & Evans, 1967). Usually, an atomic absorption spectrometer (AAS) or atomic fluorescence spectrometer (AFS) is used as the detector (Biester & Scholz, 1997; Raposo et al., 2003; Windmüller et al., 1996). Two different approaches are commonly in use to perform TPD fractionation:

- Typically, self-constructed apparatus is used consisting of sample vessel located within an electric furnace that is directly connected to a heated quartz cell (Figure 1.9).

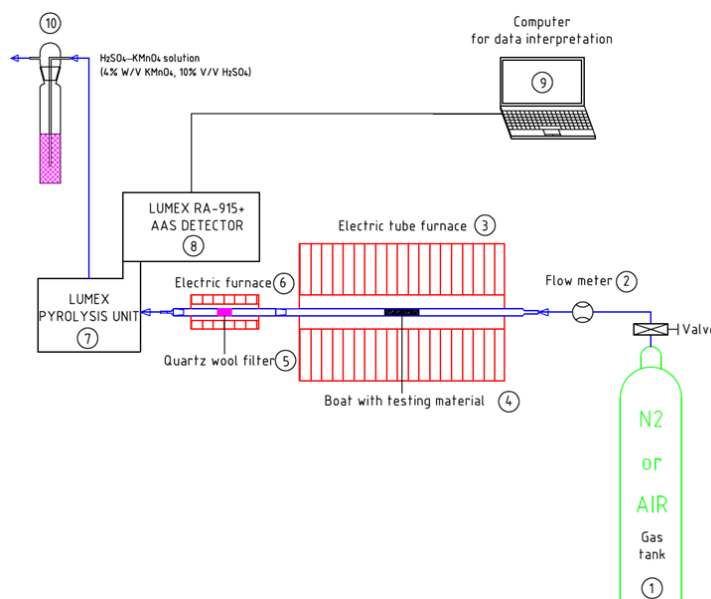


Figure 1.9: An example of the experimental set-up for temperature programmed desorption approach (Sedlar, 2014).

Samples are heated up continuously at a constant rate with a constant gas flow (e.g., Ar, N_2 , air). All released Hg-compounds were transformed to $\text{Hg}(0)$ by thermal reduction when passing through a heated quartz tube/pyrolytic cell (e.g., 800 °C) and detected by AAS using continuous detection mode with background correction (Zeeman or D_2 -background correction). In our previous studies, we used Lumex RA-915 + PYRO-915, and detail description of the

method is given elsewhere (Sedlar et al., 2015; Sedlar, Pavlin, Popovič, & Horvat, 2015).

- An alternative method for mercury fractionation by thermo-desorption consists of the use of direct mercury analysers (DMA), such as the AMA-254 (LECO) or DMA-80 (Milestone, Figure 1.10), by merely adjusting combustion temperature and the heating program (Reis et al., 2015; Saniewska & Beldowska, 2017). Measuring is not continuous, but several steps are needed to obtain complete Hg releasing profile in one sample. DMA appear to be more advantageous, as they already use thermal-decomposition for total mercury quantification, are easy to use by the non-expert analyst and, since the equipment is automated and commercially available, operational conditions are standardised and results obtained by different laboratories can be compared. However, DMA-80 is a commonly used instrument for determination of total Hg concentration.

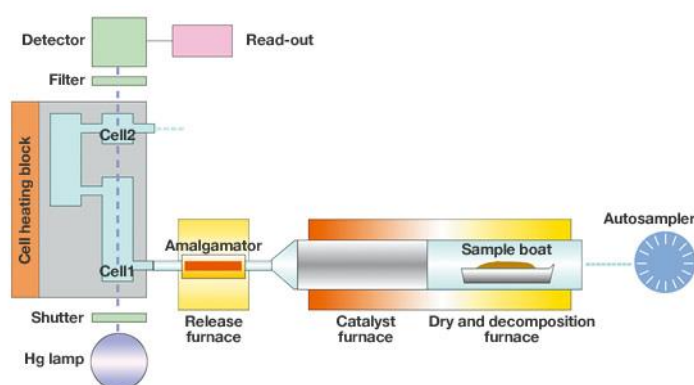


Figure 1.10: DMA-80 is based on the principles of samples thermal decomposition, consolidated mercury and detection of atomic absorption.

Identification of mercury species: Different mercury species are released at different temperature ranges (Koksoy, Bradshaw, & Tooms, 1967) as a consequence of different vapour pressures (Milobowski et al., 2001). During the analysis, heating is responsible for breaking the bonds of Hg present in the matrix, causing a successive release of the metal in its elemental form (Biester, 1994). The details of the related physical and chemical processes are still unknown. Since the AAS method detects only Hg(0), it means that Hg(I) and Hg(II) have to be reduced to Hg(0) during the release process (Windmüller et al., 1996). Investigations of Hg compounds in various solid samples are of great interest:

- to understand temperature stability of Hg in solid substrates/wastes;
- to define Hg fractions released during controlled heating as proxies for the identification of Hg compounds present in solid substrates.

In addition to melting/boiling points, the decomposition and sublimation temperatures for some mercury compounds are provided in Table 1.3. The data represent an overview of different (thermodynamic) studies. Hg(0) release at lower temperature, while Hg(I, II) show peak(s) at higher temperature(s). Moreover, the release temperature of different Hg-species may overlap with each other. Different Hg-species could have more than one peak as observed in our previous work of Sedlar et al. (Sedlar et al., 2015) and in other studies (Lopez-Anton et al., 2010; Rallo et al., 2010). Step decomposition of Hg-compounds is suggested in those cases. The data provided in Table 1.3 mostly represent the Hg releasing

temperature of pure Hg compounds. However, sample matrix affects on releasing of Hg and resulting TPD spectra of the same Hg species differ in various substrates. Evaporation of heated mercuric species was induced by the physical and chemical characteristics of the solid matrices.

Table 1.3: Hg species commonly found in gypsum according to the literature.

Mercury species	Temperature of decomposition/sublimation (°C)	Reference
Hg(0) $p_v = 2.7 \cdot 10^{-3}$ mBar	-39 <80 <150	(Lide, 2009) (Watling, Davis, & Meyer, 1972) (Bombach et al., 1994)
Hg ₂ Cl ₂ $p_v = 1 \cdot 10^{-7}$ mBar	383– sublimation 170	(Lide, 2009) (Watling et al., 1972)
HgCl ₂ $p_v = 1.6 \cdot 10^{-4}$ mBar	276 277 – melting point, 304 – boiling point <250 220	(Lide, 2009) (W. H. Schroeder & Munthe, 1998) (Koksoy et al., 1967) (Watling et al., 1972)
HgS $p_v = \text{too low}$	344 – transforms to black HgS 584 – sublimation 300 280-400 210-340 400 265-345	(Lide, 2009) (W. H. Schroeder & Munthe, 1998) (Watling et al., 1972) Biester, 1994 (Koksoy et al., 1967) (Bombach et al., 1994) (Leckey & Nulf, 1994)
HgO(red)/HgO(yellow) $p_v = 3.2 \cdot 10^{-12}$ mBar	500– decomposition 270-535 160-495	(W. H. Schroeder & Munthe, 1998) (Koksoy et al., 1967) (Watling et al., 1972)
HgSO ₄	450 °C decomposition 500 °C decomposition	(Lide, 2009) (Tariq & Hill, 1981)
Hg ₂ SO ₄	335 – 500– decomposition	(Tariq & Hill, 1981)

* p_v obtained by (Lindquist et al., 1991)

Methodological problems: Stability of mercury compounds refers to the temperature at which the Hg signal attains its maximum (peak temperature). In general, this approach based on the mathematical treatment (peak fit) of the different mercury standards TPD spectra (curves, thermograms) and the spectra of actual (authentic) samples. There is no direct correlation between the physicochemical properties of the pure mercury compounds, i.e., melting and sublimation point and vapour pressure (Table 1.3), with the temperature range in which they release from the solid matrices reported in the literature (Windmüller et al., 1996). There are, however, several reasons why the TPD method should be used with the greatest care, as follows:

1. Standards are typically prepared by dry mixing pure mercury compounds with the matrix (substrate), for example, CaSO₄ · 2H₂O, where adsorption on the surface of the crystals takes place. In case of WFGD gypsum, Hg compounds can be present within the crystal bulk because they exist in the solution as the crystals formed.

Additionally, WFGD gypsum slurry contains several other types of particulate matter that varies in adsorption affinity (particles coming into the system via fly ash and through the addition of limestone, e.g., Fe oxides), so it is reasonable to expect that neither the same peak temperature nor the same peak forms in both cases.

2. The sample matrix and its particle size distribution, the heating ramp, type of the carrier gas, flow rate velocity of the carrier gas, the weight of the sample, sampling procedure and analysis (sampling) time affect the release of Hg by shifting the peak toward lower or higher temperatures, and might change the peak intensity (Biester & Scholz, 1997; Feng et al., 2004; X. Liu et al., 2013; Lopez-Anton et al., 2010; Luo et al., 2011; Rallo et al., 2010; Raposo et al., 2003; Sedlar et al., 2015; Shuvaeva et al., 2008; Windmüller et al., 1996; Z. Zhu, Zhuo, Fan, & Wang, 2016). All these factors are responsible for the discrepancies observed in the measurement of Hg species among various laboratories, and unfortunately, as yet, no standardised method has been established for determining Hg speciation/fractionation in solid samples. Validation of the methods often performed by comparing the total mercury content indicating accuracy in the range of $\pm 20\%$ (EVISA, 2017).
3. Thermograms are suitable for qualitative determination of various mercury species whereas quantitative results for different Hg species are seldom reported. Different fractions are often qualitatively reported as "mobile," "semi-mobile" and "non-mobile" rather than true species identification. In cases where quantitative results assign to different species, authors are very vague in describing which part of the thermogram was assigned to which species and how signal integration was performed (EVISA, 2017).

1.5.1.4 Temperature programmed desorption/decomposition method using a mass spectrometer

The mass spectrometer (MS) is rarely applied to detect mercury and mercury compounds in different environmental samples (Ozaki et al., 2008; Sedlar, Pavlin, Popović, & Horvat, 2015; Uddin, Ozaki, Sasaoka, & Wu, 2009; Wu, Uddin, Nagano, Ozaki, & Sasaoka, 2011). In our recent study, we compared the desorption/decomposition temperatures and thermograms of various pure Hg-compounds and those mixed with SiO_2 and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ by using either a mass spectrometer and AAS (Sedlar, 2014). Since MS could measure different volatile compounds at the same time, in theory we could predict the decomposition reactions that help in the identification of mercury compounds present in the solid samples.

Theoretical background of TPD method: Basically, TPD is the method for observing desorbed molecules from a surface (measurement of the rate of desorption) when the surface temperature is increased. This technique is important for the determination of kinetic and thermodynamic parameters of desorption processes or decomposition reactions that place at the surface of solid materials (Rakić & Damjanović, 2013; S. L. M. Schroeder & Gottfried, 2002). Moreover, this method can be useful in the identification and characterization of sites active in adsorption and catalytic reactions, in the study of adsorption states, binding energies, and surface concentration. In general, the method is usually applied to the porous material and well-defined surfaces of single-crystalline samples (Rakić & Damjanović, 2013).

Vaporization process: Mass spectrometric investigation of the vapour flux allows one to determine and monitor the vapour composition. The activation energies of vaporisation of

each vaporising species can calculate the variation of the composition with temperature. The bulk properties of the vaporising crystal samples (pure compounds) should be well characterised by changes that may significantly influence the evaporation rate (Somorjai, 1969). However, in the solid samples such as gypsum matrix, the study of mercury vaporisation is very complicated because interactions between mercury and substrate containing different species affect the final desorption profile (thermogram). The releasing behaviour of the Hg-species, as demonstrated by the thermograms, can be in part a consideration of the kinetics, the thermodynamics, and mechanisms of the vaporisation processes. These characteristics under non-equilibrium conditions are different from those in equilibrium, resulting in different volatilisation rates. Therefore, vaporisation behaviour, in non-equilibrium conditions, cannot be predicted from equilibrium measurements (Somorjai & Lester, 1967). It follows that the releasing temperature of various Hg-compounds obtained by TPD method is not the same as literature data. For example, vapour pressure data suggests the following sequence: $\text{Hg}(0) > \text{HgCl}_2 > \text{Hg}_2\text{Cl}_2 > \text{HgO} > \text{HgS}$, whereas the thermograms for Hg_2Cl_2 released at a lower temperature than HgCl_2 (Windmüller et al., 1996).

Adsorption/desorption process: Adsorption takes place when an attractive interaction between a particle and a surface is strong enough to overcome the disordering effect of thermal motion (S. L. M. Schroeder & Gottfried, 2002). There are two principal modes of adsorption of molecules on surfaces where the basis of distinction is the nature of the bonding between the molecule and the surface (Nix, 2013):

- *Physical Adsorption:* the only bonding is by weak Van der Waals type forces (electrostatic interactions). There is no significant redistribution of electron density in either the molecule or at the substrate surface.
- *Chemisorption:* a chemical bond, involving substantial rearrangement of electron density, is formed between the adsorbate and substrate. The nature of this bond may lie anywhere between the extremes of virtually complete ionic or complete covalent character.

Desorption takes part as a result of thermal motion which kinetic energy is high enough to break the bond between the adsorbate and weak active sites. According to the desorption studies, the released (adsorption-desorption) peaks are denoted as weak, medium, strong and very strong. Apparently, the overlapping of desorption peaks that has its origin in the surface heterogeneity imposes the necessity to resolve the complex TPD curve and to assign particular desorption profiles to the sites of definite strength. Typically, the mathematical procedure of deconvolution is applied (Rakić & Damjanović, 2013). In the study of Sedlar et al. (Sedlar, 2014) it was observed that different substrates might significantly change the decomposition temperature and the peak shape for various investigated Hg-species. This is even more complicated in the actual samples such as gypsum.

An adsorbed species present on a surface at low temperatures may remain almost indefinitely in that state. As the temperature of the substrate increases, however, there will come the point at which the thermal energy of the adsorbed species is such that one of the several things may occur (Nix, 2013):

- a molecular species may decompose to yield either gas phase products or other surface species;
- an atomic adsorbate may react with the substrate to yield a specific surface compound, or diffuse into the bulk of the underlying solid;
- the species may desorb from the surface and return to the gas phase (desorption process).

In the absence of decomposition, the desorbing species will be the same as that adsorbed initially, but this is not always the case.

The principle of operation of mass spectrometer: Quadrupole mass spectrometer (QMS) is typically used in the modern implementation of the TPD technique. The whole process is carried out under computer control with simultaneous monitoring of a vast number of possible by-products (volatile species of interest, decomposition fragments). Surface reactions and molecular adsorption on surfaces utilise temperature-programming to discriminate between processes with different activation parameters. The sample is heated in a controlled manner (a linear temperature ramp) while monitoring the evolution of species from the surface back into the gas phase. The set-up (Figure 1.11) is similar than in classic TPD method using AAS detection (see Subchapter 1.5.1.3), where the differences are in the detector and no need of carrier gas. In such experiments the data obtained consists of the intensity variation of each recorded mass fragment as a function of time/temperature.

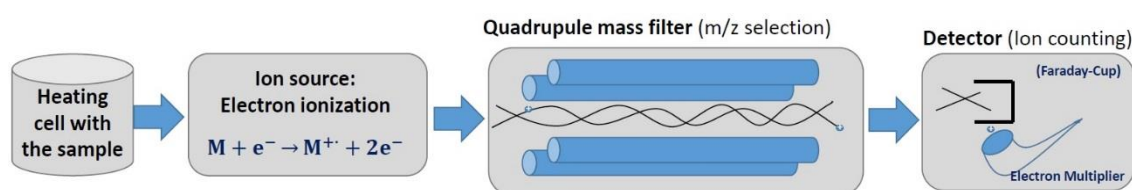


Figure 1.11: Experimental set-up using quadrupole mass spectrometer with electron ionization.

1.6 Gypsum as a By-Product of Desulphurization Process

Gypsum samples differ among the TPPs around the world. Their composition is dependent on the type of coal, APCDs and conditions in WFGD scrubber. Sampling and sample preparation are also important factors because the separation of gypsum slurry into fine and coarse part significantly differ in the final concentration of TMEs concerning bulk samples. In the present doctoral dissertation, different gypsum samples from Šoštanj and various Chinese TPP were studied. Differences in the composition can reflect in different mercury species present in the gypsum sample. Moreover, some elements such as Fe may change the releasing of Hg from the sample.

In this chapter short explanations are provided regarding the formation of gypsum, typical composition and properties of gypsum, the sources and the presence of TMEs in the gypsum, literature data related to Hg accumulation in the presence of Fe-species (minerals) and finally the overview of the existing literature describing stability and identification of Hg in various gypsum samples.

Since Hg is accumulated in the gypsum which is further reused or disposed as open stacks, Hg may be leaching by rain, resulting in the release to the surrounding groundwater and soil and causing further Hg pollution. Therefore, evaluating the Hg release for the reuse and disposal of gypsum is of environmental importance.

1.6.1 General description

Formation of gypsum: Gypsum is a major by-product of the WFGD forms when SO_2 reacts with $\text{CaCO}_3/\text{Ca}(\text{OH})_2$. The removed (and newly formed) gypsum slurry is transferred to a dewatering process immediately after the slurry is out of the absorber. This process often uses one or two hydroclones. The hydroclones separate the gypsum solids from the water using centrifuges. The underflow from the first set of hydroclones

contains the gypsum solids and is transferred to vacuum dewatering belt. The vacuum dewatering belt then removes additional water from the gypsum, drying the gypsum to its desired moisture content. The central FGD slurry dewatering device is usually shared by multiple units in many power plants. In this case, the gypsum collected in the vacuum dewatering belt does not represent the real mercury content within a specific unit. Hence, the gypsum slurry is collected from the exit of each absorber, and the water is separated to obtain the desired gypsum sample (Sui et al., 2015). Operation conditions in FGD scrubber and species entering in the system influence the formation of Hg-compounds which are later retained in the gypsum.

The composition of gypsum: In WFGD slurry, a solid fraction (gypsum) represents about 10-15% of slurry solution (Frkal, 2013; Kairies, Schroeder, & Cardone, 2006; Stergaršek et al., 2008). It is mostly composed of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ while minor amounts represent silica, alumina, iron oxide, and other minerals (Beatty, Schroeder, & Beatty, 2012; Kairies et al., 2006; Sun et al., 2014). Gypsum slurry taken from the main scrubber settles in two layers, whereby the upper has a brownish colour, with much smaller particle size, and the bottom layer is white-grey, with larger particles. The fine fraction represents about 10% of the bulk gypsum (Frkal, 2013). Literature data suggest that the upper, brownish layer (slower-settling layer) contains much greater amounts of Hg and other (trace) elements, such as Al, Fe, Mg, Mn, Ti and Ba (Kairies et al., 2006; Stergaršek et al., 2008).

It is worth mentioning that the limestone slurry used in the desulphurisation technique acts as a scavenging system not only for sulphur but also for other high volatile elements such as F, Cl, Hg, As, Se and B present either in the gas emissions or condensed on the small particles escaping to the electrostatic precipitators (ESPs) (typically <1%) before entering in the FGD installation (Cheng et al., 2009; Ito et al., 2006; Meij & te Winkel, 2007), and for other trace elements (Cd, Cr, Cu, Ni, Pb, Zn, Ba, Mo) enriched in these particles (Álvarez-Ayuso et al., 2006). Once captured, a certain proportion of the trace pollutants distributes into solid by-products (gypsum) and water streams (gypsum slurry water and filtered water) (Córdoba et al., 2011; Córdoba, Castro, Maroto-Valer, & Querol, 2015). Low proportions release in a gaseous and PM form (Stergaršek et al., 2008).

Hg and gypsum in China: A considerable amount of Hg is bound to the FGD gypsum. Hao et al. studied FGD gypsum samples from 70 coal-fired power plants in 20 Chinese provinces, and the results showed that the Hg concentrations in FGD gypsum ranged from not detectable to $4330 \pm 620 \mu\text{g kg}^{-1}$ (Hao et al., 2016). It follows that providence in the northern part of China had lower average Hg concentration in FGD gypsum than in the middle or southern part where average concentrations are relatively high. Additionally, the correlation between Hg concentrations in FGD gypsum and Hg in the coal is hard to build by taking into account the APCDs and the regional information about the Hg concentration in coal (Hao et al., 2016). Since coal in China has variant and relatively high Hg content (Mukherjee et al., 2008; L. Zheng, Liu, & Chou, 2007) and considerably lower Cl content, which plays a significant role in promoting the oxidation of Hg(0) to Hg(II), results from previous studies for other countries can hardly be considered representative of China.

Sources of elements: As already mentioned, significant sources of TMEs in the gypsum slurry are attributed to the flue gas with fly ash particles (Clarke & Sloss, 1992; Klein et al., 1975; Meij, 1994a; M. Xu et al., 2004) not retained in the particle control devices (Bunt & Waanders, 2010; Galbreath et al., 2000; López-Antón et al., 2011; Otero-Rey et al., 2003; Pavlish et al., 2003) and limestone added to the WFGD system (Ochoa-González et al., 2013; Beatty et al., 2012; Kairies et al., 2006; Liu et al., 2013; Shuetze et

al., 2012). Small particles pass through the ESP, reach the WFGD device and are retained there due to adsorption, co-precipitation or other chemical reactions (Stergaršek et al., 2010, 2013). Limestone that is continuously added into scrubber contains elements such as Mg (as dolomite, $\text{CaMg}(\text{CO}_3)_2$), Si (quartz, SiO_2), Fe, Mn, Al and other metals (Ochoa-González, Díaz-Somoano, & Martínez-Tarazona, 2013). Although TMEs significantly accumulate in gypsum (Liu et al., 2013), a smaller amount is emitted to the atmosphere through the stack gas (Helble & Sarofim, 1993; Otero-Rey et al., 2003). The control of emissions in the gaseous phase and small particulates is crucial. In power plants equipped with WFGD and WESP systems both emissions are reduced (C. Zheng et al., 2017).

Applications: Gypsum is used in the production of wallboard (Beatty et al., 2012; Heebink & Hassett, 2005; Kairies et al., 2006; X. Liu et al., 2013; Milobowski et al., 2001), as a cement replacement in concrete/grout, structural fill, stability components for waste and soil, as a road base, mineral filler, concrete block, and blasting grit (Álvarez-Ayuso & Querol, 2007; Clark, Ritchey, & Baligar, 2001; Jinman Wang & Yang, 2017; Zhou, Zhongyang, Yanqun, & Mengxiang, 2013). It could be disposed of in a landfill. These materials are getting stabilised by mixing with fly ash and lime before disposed of in landfills, structural fills, or mines (American Coal Ash Association, 2009). The fate of mercury during the management of FGD gypsum in such scenarios is mainly dependent on its species. Therefore, the stability (and identification) of Hg and Hg-compounds needs to be controlled to avoid its release/leaching into the environment. According to the Slovenian Waste regulation, the maximum permitted concentration of mercury in solid waste is 20 mg kg^{-1} and in liquid waste 0.05 mg L^{-1} (Uradni list 103/2011, 2011).

1.6.2 Mercury in relation with other TMEs in the gypsum

Fe, Al, K, Mg, Si, and S were the most common elements found in gypsum samples, indicating some of the minerals responsible for affecting the Hg-adsorption to iron oxides, iron hydroxide, phyllosilicate minerals (illite $(\text{K},\text{H}_3\text{O})(\text{Al},\text{Mg},\text{Fe})_2(\text{Si},\text{Al})_4\text{O}_{10}[(\text{OH})_2,(\text{H}_2\text{O})]$, glauconite $(\text{K},\text{Na})(\text{Fe}^{3+},\text{Al},\text{Mg})_2(\text{Si},\text{Al})_4\text{O}_{10}(\text{OH})_2$) and iron sulfides (Beatty et al., 2012; Kairies et al., 2006). These compounds are commonly present in the limestone that is introduced into a WFGD system (Beatty et al., 2012; Evans & Elmore, 2006). However, iron may be derived in the gypsum from both sources, from coal (as fine fly ash) and limestone (Gustin & Ladwig, 2010). In actual WFGD gypsum samples, a higher concentration of mercury was found to be present in the fractions enriched with iron (Beatty et al., 2012; Kairies et al., 2006). The literature indicates that some oxides and hydroxides (e.g., Fe, Al and Mn) may govern the adsorption process of Hg in solution (Inoue & Munemori, 1979; C. S. Kim, Rytuba, & Brown, 2004a, 2004b; Lockwood & Chen, 1973; Stergaršek et al., 2013, 2010; Tiffreau, Lützenkirchen, & Behra, 1995).

Leaching test proposes strong chemical adsorption rather than physical adsorption of Hg to the surface (Kairies et al., 2006). In the presence of Fe-compounds such as iron oxides and hydroxide, strong chemical adsorption could be possible in the gypsum (Beatty et al., 2012). A positive correlation between Fe (Al) and Hg was found in many studies (Beatty et al., 2012; Kairies et al., 2006; C. S. Kim et al., 2004b; Sun et al., 2014). It follows that in the iron-rich fine fraction of the FGD gypsum most of the PBM is retained (an average of $(85 \pm 15) \%$) (Kairies et al., 2006; Shuetze et al., 2012). Mercury may accumulate (adsorbed) also on precipitates of MnO_2 or Fe(oxy)hydroxides that formed during the simulation experiments of WFGD scrubber (Stergaršek et al., 2010, 2013). In the extraction procedure using diluted acid, the residue of gypsum sample demonstrates accumulation of Hg in addition to Fe and Al, whereas the proportion of gypsum as $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is small. This indicates the importance of iron or iron/aluminium phase for

Hg accumulation (K. Schroeder & Kairies, 2005). Serrano et al. (2012) found that Hg(II) could form a Hg-Al precipitate and Hg-Fe-precipitate in the presence of Ca, SO_4^{2-} and Fe or Al (Serrano, Vlassopoulos, Bessinger, & O'Day, 2012). Hg-complex with Fe and Al shows a high affinity to the materials in FGD gypsum (Hao et al., 2016). Mercury as Hg(I) mostly associated with iron oxide was proved by XAS study due to the association with the iron that leads to more stable mercury form (Al-Abed, Jegadeesan, Scheckel, & Tolaymat, 2008). In the processes where a fine fraction is not allowed to be separated, the output gypsum will contain increased Hg concentration (Shuetze et al., 2012).

Mercury and different substrates: Mn and Fe show an important role in the oxidation of mercury. They could act as a catalyst for Hg oxidation. Due to the simultaneous formation of precipitates, this should be continuously removed (Stergaršek et al., 2010, 2013). However, Hg could also be trapped there. Since WFGD gypsum from Šoštanj TPP contains an elevated concentration of Fe relative to the Hg, we performed simple experiments using FeOOH (in addition to SiO_2 , $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Al}(\text{OH})_3$). We observed the influence of different substrates on Hg TPD spectra using dry or wet mixtures. We focused mainly on Fe due to the possible catalytic role at increased temperature and adsorptive surface. For detailed studies about Hg adsorption/desorption on FeOOH (and other Fe-oxides(hydroxides)) in WFGD scrubber, we should simulate the conditions present in WFGD scrubber of Šoštanj TPP. However, this was not the main purpose of this work but rather to observe the effect and differences on Hg TPD spectra by using different substrates.

According to the literature data, all substrates used are not stable at higher temperatures. They change their crystal structure or lost structurally bound water. For example, in case of FeOOH dehydration (removal of structurally bound water) occurs at temperatures above 200 °C (226-239 °C according to (Galwey & Brown, 1999) and 275 °C (Balek & Subrt, 1995)) where Fe_2O_3 is formed. Similar dehydration appears with $\text{Al}(\text{OH})_3$ where Al_2O_3 is formed. In case of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ water is removed in two steps (around 100 and 200 °C). SiO_2 transforms from one crystal phase to another at temperatures above 500 °C. Structural changes might influence the releasing of Hg.

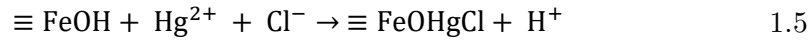
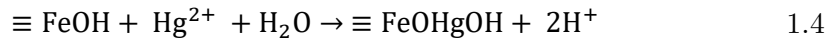
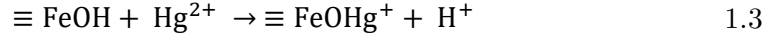
Adsorption process in solution: Mercury adsorption is an important process, which depends on the ligands and minerals (particles) present in WFGD slurry (C. S. Kim et al., 2004a, 2004b). The surface of iron oxides and hydroxides represents the sites of many sorption reactions (Al-Abed et al., 2008; Bonnisel-Gissinger, Alnot, Lickes, Ehrhardt, & Behra, 1999; Gunneriusson & Sjöberg, 1993).

Most ligands will lower or enhance the adsorption of metal cations due to several possible processes including (a) formation of stable nonadsorbing metal-ligand aqueous complexes; (b) formation of metal-ligand ternary surface complexes, which at high metal and ligand concentrations can lead to surface precipitation; (c) competitive ligand sorption to particle surfaces, effectively blocking the more reactive sorption sites at the surface; and (d) reduction of the positive charge at mineral surfaces, thereby lowering the electrostatic repulsion of cations by the surface (C. S. Kim et al., 2004a, 2004b).

Formation of sorption complexes: INNER SPHERE is the formation of a direct chemical bond between Hg(II) and the substrate surface, while OUTER SPHERE complexation of Hg(II) is sounded by a solvation shell of water molecules sorbs in a specific or non-specific electrostatic or hydrogen-bonded manner.

The importance of ligands (chloride, sulphate) presents in solutions that increase/decrease the Hg sorption to mineral sorbents such as goethite ($\alpha\text{-FeOOH}$), γ -alumina (Al_2O_3) and bayerite ($\beta\text{-Al}(\text{OH})_3$) has been demonstrated (C. S. Kim et al., 2004b). Several studies have reported a shift in the macroscopic Hg(II) adsorption edge to higher

pH levels as a function of Cl^- , indicating that Hg(II) sorption is inhibited as Cl^- increases (Gunneriusson & Sjöberg, 1993; C. S. Kim et al., 2004b). This inhibition is considered to be due to the formation of HgCl_2 (aq) ($\text{Cl}^- > 10^{-3}$), which is stable in solution and less prone to sorption (Mac Naughton & James, 1974). Hydrolysis reactions with the formation of HgOH^+ and Hg(OH)_2 prevail when the pH raised (C. S. Kim et al., 2004a). If no other ligands are present in water solution, Hg(OH)_2 is the dominant phase at pH around 3 (Gunneriusson & Sjöberg, 1993; C. S. Kim et al., 2004a; Lockwood & Chen, 1973; Mac Naughton & James, 1974). In the presence of competing ligands such as Cl^- , $3 < \text{pH} < 8$ three complexes are suggested ($\equiv$ surface) (Gunneriusson & Sjöberg, 1993):



Also, higher adsorption of Hg(II) was observed with increasing SO_4^{2-} which suggests inner-sphere sorption of Hg(II) rather than outer-sphere sorption. In the absence of ligands, the prevailing mechanism is hydrolysis, at a higher pH ($\text{pH} > 3$) Hg(OH)^+ and Hg(OH)_2 form (Bonnissel-Gissinger et al., 1999; Gunneriusson & Sjöberg, 1993; C. S. Kim et al., 2004a). Higher adsorption of Hg(II) occurs at an elevated concentration of FeOOH and low chlorine concentration. (Gunneriusson & Sjöberg, 1993).

Molecular-scale knowledge of the interactions between Hg(II) , complexing ligands, and particles found in WFGD scrubber is necessary for understanding the roles of these ligands in metal-ion sorption processes at gypsum–water interfaces. However, the chemistry in WFGD is very complicated, and a lot of factors might influence the identity and the presence of mercury species. This information is also important in predicting the effect of changes in ligand concentrations on Hg(II) adsorption/desorption processes during Hg transport in the desulphurization process. All the studies describing the adsorption of Hg to Fe-matrices used pure adsorbent, and thus the results could not be fully implemented to the actual samples. WFGD gypsum are very complicated matrices containing a lot of other species not only Fe. Nevertheless, adsorption studies of Hg to Fe-oxide(hydroxides) are important to better understand this process in the solution, thus suggesting a possible mechanism of Hg -adsorption and formation of different Hg -complexes in the WFGD slurry.

1.6.3 A review of existing literature based on the identification of mercury compounds in gypsum using TPD method

In the previous subchapter different authors suggest the importance of Fe in the accumulation of Hg in the gypsum and the formation of various Hg species in solutions where different adsorptive surfaces exist. Mercury reactions in gypsum slurry are very complicated (see a more detailed description in Chapter 1.4.4) and the absorbed Hg(II) in the slurry may also be reduced and released as Hg(0) (Ochoa-González, Díaz-Somoano, & Rosa Martínez-Tarazona, 2013; T. Tang et al., 2010; Wo et al., 2009). In the study of Sun et al. it is suggested that the excess sulphite and chloride would react with Hg(II) to form HgSO_4 , HgSO_3 , $\text{Hg(SO}_3)_2^{2-}$, ClHgSO_3^- and $\text{Cl}_2\text{HgSO}_3^{2-}$, which could inhibit Hg(II) reduction. These compounds, together with those that are formed by the addition of additives, seem to be readily retained by the gypsum (Sun et al., 2015; Q. Tang et al., 2013). In the absence of chlorine formation, HgSO_4 is suggested to form which would be hydrolysed in water, precipitating to the basic sulphate, $\text{Hg}_3\text{O}_2(\text{SO}_4)$ (Acuña-Caro et al., 2009; Y. Wang, Liu,

Wu, Mo, & Cheng, 2010). On the other hand, oxidised mercury can be absorbed by the solid particles present in the slurry after SO_2 -CaO reaction (Akiho, Nunokawa, & Shiras, 2003). On the other hand, some other Hg-compounds (typically HgCl_2 , Hg_2Cl_2 , HgO , HgS and HgSO_4) have been identified by many authors using TPD approach (Córdoba, Maroto-Valer, et al., 2012; J.-Y. Lee et al., 2009; X. Liu et al., 2013; Milobowski et al., 2001; Rallo et al., 2010; Sedlar et al., 2015; Sui et al., 2015; Z. Zhu et al., 2016; Zou et al., 2016).

In general, thermograms of different gypsum samples obtained by using TPD method reveal various mercury compounds present. According to the Heebink and Hassett, (2005), three mercury species are the primary Hg compounds likely to be incorporated into WFGD gypsum: HgCl_2 , HgO , and possibly $\text{Hg}(\text{NO}_3)_2$. However, HgCl_2 is the most probable mercury species present in bulk. Lower concentrations of $\text{Hg}(0)$ can also be present. Even $\text{Hg}(0)$ incorporated into FGD material is likely to be complexed or bound in some manner. The low concentrations of free $\text{Hg}(0)$ emitted by unheated FGD material confirm its presence (Heebink & Hassett, 2005).

In the study of Zhu et al. (2016), TPD and SEP methods were employed to identify the Hg species in FGD gypsum from China. Hg-compounds determined by TPD method showed the presence of HgCl_2 , Hg_2Cl_2 , Hg_2SO_4 , black HgS and red HgS , among which both HgS species prevail. The author suggested no direct connection between Hg-compounds present, coal types and APCDs. Hg in FGD gypsum would release as $\text{Hg}(0)$ later in industrial heating processes. The results of SEP show that the Hg in FGD gypsum was relatively stable (extracted in Fractions 4 and 5) and thus the leaching of Hg should be very low in the natural environment (Z. Zhu et al., 2016). However, low Hg concentration in gypsum sample made results of SEP questionable and the TPD method seems to be more appropriate (Reis et al., 2012).

Milobovski et al. found two distinct Hg compounds in FGD slurry, released at about 300 and 400 °C. HgSO_4 released at higher temperatures while at 300 °C either HgS or HgO could be present. They used only four different standards to identify Hg compounds present where HgS and HgO overlapped each other (Milobowski et al., 2001).

Thermograms of two different gypsum samples from Spanish power plants indicate the presence of two distinct Hg-species as well. Sample with Hg releasing at about 120 °C might be attributed to HgCl_2 while the one released at a higher temperature may be HgS (Rallo et al., 2010).

In the study of Lee et al. (2009) none of the standards fits with thermograms obtained from gypsum samples but the possible species to be present in gypsum were HgCl_2 and Hg_2Cl_2 (J.-Y. Lee et al., 2009).

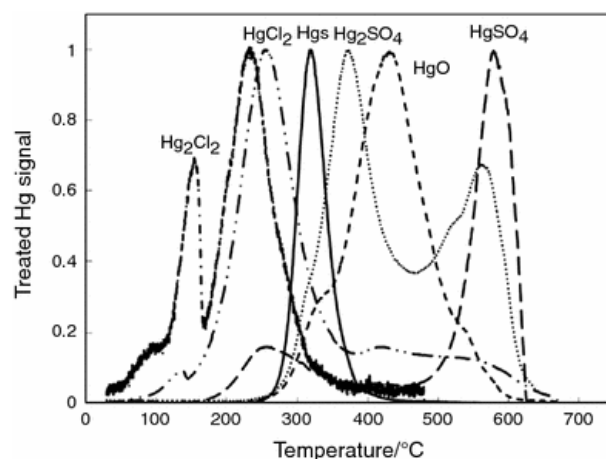


Figure 1.12: The thermal release of mercury standards presented in the study of Sui et al. (Sui et al., 2015).

Sui et al. (2015) analysed WFGD samples from five power plants in China all using the WFGD process with forced oxidation. All samples exhibit similar thermograms' form, where the predominant mercury species are suggested to be HgS, followed by HgO, Hg-chlorides, and also a small amount of Hg₂SO₄ and HgSO₄. The origin of HgS was explained by possible disproportionation of sulphite ion to sulphate and sulphide ions (Sui et al., 2015).

In a similar work of Liu et al. (2013), WFGD samples from eight Chinese power plants were analysed. HgCl₂ and black HgS were found as the primary species present in the gypsum sample, but Hg₂Cl₂, red HgS, HgO and HgSO₄ could be present as well. In the wallboard production process, 10–50% of mercury could be released from the FGD gypsum into the atmosphere. Releasing of mercury compounds at higher temperatures is related to the more stable Hg-compounds present in the gypsum, such as HgSO₄ and HgS compared to less stable HgCl₂ (X. Liu et al., 2013).

Both author groups (Liu et al. (2013) and Sui et al. (2015) used “treated gypsum” (preheated WFGD gypsum, Figures 1.12 and 1.13) as a matrix to prepare standards instead of pure CaSO₄ · 2H₂O reagent. These two works seem to be state of the art in the field since no other author group successfully measured thermograms of real WFGD samples that could provide reliable application of peak-fit approach/method.

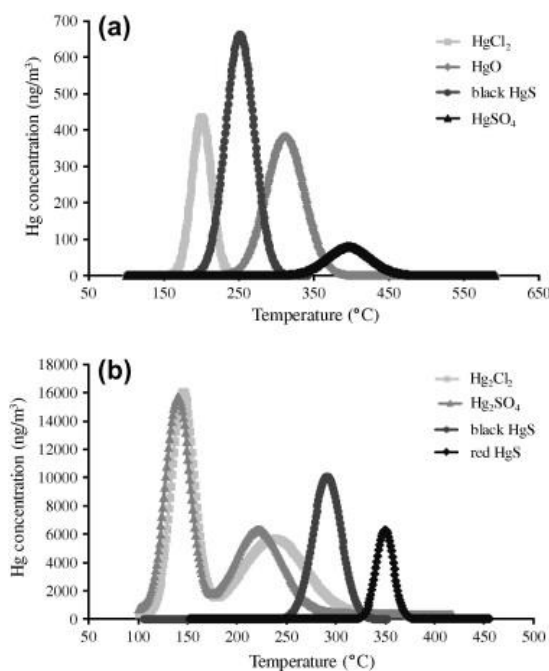


Figure 1.13: Thermal decomposition profiles of mercury standards: (a) HgCl₂, HgO, black HgS, and HgSO₄; (b) Hg₂Cl₂, Hg₂SO₄, black HgS and red HgS (X. Liu et al., 2013).

Similar results for mercury standards are provided in our previous studies of Sedlar et al. (2015) (Sedlar et al., 2015; Sedlar, Pavlin, Popović, & Horvat, 2015). For identification of Hg compounds in gypsum samples from the Šoštanj TPP, standard addition procedure using synthetic gypsum spiked with pure Hg compounds was applied. It was revealed that the substantial proportion of Hg in gypsum belongs to Hg-Cl and Hg-Br compounds are appearing at 160 to 200 °C, followed by smaller amounts of HgO, HgS and Hg sulphates appearing at 300 and 450 °C. Industrial gypsum samples were compared with pure Hg compounds (mercury standards, Figure 1.14), and the compounds mixed with different substrates (SiO₂ and CaSO₄ · 2H₂O), for calibration purposes.

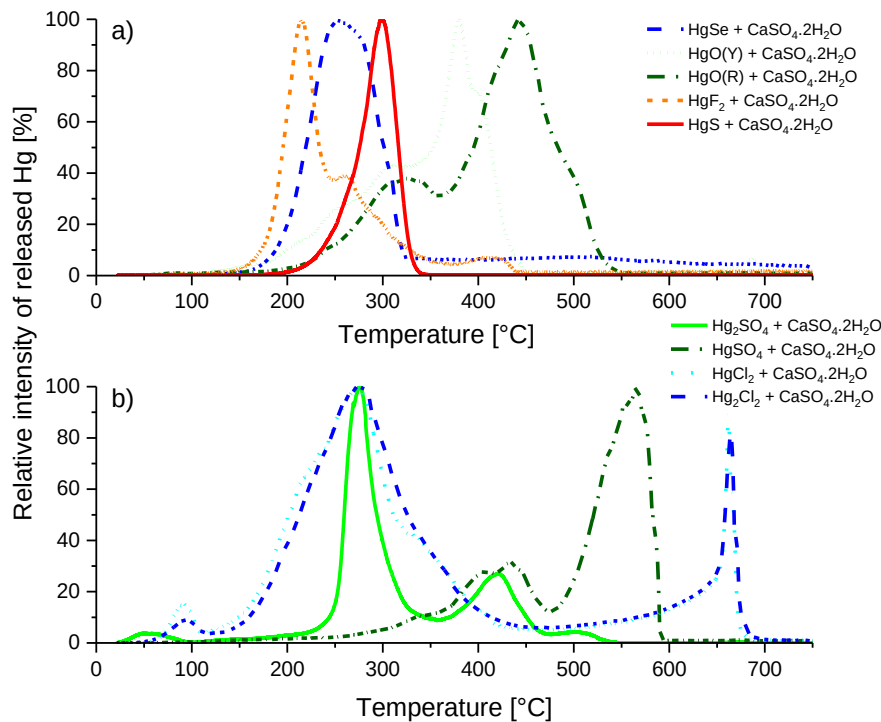


Figure 1.14: Thermal decomposition profiles of mercury standards, mixed with $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$: (a) HgSe , HgO(Y) , HgO(R) , HgS , and; (b) HgCl_2 , Hg_2Cl_2 , Hg_2SO_4 and HgSO_4 (Sedlar et al., 2015).

In the investigation of Z.-W. Zhu et al. (2017), HgS represents the species that is mainly present in the gypsum samples. Although HgS is thought to be a stable compound, detectable amounts of Hg were continually emitting from all the samples probably due to mercury reduction of oxidised Hg in FGD gypsum and desorption/diffusion of $\text{Hg}(0)$ among gypsum particles. Moreover, study shows higher releasing during the day than in the dark at room temperature with UV radiation being the primary factor for re-emission. However, those emissions are low. On the other hand, enhanced Hg releasing from the gypsum is observed in the presence of water (e.g., precipitation events in the environment), when gypsum is exposed to the solar radiation and at increased temperature (Z.-W. Zhu, Zhuo, Fan, & Wang, 2017). Temperature, solar radiation, and soil moisture content have been found to be critical parameters that influence Hg release from solid samples such as gypsum (Briggs & Gustin, 2013; Gustin & Ladwig, 2010; Moore & Carpi, 2005).

Stability and identification of Hg species in gypsum samples are important due to the environmental exposure (after disposal) and when it is used in further production. Most of the authors determine Hg -species according to "calibration standards" using pure Hg -compounds mixed with different substrates or with "treated" gypsum samples containing no mercury. However, this approach is not the best one due to the sample matrix that contains different species which may influence Hg releasing. Moreover, identification of mercury compounds is difficult and overlapping of the peaks may occur in actual samples compared to a separated peak of standards. Until now, there is no standardized method to calibrate the measuring system and differences among laboratories exist.

Heating of gypsum to higher temperatures may induce a substantial change in the solid characteristics. Moreover, all Hg compounds (also the most stable) start to evaporate when the appropriate temperature is achieved. In the presence of a catalyst (e.g. FeCl_2), a

sufficient amount of Hg is removed quickly, at lower temperatures (Matsuyama et al., 1999). It follows that sample matrix could change TPD spectrum, and the mercury species which would originally release at lower/higher temperatures show completely different TPD spectrum. Similar is the peak shape that becomes narrower, broader or changed the shape. Therefore, the results obtained by the TPD method are sometimes questionable. Many researchers indicated the presence of different Hg species in their gypsum samples, but only a few of them take into account the importance of matrices and thus the presence of other species in the sample. It follows that interpretation of the TPD spectra provided by different authors is not necessarily correct. Hence, additional characterization of the samples may give useful information for better identification of mercury compounds; for example to get the data for i) sample composition (the presence of different chemical elements, multielemental analysis), ii) particle size distribution due to the higher accumulation of most TMEs in fine particles, iii) chemical/physical phenomena and structural information about the sample (TGA, SEP, SEM, TEM, XRD, direct methods using XAS and other methods).

An important part in the determination of mercury species in solid samples is also sampling, sample preparation and handling. With inappropriate sampling, the sample may change the original composition (presence and concentration of TMEs). It follows that due to different properties and conditions in the sample, Hg-compounds may change, and identification becomes more difficult. Moreover, manipulation of the samples may change TPD spectra, and thus the original identity of mercury compounds present in the raw sample is unknown.

In the doctoral dissertation of Matej Sedlar (Sedlar, 2014) we investigated the stability of various mercury compounds in solid samples at higher temperatures by mixing of different mercury compounds with two different substrates (SiO_2 and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). We found out that stability of mercury compounds is not dependent only on their decomposition/sublimation temperatures but rather by other factors such as matrices, heating rate, carrier gas, flow rate, etc., which affect their releasing temperature. The present doctoral dissertation represents a continuation and upgrading of the work of Sedlar (Sedlar, 2014). Overall, the main aim of this study was to evaluate the possibility of identification of mercury compounds in solid samples, in particular in the gypsum, by using MS instead of CV AAS. Regarding this, we try to identify mercury compounds present in the gypsum by observing other decomposition fragments (volatile species) and thus predict the decomposition reactions (reaction pathway) present at elevated temperatures. However, doctoral thesis encompasses different fields such as sampling and sample preparation, studying the stability of mercury compounds and effect of different substrates on mercury releasing during the TPD process, compare dry and wet method for preparation of mercury standards and observe their TPD spectra during the thermal process, and to see the effect of sample manipulation and aging of the sample on TPD spectra. Because fine fraction in gypsum samples from Šoštanj TPP contains higher concentrations of most of the TMEs compared to coarse fraction, the effect of particle size and the presence of other metals (e.g., Fe and Al) were studied to see the influence on Hg releasing. Distribution of TMEs (not only mercury) during coal combustion was examined for a better understanding of the behaviour and their partitioning/accumulation in the gypsum and other by-products of the combustion process and flue gas cleaning.

Chapter 2

Aims and Hypothesis

The main objective of the present work was to develop and validate a new method for identification of mercury compounds present in solid samples, in particular gypsum, by using temperature programmed desorption (TPD) coupled with mass spectrometry (MS). Typically cold vapour atomic absorption spectrophotometry (CV AAS) is used to detect released Hg(0), however, in the present work CV AAS detection was replaced by the quadrupole mass spectrometer (QMS) approach. MS has several advantages over CV AAS such as better sensitivity and a possibility to detect mercury species and other volatile compounds released during increasing temperature programme. Based on these facts the hypothesis and specific aims have been identified and guided the work of the present research.

The main aims and goals of this doctoral dissertation are:

- To characterize different gypsum samples from Šoštanj TPP with respect to TMEs in different grain sizes;
- To develop and optimize TPD methodology by using QMS as a detector;
- To study the decomposition of mercury compounds and compare the experimental data with theoretical calculations (e.g., HgCl₂);
- To identify mercury compounds present in solid samples and to understand the decomposition pathways of some mercury compounds at higher temperatures based on decomposition fragments (volatile species other than Hg);
- To differentiate between weakly adsorbed mercury (e.g. Hg(0)) and mercury strongly bounded in the matrix;
- To compare the results obtained by TPD-QMS method with a direct method based on X-ray Absorption Spectroscopy (XAS) method;
- To evaluate the influence of other compounds (substrates) on mercury adsorption/retention during the TPD process (SiO₂, CaSO₄ · 2H₂O, FeOOH, Al(OH)₃);
- To study the stability of mercury compounds in gypsum samples obtained from Chinese TPP.

Hypotheses:

- The presence of TMEs in gypsum is strongly dependent on the gypsum particle size, FGD set-up and APCD processes in coal-burning power plant;
- MS offers better detection limits compared to CV AAS, and apart from mercury species it allows identification of other decomposition products released during temperature programmed heating;

- Sampling of gypsum, its preparation procedures prior TPD analysis and age of the sample may affect gypsum properties and consequently affect the Hg TPD curves;
- Due to different concentrations of TMEs in gypsum, the TPD spectra from different power plants as well as from different blocks of the same power plant differ significantly.
- TPD coupled with CV AAS and/or QMS is an indirect method and is not a reliable method for the identification of Hg compounds in gypsum due to matrix interferences during the heating process.
- The elevated concentrations of selected elements (Fe, Al) may considerably effect the TPD spectra, which limits the identification of Hg compounds;
- TPD is a useful method for studying the temperature stability of mercury in gypsum.

Chapter 3

Materials and Methods

3.1 Materials

Nine different **mercury compounds** were used for standards and mixture preparation. Hg-compounds, suppliers and declared purity are described below:

- HgCl_2 – old chemical, Kemika d.d., Zagreb (99%)
- HgCl_2 – new chemical, Sigma-Aldrich Co. LLC. ($\geq 99.998\%$)
- Hg_2Cl_2 – Sigma-Aldrich Co. LLC. ($\geq 99.5\%$)
- $\text{HgO}(\text{red})$ – Sigma-Aldrich Co. LLC. ($\geq 99.5\%$)
- $\text{HgO}(\text{yellow})$ – May & Baker Ltd. ($\geq 99.5\%$)
- $\text{HgS}(\text{red})$ – Mallinckrodt Chemical Works (99%)
- HgSe – Sigma-Aldrich Co. LLC. (99.9%)
- Hg_2SO_4 – Sigma-Aldrich Co. LLC. (98.0%)
- HgSO_4 – Sigma-Aldrich Co. LLC. ($\geq 99\%$)

Other chemicals used for experiments:

- Quartz, white powder, fine granulated, washed and calcined for analysis; Merck KGaA (99 – 100.5% purity of substance is calculated on calcined substance)
- $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, white powder; Sigma-Aldrich Co. LLC. (99 – 101% purity of substance is based on anhydrous substance)
- $\text{FeO}(\text{OH})$ -, Iron(III) hydroxide, brown powder; Alfa Aesar (-phase, 99+ %)
- Aluminium hydroxide, white powder; Acrös organics (extra pure).

All aqueous solutions and reagents used in the experimental work were prepared with MilliQ water (18.2 M Ω cm) (Millipore, Bedford, MA, USA).

Equipment used for sample preparation:

- pH-indicator strips, pH 0 - 14; Universal indicator, Merck
- Mass balance: Mettler Toledo AT201 (max 210 mg, d = 0.01 mg)
- Centrifuge: Tehnica, Železniki, LC-320
- Ultrasonic Homogenizer 4710 Series; Cole – Parmer Instrument Co.; Chicago, Illinois 60648 U.S.A.
- Glassware and other equipment.

3.2 Instrumentation

3.2.1 Experimental apparatus for mass spectrometry

Nier type mass spectrometer (NT-MS): In the initial stage of experimentation, a single focusing magnet MS equipped with Nier type ion source was used. The spectrometer was earlier employed in Knudsen effusion experiments (KEMS method) (Knudsen, 1915). The detailed description can be found elsewhere (Popovič, 2003). For the present purposes, the solid sample was placed into one end of a semi-closed quartz tube (introduction tube with a length of 10 cm and 3 mm of inner diameter; instead of the Knudsen cell) while the open end was tightly fit into the ionization volume of the Nier ion source (Figure 3.1). The sample end of introduction tube was heated by nozzle type resistivity heater equipped with B type thermocouple (Ni/CrNi). Typical mass of the sample is 1-10 mg. The sample was then heated to 750 °C at 10 °C min⁻¹ and regulated using an EUROTHERM regulator. The desorbed atom or molecular species were ionised at 35 eV, mass separated in a 60° magnetic separator and the ion abundances measured with an electron multiplier. The desorbed molecules (atoms) were introduced directly into the ion source of the mass spectrometer under a high vacuum (<10⁻⁵ Pa) without a carrier gas. The interactions of the desorbed species with the walls of the quartz cell were minimized, and any sudden changes in desorption were instantly registered without being smeared by the mixing effect due to the carrier gas. In addition, all desorbed species enter an almost closed ion source (resulting in a higher concentration of ions), which increases ionisation, and in turn enhances sensitivity.

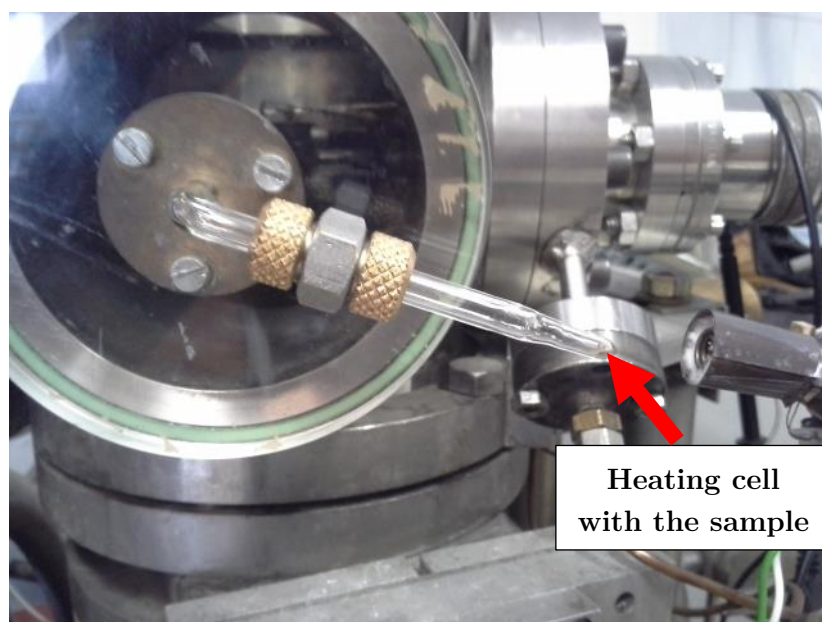


Figure 3.1: A heating cell with the sample (NT-MS).

Quadrupole mass spectrometer (QMS): For the majority of TPD measurements, the Quadrupole mass spectrometer (QMS) was employed (Pfeiffer QMS 700). The desorbed atoms or molecular species were ionized at 70 eV, mass separated in a quadrupole mass analyzer and the ion abundances measured with an electron multiplier. The QMS's high dynamic range enables the measurement of ions with an abundance ratio of 10⁷, which is a definite advantage over the Nier-type instrument. An additional benefit of using QMS is the possibility to identify different molecular species that might evolve from the sample upon heating at the same time. Sample introduction into its ionisation chamber was carried out similarly as with NT-MS, *via* thick wall quartz tube. The quartz tube was heated the

same as in the NT-MS. It also serves as a manipulator to insert the sample from the vacuum compartment close to the ion source. The declared sensitivity of the QMS is 10^{-6} A Pa $^{-1}$, which is sufficient to measure samples containing Hg concentrations as low as 5 ng g $^{-1}$. An additional benefit of using an MS as a detector is its ability to identify various molecular species that evolve from the sample when heated.

Experimental set-up: QMS is separated into two parts, pre-chamber and the central part (the main) of the spectrometer (Figure 3.2). The central part consists cross beam ion source, quadrupole mass filter (four parallel rods for filtering sample ions) and detector (Faraday-cup or secondary electron multiplier, SEM). It is tightly closed, and ultra-pump is responsible for maintaining constant vacuum during the introduction of the new sample in pre-chamber. In the second part (pre-chamber) is the quartz tube for sample introduction and the valve that should be open when the sample is inserted toward the ion source. With the aim to reduce the pressure difference between part one and two, rotary pump maintains the desired vacuum in the pre-chamber. Too big difference in a pressure could damage the device. The sample (Figure 3.2) was then heated to 750 °C at 10 °C min $^{-1}$ under high vacuum ($<10^{-5}$ mBar). The heating system is the same as in NT-MS using EUROTHERM regulation. The method is based on sample heating where volatile species go to the ion source, become ionised and then pass through the quadrupole rods where only ions of a specific mass-to-charge (m/z) ratio reach the detector. In this study, multiple ion detection mode (MID) was typically used for observation and detection of Hg and other volatile species in gypsum samples. Faraday counter was used for detection of H $_2$ O, CO $_2$, SO $_2$ that released in higher concentrations.

All TPD spectra obtained by QMS were corrected (fitted) to the real thermocouple temperature while in the case of NT-MS, peaks were not corrected and all maximum temperatures (peaks) appeared at the slightly lower positions (temperatures).



Figure 3.2: A heating cell with a sample (QMS). During analysis the cell is covered with the glass wool.

Interpretation of the results using QMS: Computer software QUADERA interprets the data as graphs continuously show the concentration of Hg ion (and other ions of interest) in the signal of ion current (A) as a function of time. The temperature is measured with analogue input.

All mass and TPD spectra (thermograms) were prepared using Origin 2017 software. Two different Hg isotopes, ^{200}Hg and ^{202}Hg , were measured simultaneously. The data for the ^{200}Hg isotope was used to prepare the TPD spectra due to its lower background compared to ^{202}Hg . The data are presented as a signal for the continuous measurement of Hg concentration in counts per second (CPS) on the ordinate axis *versus* temperature, °C on the abscissa axis. In this way it is possible to observe the release of Hg with incremental increases in temperature (thermograms, TPD spectra). For more straightforward comparison between the mercury species with different intensities, the intensity of a signal in a period was normalized to match the highest release of the peak to 100%.

CPS is recalculated according to ion current and the amplifications between Faraday cup and an electron multiplier. Amplification is typically between 5000 and 10000 and is determined in the separate test by observing various gases continuously present in the mass spectrometer (N_2 , O_2 , CO_2 , He, H_2O , Ar, etc.). Amplification should regularly be controlled.

3.2.2 Multi-elemental analysis of lignite, bottom ash, fly ash, limestone and gypsum samples using k_0 -INAA

The concentrations of major, minor and trace elements were obtained using the k_0 -standardisation neutron activation analysis method (k_0 -INAA). Homogenized samples (160–200 mg) were sealed into clean polyethylene ampoules (SPRONK system, The Netherlands), stacked together in sandwich form with an Al–0.1% Au alloy (IRMM-530R) standard and irradiated in a 250 kW TRIGA Mark II reactor (Jožef Stefan Institute, Ljubljana, Slovenia). Two irradiations were performed at a thermal neutron flux of $1.1 \cdot 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$: a short irradiation (5 minutes) to determine elements *via* their corresponding short half-life radionuclides and a second irradiation (12 hours) to determine elements *via* their corresponding medium or long half-life radionuclides. For QA/QC purposes, the certified reference material BCR-320R channel sediment was used. After an appropriate cooling time, samples were measured on a calibrated HPGe detector (45% relative efficiency). HyperLab software was used to evaluate peak area and the Kayzero software package to determine the elemental content and calculate the effective solid angle (Jaćimović, Smodiš, Bučar, & Stegnar, 2003; Smodiš, Jaćimović, Medin, & Jovanović, 1993; Xilei, Corte, Moens, Simonits, & Hoste, 1984).

The k_0 -INAA at the Department of Environment Sciences is accredited according to ISO/IEC 17025 since 2009 under accreditation certificate LP-090 awarded by Slovenian Accreditation (SA).

3.2.3 Statistical analysis

Correlations between separate elements were assessed using Pearson's correlation coefficients where P values of <0.05 were considered statistically significant. Statistical analyses were performed using STATA (version 12, StataCorp, TX, USA).

3.2.4 Determination of mercury in gypsum samples using DMA-80

DMA-80 (Direct Mercury Analyser; Milestone): About 20–40 mg of gypsum samples were weighed into the sample boat and placed in the auto-sampler. The sample is initially dried and then thermally decomposed at 650 °C in a quartz tube located inside a controlled heating coil. An oxygen stream passing through the tube carries the released Hg through the catalytic column, where Hg is reduced to $\text{Hg}(0)$. Hg vapour is collected on a gold amalgamation trap and subsequently desorbed into the absorption cell. Hg content is determined using atomic absorption spectrometry at 253.7 nm (Figure 1.10).

Table 3.1: Concentration of Hg in certified reference material BCR-277R (Estuarine sediment), ERM-CC141 (Loam soil), BCR-320R (Channel sediment) analysed at least in parallel with the determination of total Hg in gypsum samples.

Certified reference material	Certified value ($\mu\text{g kg}^{-1}$)
BCR-277R	128 ± 17
BCR-320R	850 ± 90
ERM-CC141	83 ± 17

The analytical quality of total Hg measurements was assured by regular analysis of the certified reference materials: BCR-277R (Estuarine sediment), ERM-CC141 (Loam soil), and BCR-320R (Channel sediment). Measured values were within the certified ranges (see Table 1.3). Unfortunately, gypsum reference material is not available.

3.2.5 Scanning electron microscopy (SEM)

Structural imaging and chemical characterisation of the solid particles (fine and coarse fractions) were obtained by field-emission-gun scanning electron microscopy (FEGSEM) performed on a JEOL JSM-7600F SEM equipped with an energy dispersive spectrometer (EDS) INCA Oxford 350. The samples were fixed with carbon tape and coated with amorphous carbon by evaporation (Balzers CED) and then morphologically and chemically characterised using the SEM. Images were obtained at a 5 kV accelerating voltage and 0.1 pA electron beam current, measured with an inside column Faraday cup.

3.2.6 Thermal gravimetric analyses (TGA)

Thermogravimetric (TG) and differential thermal analysis (DTA) were conducted on a Netzsch STA 409 C/CD coupled to a Balzers Quadstar 422 quadrupole mass spectrometer. Approximately 50 mg of the reagent mixture was heated in a Pt/Rh crucible. Thermal changes were recorded under a dynamic flow of synthetic air of 100 mL min^{-1} . Measurements were made from 25°C to 550°C at a rate of $10^\circ\text{C min}^{-1}$.

3.2.7 Particle size distribution

Particle size distributions were performed by Microtrac PSA FRA 9200 based on the Fraunhofer laser diffraction method. Each fraction was dried to a constant weight at 38°C in an electric dryer (MEMMERT UFE 500). All fractions were then oven dried to constant weight at 38°C in an electric drier/oven MEMMERT UFE 500. After drying, samples were homogenized in agate containers of a planetary mill (Fritsch planetary mill Pulverisette 7) or by grinding in an agate pestle and mortar.

3.2.8 X-ray absorption spectroscopy

Mercury L₃-edge XANES spectrum of the gypsum pelletized sample was measured at room temperature in fluorescence detection mode at XAFS beamline of the Elettra Sincrotrone Trieste, Italy, utilizing a silicon drift diode detector to collect the fluorescence signal. A double crystal Si(111) monochromator with an energy resolution of about 1.5 eV at 12 keV was used for the experiment and it was initially calibrated at Au L₃ absorption edge. The intensity of the monochromatized beam was monitored with three ionization detectors filled with Ar and N as follows: 70 mbar Ar + 1000 mbar N₂, 650 mbar Ar + 1350 mbar N₂, and 1620 mbar Ar + 380 mbar N₂. In the first detector, He was added to get a total pressure of 2 bars. The sample was placed between the first pair of detectors, and the reference

tungsten metal foil between the posterior pair, to check the stability of the energy scale and to obtain the exact energy calibration (W L_1 absorption edge: 12098 eV). The absolute energy reproducibility of the measured spectra was ± 0.02 eV.

The absorption spectra were measured within the interval $[-200$ eV to 857 eV] relative to the investigated absorption edge. In XANES region, equidistant energy steps of 0.3 eV were used. In total twelve absorption spectra were collected in the fluorescence detection mode; eight spectra were collected with an integration time of 10 s/step, while for the next four spectra the integration times were 9 s/step. Due to low Hg concentration, the repetitive spectra measurements last cumulatively 36 hours. The spectra of all identical runs were superimposed to improve the signal-to-noise ratio and to check the stability and reproducibility of the detection system. The XANES spectra were analyzed with the IFEFFIT package (Ravel & Newville, 2005).

3.3 Sampling and Sample Preparation

Dry gypsum samples were prepared from gypsum slurries taken from different batches (blocks 4, 5 and 6). Lignite was sampled in 2012 (LIG12). Additionally, ten gypsum samples were obtained from various power plants of China. All gypsum fractions/samples were subject to multi-elemental analysis, particle size distribution analysis and TPD method while for some samples also micrographic and thermogravimetric analysis was performed. The multielemental analysis was also done for LIG12.

3.3.1 Lignite samples

Two different lignite samples were obtained (LIG07 and LIG12) at random from a conveyor belt during a typical working day to ensure that they were representative. LIG12 was randomly sampled in 2012 from a conveyor belt during a normal working day to ensure representative samples. The combined mass of the samples was around 3 kg. They were dried to constant weight at 38 °C for a week in an electric oven (MEMMERT UFE 500). After the drying process, they were ground with a ball mill and sieved with a Fritsch Pulverisette 0 Vibratory Micro Mill to a particle size of less than 250 μm .

Lignite samples contained 36.4% of moisture, 13.8% of the mineral matter and 49.7% combustibles (66.2% C, 5.0% H, 1.4% N and 26.4% O) and had 11.137 kJ kg^{-1} lower caloric value (Stergaršek et al., 2008). The procedure and the data for LIG07 were taken from a study of Stergaršek (Stergaršek et al., 2008).

3.3.2 Fly and bottom ash, limestone

Samples were taken immediately after exiting from the boiler and the ESPs. They were placed in PVC zip lock bags at 4 °C and transported to the laboratory immediately. Limestone flour was taken before introducing into the desulphurization process. In the laboratory the samples were stored at -20 °C. Moisture content was determined in each sample by weighing before and after drying at 105 °C. All further results are expressed on a dry weight basis. The procedure and the data were taken from a study of Stergaršek (Stergaršek et al., 2008).

3.3.3 Preparation of gypsum samples

In this doctoral dissertation, the terms gypsum slurry, gypsum and slurry water are used. Gypsum slurry represents total slurry solution (liquid together with solids) while gypsum consists only moist solid fraction (bulk sample, a mixture of the coarse and fine fraction). The solid fraction in gypsum slurry is settled, and slurry water represents the liquid above

the solid fraction that contains dissolved pollutants together with small particles, typically not seen or seen as an opaque solution. All samples were taken when the process in desulphurization scrubber was in steady-state to obtain representative samples.

3.3.3.1 Gypsum from Šoštanj Thermal power plant

Block 4 (sampling in April 2015): Gypsum slurry of about 50 liters was sampled from the WFGD scrubber and stored in a barrel. Different aliquots of gypsum slurry were taken to prepare dry gypsum samples for analysis:

- The mixed fraction with "normal" particle size distribution was taken. The slurry bottle was first homogenised (by shaking) and sample aliquot was taken immediately before coarse particles settle. Random sample, TEŠ4-MSN, was divided into three aliquots. Aliquots were not washed (TEŠ4-MSN_{notw}) or washed (rinsed) with distilled water (TEŠ4-MSN_w) or ethanol (TEŠ4-MSN_{et}). TPD spectra of different washing procedures were recorded.
- Additionally, TEŠ4-MSN was separated into finer and coarse fraction. Samples were centrifuged, dried and separated according to the different colour. Gypsum with the majority of coarse fraction (TEŠ4-CSN) was taken from the bottom. Coarse fraction was divided into two subsamples; one unwashed (TEŠ4-CSN_{notw}) and the second highly washed (TEŠ4-CS_{dw}, rinsed four times with distilled water). Finer fraction of TEŠ4-MSN was separated into upper lighter and bottom brown fine fractions to see if there are any differences according to the colour of the fine fraction (TEŠ4-FSN_{up} and TEŠ4-FSN_{down}). To see the effect of washing on TPD spectra of finer particles, one sample was not washed (TEŠ4-FSN_{downnotw}).
- After homogenisation, bigger particles of gypsum slurry settle and a small part above coarse fraction was taken (sample labelled as TEŠ4-FS). This aliquot contains mostly fine particles (less coarse fraction). Samples were centrifuged, dried and separated according to the different colour. The fine fraction was separated into three fractions, TEŠ4-FFS, TEŠ4-MFS and TEŠ4-CFS.

In all gypsum samples total Hg concentrations were provided by CV-AAS (DMA 80, Milestone). Also, TPD spectra were obtained for mercury compounds characterisation.

Block 5: Three samples of gypsum slurry were taken from an agitated tank (main scrubber) of the WFGD absorber. Each gypsum slurry was separated later according to the size fraction into a fine and coarse fraction. Two different separation techniques were conducted:

- a.) The first approach was based on separation of gypsum slurry particles with the help of a hydrocyclone (pilot version, laboratory set-up, Figure 3.3) into fine (FF) and coarse (CF) fractions labelled as TEŠ5-FF and TEŠ5-CF. Fractions separation is based on centrifugal force where denser coarse fraction settles at the bottom (underflow, TEŠ5-CF) and a lighter fine fraction at the top (overflow, TEŠ5-FF), of which the latter in actual WFGD hydrocyclone systems is recirculated back into the agitated tank as a recirculated slurry. Also, slurry water was also taken for elemental analysis (TEŠ5-W₁, TEŠ5-W₂). Samples were collected in May 2013.

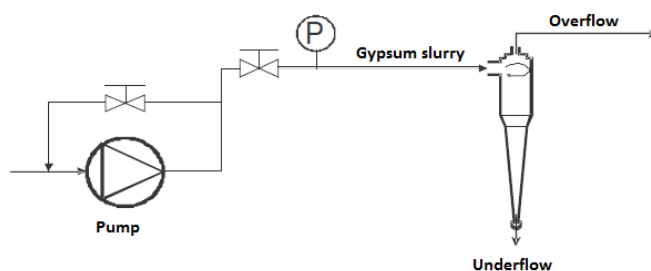


Figure 3.3: Scheme for separation of the finer (overflow) and coarse fraction (underflow).

- b.) The second separation involved two samples. Gypsum slurries were homogenised by shaking and left 72 hours to settle until two well-defined layers were formed. While the bottom layer consolidated rather quickly, it took several hours for the upper layer to separate particulates from clear water phases. After decantation, the water layer was extracted with a pipette yielding a creamy brown material. Using this approach, two particulate fractions were obtained, labelled as TEŠ5-FF1 and TEŠ5-CF1 for the first sample and TEŠ5-FF2 and TEŠ5-CF2 for the second sample. Samples were collected in December 2013 and January 2014. In this case, slurry water was not obtained for further analysis.

All samples were analysed for multielemental analyses, particle size distribution, micrograph structure and TPD analyses. The samples were not washed before measuring with MS.

Block 6 (sampling in July 2015): Three slurry samples were collected at different sampling points: one from the main scrubber (the absorber), and two from the hydrocyclone. The original gypsum slurry (ORIG) comprises a sample of the WFGD slurry from the main scrubber. Within the hydrocyclone, the gypsum slurry is separated into disposal gypsum (DISP), which escapes the hydrocyclone and is further processed for disposal and recirculated slurry water (RECY), which contains the finest particles and is pumped back into the main scrubber.

Once at the laboratory, each sample was homogenised (by shaking), transferred into a centrifuge tube (50 ml) and left to settle under gravity for 48 hours until two distinct layers were formed. Although the bottom layer representing the coarse fraction (CF) consolidated within minutes, it took at least 48 hours for the upper layer, i.e., the fine fraction (FF) to separate entirely from the water phase. Then, the water was decanted, and the remaining brownish slurry (FF) transferred to a clean centrifuge tube and centrifuged at 2500 rpm for 30 minutes. After again removing the water, the residual paste was transferred to four Teflon containers where it was left to dry. This resulted in four separate fractions: ORIG-FF, ORIG-CF, DISP-FF and DISP-CF. The RECY sample contained the finest particles and only one fraction was formed. A whole gypsum sample (ORIG gypsum, bulk; not separated;) was also prepared from gypsum slurry.

All samples were analysed for multielemental analyses, particle size distribution, micrograph structure, thermogravimetric analyses and TPD analyses. All samples were washed before TPD analysis.

In addition, one aliquot of ORIG gypsum slurry was separated into five different fractions later, four finer fractions (the finest fraction ORIG_S-FFF; a mixture of the finest and fine fraction ORIG_S-FFF + ORIG_S-FF; ORIG_S-FF, fine fraction; finer fraction brown precipitate ORIG_S-FF_{brown},) and one coarse fraction, ORIG_S-CF. Information about mercury content and the TPD spectra are provided for these samples. Samples were not washed before TPD analysis.

3.3.3.2 Gypsum samples from various Chinese thermal power plants

Ten gypsum samples from different power plants, packed in duplicate into plastic ZIP-lock bags (about 50 g each) were obtained. Samples differed in colour, odour, and humidity. The moisture content was determined by heating a few grams of samples at 38 °C for a week until a constant weight was achieved. Total mercury concentration was measured by CV AAS (DMA-80, Milestone). Also, multielemental analysis for TMEs was obtained. TPD method was applied in all samples.

In addition to gypsum samples, gypsum slurries from two Chinese TPP were obtained and separated into fine and coarse particles. TPD spectra of finer fractions were recorded.

3.4 Preparation of Different Dry and Wet Mercury Compound Mixtures

Dry preparation of Hg compounds with $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and SiO_2 : Eight pure Hg compounds (HgCl_2 , Hg_2Cl_2 , $\text{HgO}(\text{Y}, \text{R})$, HgS , HgSe , HgSO_4 , and Hg_2SO_4) were prepared by mixing with two different substrates (SiO_2 or $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ powders). A few milligrams (1-5 mg or 10-12 mg for SiO_2 and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ respectively) of Hg compound was added to 5 g of substrate powder. The mixtures were carefully homogenised by mixing in a zirconium container and mixed using a planetary mill (Fritsch planetary mill Pulverisette 7). Mercury content was approximately 1.5-2 mg g⁻¹. 0.5-1 mg was taken for measurement. Detail preparation procedure for both substrates is described in the doctoral dissertation of Sedlar (Sedlar, 2014).

Dry preparation of Hg compounds with FeOOH : Four different mercury compounds were selected (HgCl_2 , Hg_2Cl_2 , $\text{HgO}(\text{Y})$ and $\text{HgO}(\text{R})$). About 1 mg of each mercury compound was diluted with 5 mg of FeOOH powder and mixed in a zirconium container using a planetary mill (Fritsch planetary mill Pulverisette 7). The Mercury content was approximately 0.2 mg g⁻¹.

Wet preparation of Hg compounds with $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$: Six different Hg compounds were selected (HgCl_2 , Hg_2Cl_2 , HgO , HgS , HgSO_4 and Hg_2SO_4). Each solution was prepared separately by dissolving 1 mg of the pure mercury compound in 1 L of a saturated solution of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. An aliquot (50 ml) was then left to dry to leave a precipitate of Hg compound/ $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. This was then analysed using TPD – MS.

Wet preparation of Hg compounds with $\text{FeOOH}/\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$: In a 100 ml of each saturated solution of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ with added Hg-species: HgS , HgSO_4 , Hg_2SO_4 , $\text{HgO}(\text{Y})$, HgCl_2 and Hg_2Cl_2 , 0.5 g of FeOOH was added. The resulting brown solution containing non-soluble FeOOH was stirred, centrifuged and finally dried at 38 °C. The mass of FeOOH added was calculated according to the amount of Fe and Hg present in original WFGD gypsum sample (ORIG-FF). From this 5 mg was taken for TPD – MS analysis.

Wet preparation of Hg compounds with FeOOH : Separately, 1 mg of pure $\text{HgO}(\text{Y})$ and HgCl_2 were added to the FeOOH solution (0.5 g FeOOH in 100 mL⁻¹ of distilled water). The mixture was stirred, centrifuged and then dried.

Wet preparation of Hg compounds with $\text{Al}(\text{OH})_3$: Two different experiments using HgS and HgCl_2 were performed. First 0.6-0.7 mg of pure HgS and HgCl_2 were added in 100 mL of water solution with $\text{Al}(\text{OH})_3$ (0.6 g added in distilled water). A small aliquot of each

species was taken from solution and dried afterwards to obtain crystalline phase. Crystals were ground then and analysed with QMS. 3-5 mg were taken for measurement.

Wet preparation of Hg compounds with $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}/\text{Al}(\text{OH})_3$: Secondly, those two Hg-compounds were added in a 100 mL of saturated solution of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. 0.6 g of $\text{Al}(\text{OH})_3$ was added, stirred, centrifuged and finally dried at 38 °C. The concentration of mercury in each standard was about 10 mg kg⁻¹. From this, 3-5 mg were taken for analysis.

Spiking with HgS: Dry prepared HgS standard was first added to a mercury standard solution ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}/\text{FeOOH}$ including HgCl_2 , Hg_2Cl_2 , HgSO_4 or $\text{HgO}(\text{Y})$). Secondly, it was mixed (spiked) with dry gypsum samples (gypsum sample ORIG-FF from block 6 and one sample from China).

Addition of NaCl in a solution of $\text{FeOOH}/\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$: To a solution of HgCl_2 - $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ 0.5 g of FeOOH was added. A sufficient amount of NaCl was then added to give two different concentrations of NaCl, namely, 0.006 and 0.17 M.

Experiments with HgCl_2 : Highly pure HgCl_2 was used. Pure HgCl_2 was mixed with two different mixtures (SiO_2 and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) to obtain reproducible NIST mass spectrum obtained by electron ionisation (NIST Chemistry WebBook, 2014). A known weight of ultra-pure HgCl_2 (100 mg) was placed in the ion source of the NT-MS. The cell was then cooled to -15 °C to prevent excessive sublimation during evacuation to a working pressure of 10⁻⁵ Pa. The sample was then allowed to reach room temperature (20 °C).

Chapter 4

Results and Discussion

4.1 Properties and Distribution of Mercury and Other Elements in Gypsum and Other Samples of Coal Combustion

The main focus of this chapter is a characterization of the different gypsum samples from the Šoštanj TPP. Gypsum composition is a consequence of the cleaning of the flue gas (including different APCDs), conditions in the WFGD scrubber, sampling and sample preparation. Gypsum contains different TMEs coming into the system *via* flue gas (because of coal combustion) and with the limestone. Although we are interested mainly in mercury, the information about other TMEs gives us an important overview about their volatility/condensation and accumulation under different conditions and if there are some relations with mercury.

The results in Chapter 4.1 are organised into three main parts. The first part shows the distribution of elements in different by-products of coal combustion and potential sources of TMEs in the gypsum samples. The second and third part consists the behaviour and partitioning of TMEs in finer and coarser gypsum fractions of block 5 and 6 of Šoštanj TPP. Characterization of different gypsum samples are described as well. Some parts have not been published yet, but represent an important contribution to the understanding of the processes taking place after coal combustion and in the WFGD system. All these results help in interpretation and understanding of the TPD spectra described in Chapter 4.2.

4.1.1 Distribution and accumulation of major and trace elements in block 4 of Šoštanj thermal power plant

Mercury chemistry during the combustion process is very complex. Therefore, it is important to understand the chemical and physical conditions that may affect mercury speciation and behaviour in the flue gas. WFGD scrubber and gypsum as by-product represent the last step in the "cleaning" of the flue gas in most of the TPP, also in Šoštanj TPP. Distribution of TMEs in different combustion by-products and the contribution of those elements into the gypsum coming either with the limestone or particles alongside with the flue gas represents an important overview of the chemistry taking place in the post-combustion zone. In most publications, data are available for a limited number of elements present in various by-products, while in the present study information for 45 elements is provided, including some strategic rare earth elements (REEs) that are rarely discussed. This information enables us to estimate the contribution of different mass flows that come into the gypsum slurry. This section aims to put together the data from previous

studies to evaluate the main sources of TMEs into the WFGD gypsum and to estimate the distribution of these elements along the combustion process. Unfortunately, the data for the bottom and fly ash, limestone, and bulk gypsum exist only for block 4. Due to the similarity between blocks 4 and 5, some data were applied in block 5.

The data for total elemental concentrations and corresponding uncertainties in lignite samples (LIG08), fly ash, bottom ash (slag), limestone, slurry water, and bulk gypsum are provided in the Appendix A, Table A.1. Lignite samples taken from Velenje mine were analysed several times within the last decades (Sedlar et al., 2015; Stergaršek et al., 2008; Stropnik, Byrne, Smodiš, & Jaćimović, 1994). The multielemental analysis in lignite samples shows no considerable differences in the composition of all samples measured. Therefore, the interpretation of the results described in the following subchapter includes some characteristic data from the previous study including block 4 of Šoštanj TPP (Stergaršek et al., 2008), where the same coal and APCDs as in block 5 were used. Considering this, all results provided here serve for a better understanding of behaviour and partitioning (accumulation) of Hg and other elements during the lignite combustion in Šoštanj TPP.

The importance of particle size regarding mercury accumulation in WFGD gypsum from a Šoštanj TPP has been examined in the previous study (Sedlar, et al., 2015; Stergaršek et al., 2008). As already mentioned, grain size distribution revealed a significantly higher proportion of Hg in smaller particles (Stergaršek et al., 2008). In the present work, in addition to mercury, the concentrations of other 44 TMEs were determined in various size fractions of gypsum. Instead of studying all water streams in WFGD system, we decided we would focus on particles in the gypsum slurry samples (gypsum). Although bulk gypsum is typically used to characterize gypsum samples, in our work all gypsum slurry samples were separated into fine (recirculated gypsum slurry, overflow) and coarse (mostly consisted of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, underflow) fractions. Our study revealed several important findings with regards to the distribution, accumulation and sources of TMEs in the different particle size fractions. We also emphasized the importance of sample preparation when separating gypsum slurry into fine and coarse fractions.

4.1.1.1 Comparison of the data for elements in coal, fly ash and bottom ash with the literature data

The concentrations of elements in lignite sample from Velenje (LIG08) were compared with different samples from all around the world. It was observed that TMEs in lignite from Šoštanj TPP show the concentrations that correspond to the range determined for the global lignite content with consideration of different coal ranks (Vassilev, Kitano, & Vassileva, 1996). Molybdenum is the only element that exceeded the upper value. The content of elements in European fly ash has also been reported (Swaine, 1990). Concentrations for some TMEs from Šoštanj TPP (As, Ba, Co, Cr, Mo, Rb, Sb, Se, Sr, Th, U, V and Zn) are mostly in the range of European fly ash. Differences were found for Co, Se, Th that were below the lower limit determined for European fly ash, and for Mo and U, which occur in higher concentrations. Hg concentrations in Šoštanj TPP fly ash belong to the group of samples containing lower concentrations. So far, there are only few literature data (the multielemental analysis) to compare the gypsum samples (S. J. Lee et al., 2006; Meij, 1994b; Pudasainee, Kim, Yoon, & Seo, 2012; Yokoyama et al., 2000).

Figure 4.1 shows the concentration of elements in samples of lignite, fly and bottom ash where elements are partitioned into different groups according to their volatility (Clarke & Sloss, 1992; Klein et al., 1975; Meij, 1994a; M. Xu et al., 2004). Comparing coal, fly and bottom ash, the differences between the groups exist. The first group including non-volatile elements shows the same behaviour for all classified elements. Concentrations

of TMEs in coal are lower compared to slag (bottom ash) and fly ash. It follows that the enrichment (accumulation) of elements during the process of coal combustion is distributed equally between fly and bottom ash (Ca, Mn) or shows a slightly higher concentration in fly compared to bottom ash. Further, elements classified into group two (semi-volatile elements), show comparable concentrations in coal and bottom ash whereas fly ash shows enrichment. Elevated concentrations of those elements in fly ash are consistent with the literature data where the elements in the second group volatilize during coal combustion and then condense onto the particles in the flue gas stream. The third group of elements representing volatile elements that show completely different behaviour; concentrations in coal are higher than in ash samples due to the volatility. The only exception is iodine showing the highest concentration in bottom ash. Group of elements such as Na, Cs, V, Cr and U show behaviour between group one and two. Few elements (Zr, W, In, S, Nd, Tb, Dy and Yb) have not been classified in the literature and are located separately in Figure 4.1. They reflect a similar distribution of elements between fly and bottom ash as elements in the first group, with only exceptions of Zr, In and volatile S. Zr and In show a similar concentrations pattern as iodine.

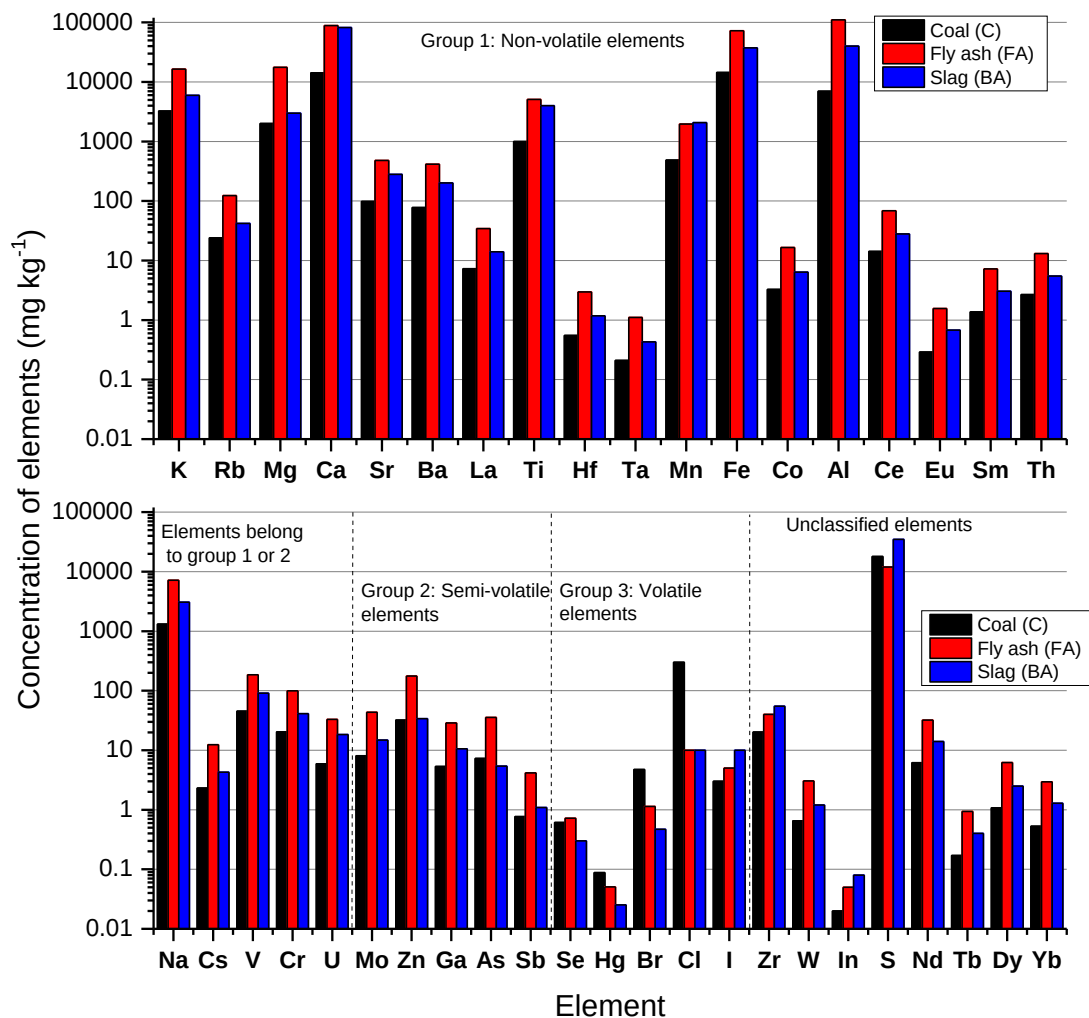


Figure 4.1: Concentration of elements in coal, fly and bottom ash distributed regarding the group in which each element belongs.

4.1.1.2 Distribution of elements between fly ash and bottom ash (slag)

The enrichment factors (EF) for fly (EF_{FA}) and bottom ash (EF_{BA}) concerning the lignite were calculated to express the element partitioning using the following equation:

$$EF_{FA}, EF_{BA} = \frac{\text{Conc. of the X in FA or BA} / \text{Conc. of Sc in FA or BA}}{\text{Conc. of the X in coal} / \text{Conc. of Sc in coal}} \quad (4.1)$$

EF refers to the ratio of the concentration of an element in fly ash (FA) and bottom ash (BA) to its concentration in coal (Figure 4.2). X represents the concentration of an element used in the calculation. Scandium, as a non-volatile element, present in low concentrations in all samples, was used for normalisation. Typically, Al and Fe are used (Esenlik et al., 2006; Germani & Zoller, 1988; Gordon & Zoller, 1973; Meij, 1992; Querol et al., 1995; Ratafia-Brown, 1994; Smith M., 1987; Vassilev, Eskenazy, & Vassileva, 2001) for normalization purpose, although in geochemical normalization Sc is preferred due to its unique presence in geochemical settings and non-anthropogenic origin (Ackermann, 1980; Grousset et al., 1995).

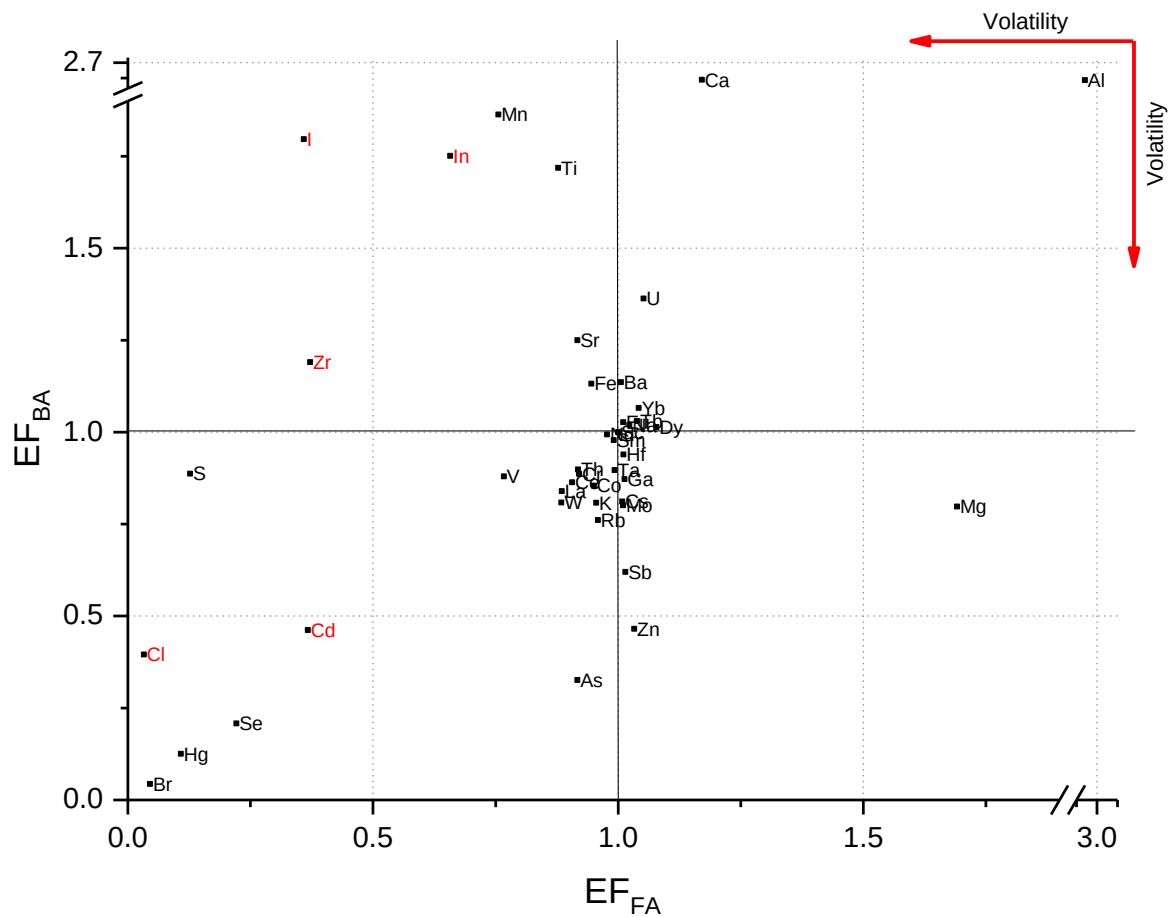


Figure 4.2: The enrichment factors for fly (EF_{FA}) and bottom ash (EF_{BA}) relating to lignite. Elements in red represent orientational value since the concentrations are below the limit of detection.

As shown in Figure 4.2 the physical-chemical processes result in the dynamic distribution of elements between FA and BA is similar with the data (Klein et al., 1975;

Meij, 1994a). Elements with EFs close to 1 are considered conservative whereas EF factors above 1 indicate enrichment. For example, Al and Ca are enriched in both fractions, which can be explained by the presence of Al minerals in FA (Al-Si glass and Fe bearing phases) and silicate and alumina-silicate glass fractions in BA (Z. Li et al., 2005). Elements such as I, Zr, In, Mn, Sr, Fe, Ti, Ba and U enrich in BA. Some of them (Fe, Mn, Zr) have higher density and low volatility (J. Li et al., 2012) while Mn is probably enriched due to high affinity for Fe oxides (Q. Tang et al., 2013) abundant in BA (Querol et al., 1995). Mg is classified as a non-volatile element. Enrichment of Mg in FA and its depletion in BA is possibly due to the formation of its volatile compounds (Neville, Quann, Haynes, & Sarofim, 1981). Non-volatile elements are significantly depleted in FA (I, Zr, In, Mn) and show high enrichment in BA indicating scavenging processes (J. Li et al., 2012). As, Sb, Zn classified in Group 2 show typical depletion in BA (Esenlik et al., 2006). A number of elements are depleted in both fractions, because of their volatile nature (Hg, Se, Br and Cl) (Clarke & Sloss, 1992; Klein et al., 1975; J. Li et al., 2012; Meij, 1994a; Querol et al., 1995, 1996). Cd shows similar behaviour to volatile elements although it belongs to the second group according to the literature.

The partitioning of elements obtained in this study is similar to the literature data with some exceptions. For example, the enrichment of iodine in BA is not consistent with its volatile nature. Zr and In, which are not volatile, show a similar partition as I. It should be taken into consideration that for elements such as Cd, Cl, I, In and Zr with concentrations below the limit of detection (LOD) half the value of concentration was taken for calculations (Table A.1). REEs also demonstrate the conservative behaviour.

Literature shows that the highest concentrations of trace elements are associated with the fine fraction of fly ash (Clarke & Sloss, 1992; Klein et al., 1975; Meij, 1994a; M. Xu et al., 2004) that is not captured by particulate control devices. The finest particles in the flue gas stream, therefore, pass through and reach the WFGD device (Galbreath et al., 2000; Otero-Rey et al., 2003; Pavlish et al., 2003). These particles can be retained in the WFGD due to adsorption and co-precipitation (Stergaršek et al., 2010, 2013), while a smaller fraction is emitted to the atmosphere through the stack gas (Helble & Sarofim, 1993).

4.1.1.3 Accumulation of elements in bulk gypsum and their sources

The data of sampling campaign from 2007 (Stergaršek et al., 2008) were used to evaluate the primary sources and contribution of TMEs in WFGD gypsum. Trendlines (best-fit of the concentration of elements) for FA, bulk gypsum, limestone and slurry water versus lignite (LIG08) are shown in Figure 4.3. Enrichment/depletion of TMEs in gypsum (concentrations above or below the expected trend line) is a consequence of solubility effect or co-precipitation and adsorption in WFGD gypsum slurry. In the bulk gypsum, accumulation of elements reflects the chemistry of elements/species taking place during the desulphurization and recirculation process. Most of the elements in bulk gypsum are located (distributed) close to the trend line. On the other hand, accumulation is observed for Hg, Se and halogens, while Mn shows depletion. The trendline for FA is positioned above all others and shows a linear correlation with elements present in lignite. FA was taken from ESP, and the elements represent the concentrations present there and not the particles entered in the gypsum slurry. However, the smallest particles passing through the ESP have not been sampled, except in case of Hg where most of PBM is retained in gypsum slurry (Stergaršek et al., 2008). On the contrary, depletion of volatile elements in FA indicates accumulation of those elements in WFGD scrubber (Hg, Se, and halogens). The trendline for limestone versus coal points to the relative contribution of elements into the system (e.g., Ca, Sr) as another source of elements. Parallel lines of limestone and FA show

the natural presence of most elements in those fractions. Also, the data of slurry water was obtained demonstrating a higher concentration of Cl, Br, Na, Mg and Ca due to the high solubility of these elements (compounds), for which the recirculation process plays a significant role in their concentrating (accumulation) in the WFGD scrubber.

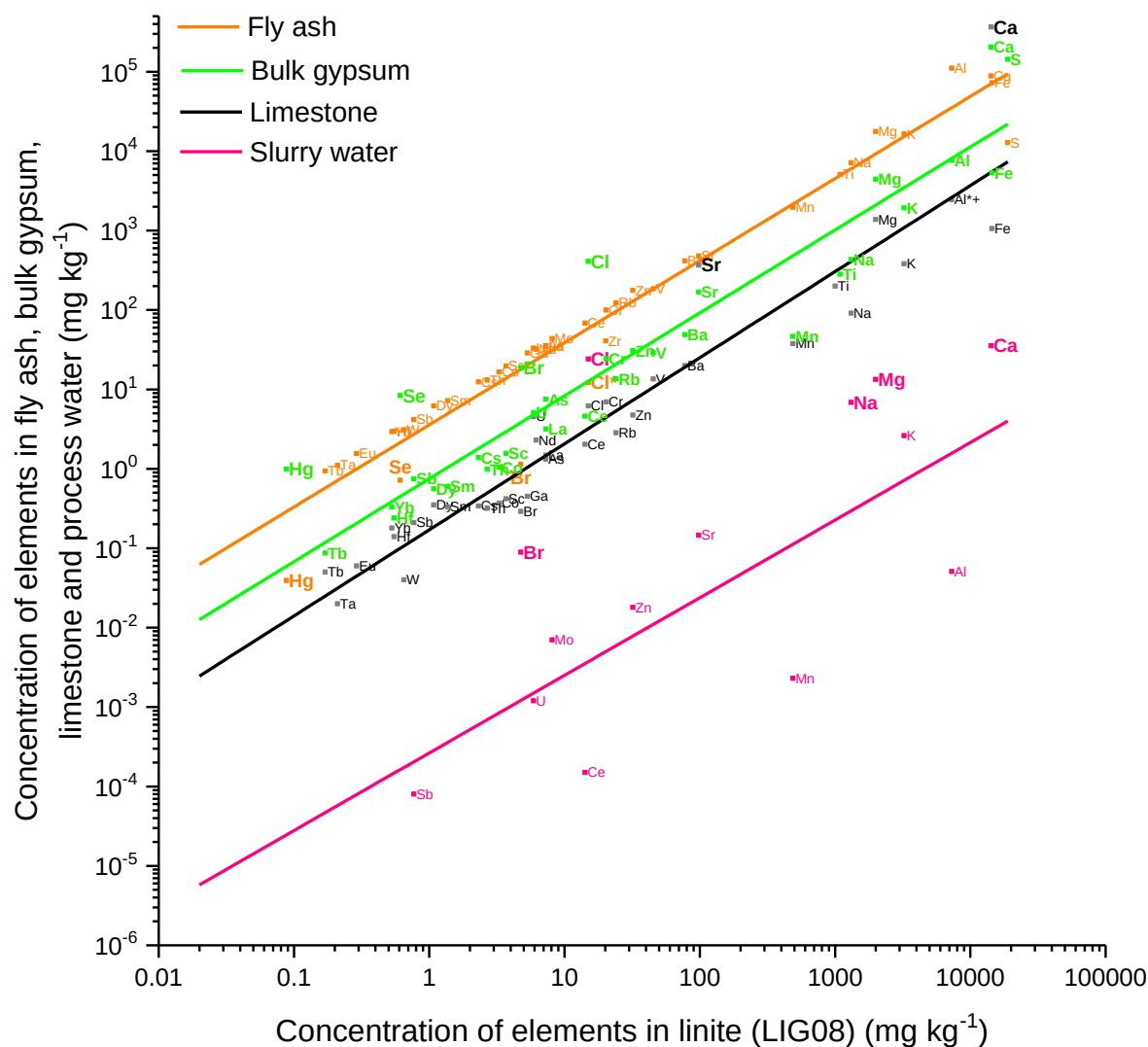


Figure 4.3: Concentration of elements in Velenje lignite (LIG08) versus concentration of elements in limestone, fly ash, bulk gypsum, and gypsum slurry water.

The data provided above assists more as an insight into the sources of TMEs in the gypsum and shows the distribution of elements in various by-products. Unfortunately, detailed study of all income/outcome sources was done only in block 4. Gypsum was not separated into various size fractions to see the distribution of TMEs there, except for Hg. In further chapters more information about the distribution of TMEs in gypsum samples of block 5 and 6 is provided.

4.1.2 Distribution and accumulation of major and trace elements in gypsum samples – block 5

The results and discussion in this section are based on a) the properties of fine and coarse fractions of gypsum samples, b) enrichment of elements in fine fraction with respect to the coarse fraction of gypsum, c) input of elements with the limestone as a source of TMEs into the system, and d) comparison between fine and coarse fractions versus lignite and among the different preparation procedures. Sample preparation is a key step in obtaining detailed information about the distribution of elements and for better prediction of reactions taking place in WFGD system.

4.1.2.1 Characterization of a fine and coarse fraction

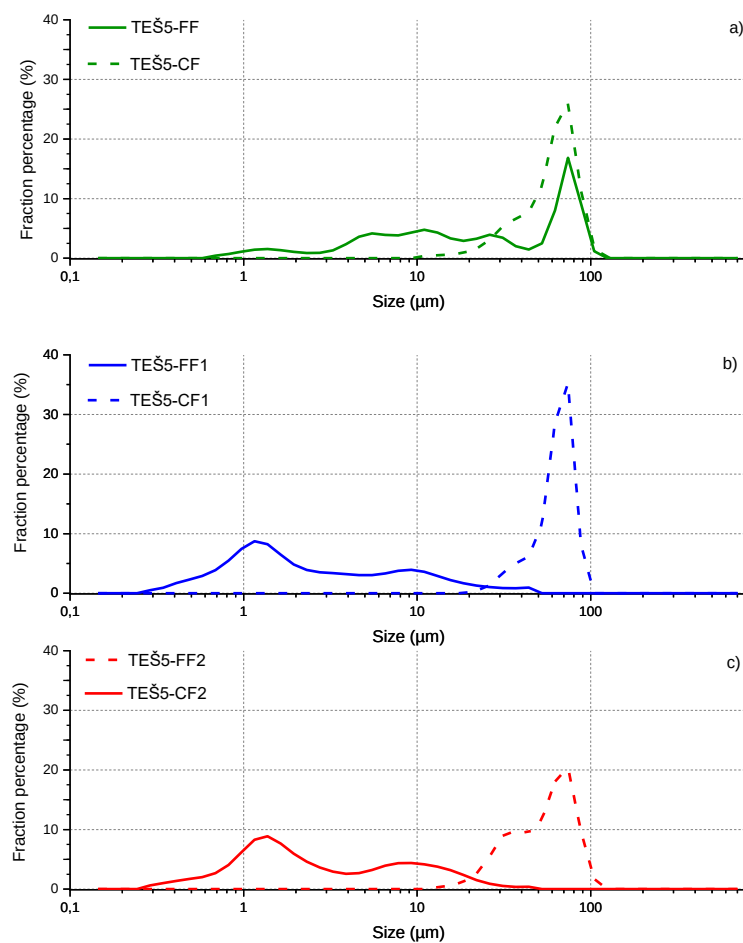


Figure 4.4: Distribution of particles in fine and coarse fractions from block 5: separation by hydro cyclone (TEŠ5-FF, TEŠ5-CF) and separation by sedimentation approach (TEŠ5-FF1, TEŠ5-FF2, TEŠ5-CF1, TEŠ5-CF2).

Gypsum slurry in WFGD system is a complex matrix containing mainly $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, alongside with unconsumed, insoluble and soluble constituents of limestone, and particles washed out of the flue gas. In this study, each slurry sample was separated into fine and coarser fraction.

Particle sizes determined by grain size distribution analyses are presented in Figure 4.4. Gypsum samples demonstrate differences that are most likely caused by sample preparation procedures as well as different sampling time, locations and conditions within the WFGD system. The differences are more pronounced in the composition of the fine fractions. The fine fraction of TEŠ5-FF contains a relatively high amount of coarse fraction (green distribution in Figure 4.4). This indicates that sedimentation technique provides better separation of fine and coarse fractions concerning the separation using hydrocyclone. Within sedimentation, almost no bigger particles were found in fine fraction (TEŠ5-FF1, TEŠ5-FF2). Coarse fractions slightly differ between subsamples where TEŠ5-CF2 contains a greater proportion of particles smaller than 50 μm .

SEM technique gains insight into the structure of fine and coarse particles (Figure 4.5). Differences between fractions are seen. $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ crystals represent the main stream in coarse fraction (Figure 4.5b). Non-uniform size distribution of fine fractions illustrates a different structure, presumably consisting of unburned particles and various minerals originating from fly ash, agglomerates and precipitates (Figure 4.5c). Bigger agglomerates are typically found in fine fraction (Figure 4.5d). However, the fine fraction may also contain some bigger crystals of gypsum (Figures 4.5a and c) that could be present as a consequence of the incomplete separation of the original gypsum slurry sample.

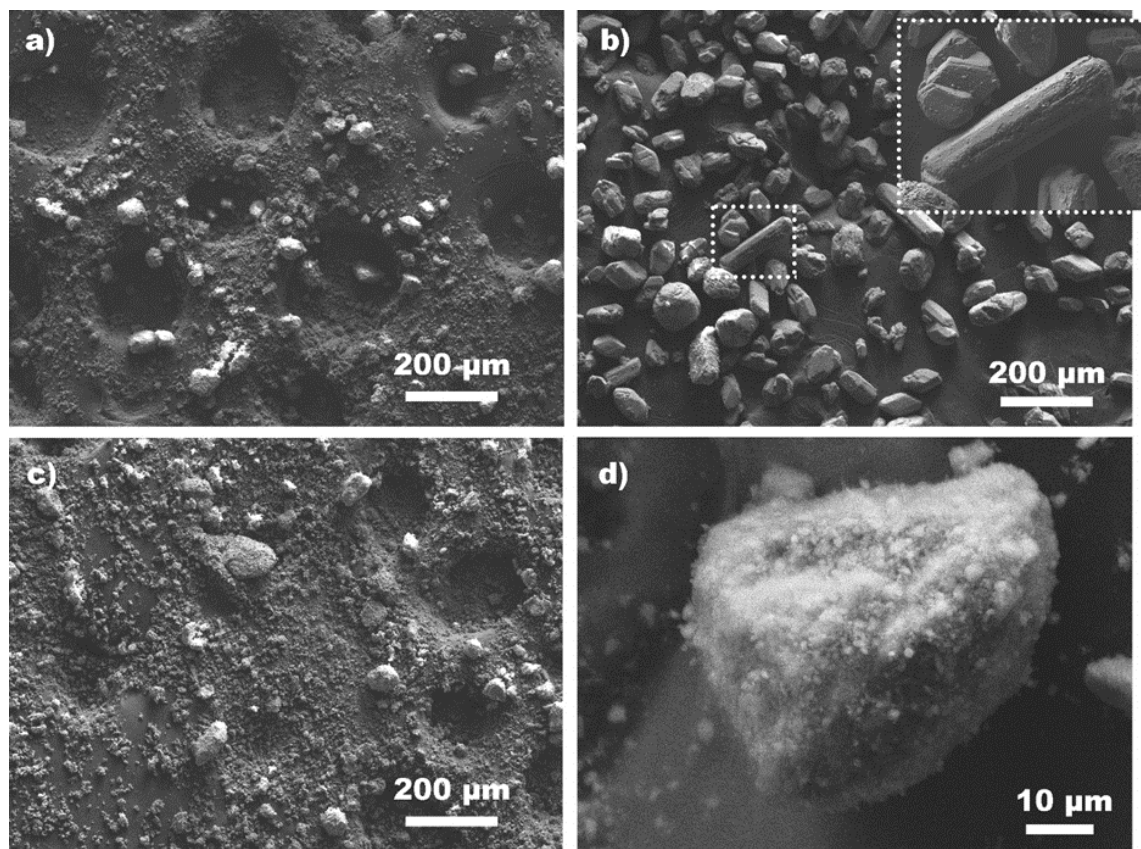


Figure 4.5: Scanning electron microscope (SEM) images of solid particles in gypsum from block 5: (a) fine fractions TEŠ5-FF, (b) coarse fraction TEŠ5-CF, (c) fine fraction of TEŠ5-FF1), and (d) typical example of agglomerate present in both finer fractions.

Table 4.1 shows the proportion of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ crystals present in bulk gypsum and in each separated fraction calculated according to the measured concentration of Ca present in the sample (multielemental analysis Tables A.1 and A.3 in Appendix A). The bulk

sample represents an average between coarse and fine fraction containing a lower amount of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ concerning the coarse fraction. Coarse fraction is predominantly in a form $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ while in fine fractions its proportion is much lower. The fine fraction TEŠ5-FF differs from TEŠ5-FF1 and TEŠ5-FF2 according to a higher proportion of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. Due to the incomplete gypsum slurry separation into TEŠ5-FF and TEŠ5-CF as observed in Figure 4.4, it follows that there is a lower amount of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in coarse fraction and consequently elevated proportions in a fine fraction. Table 4.1 indicates far less $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in TEŠ5-FF2 than in TEŠ5-FF and TEŠ5-FF1. In general, less $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ present in fine fractions is consistent with a lower particle size and increasing proportion of other species (elements) comprising in the sample.

Table 4.1: Percentage of Ca and calculated proportion of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ crystals in gypsum samples.

Sample	Percentage of calcium finer/coarse fraction (%) [*]	Proportion of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in gypsum (%)
Bulk gypsum	20.4	87.6
TEŠ5-CF	22.3	95.6
TEŠ5-FF	14.4	61.9
TEŠ5-CF1	23.2	99.6
TEŠ5-FF1	11.8	50.5
TEŠ5-CF2	23.2	99.6
TEŠ5-FF2	4.31	18.5

^{*} Theoretical molar proportion of Ca in $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is 23.3%.

4.1.2.2 Partitioning of elements in different size fraction of gypsum

Accumulation of TMEs in gypsum depends on particle sizes. The elements are partitioned between fine and coarse fractions (Figure 4.6). Most of the elements are considerably enriched in the fine fractions, with some exceptions (Ca, Sr, S) that constitute the bulk of gypsum. Strontium introduced into the system alongside limestone usually occurs as SrCO_3 (Ochoa-González, Díaz-Somoano, & Martínez-Tarazona, 2013). In general, enrichment of elements in TEŠ5-FF is smaller concerning TEŠ5-FF1 and TEŠ5-FF2. A larger proportion of bigger particles in the fine fraction TEŠ5-FF causing a “dilution” effect (Figure 4.4). However, much higher enrichment for most TMEs is observed in TEŠ5-FF2 concerning TEŠ5-FF1 and TEŠ5-FF fraction of gypsum, suggesting the importance of sampling and preparation procedures. Higher enrichment of most TMEs is consistent with Table A.3 (Appendix), where the proportion of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is significantly lower as a consequence of other particles present in the sample.

Alkali elements show similar enrichment except for Na, while earth-alkaline elements show enrichment for Mg and Ba, but not for Ca and Sr (Figure 4.6). Additionally, Ba is highly enriched in finer fractions of TEŠ5-FF2. Since the salts of alkali and earth alkali elements have a solubility several orders of magnitude higher than the salts of the transition elements, the precipitation reactions alone cannot explain these findings. Adsorption is probably the prevalent mechanism. Aluminium is enriched in all finer fractions and is one of the most enriched elements. A small part is supplied with limestone while mostly entering with fly ash that escapes the ESP and could be present as small aluminosilicate cenospheres with the high specific surface for adsorption/condensation. On the other hand, it could enter as sulphate (oxide) aluminium species, where some are well soluble, and therefore TMEs can be released (Córdoba et al., 2015; Querol et al., 1995). Al can be

introduced by different insoluble, saturated species as well (Córdoba et al., 2012; Ochoa González et al., 2015). As, Sb and Se show similar enrichment in all fractions. Enrichment of transition elements is comparable, except for La, Hf and Mn. Mn as a non-volatile element is typically retained in bottom ash and therefore its presence in gypsum is mostly the consequence of limestone addition (Ochoa-González, Díaz-Somoano, & Martínez-Tarazona, 2013) and only minor part could enter with the smallest particles. Furthermore, Mn can form precipitates such as MnO_2 in WFGD slurry tank (Stergaršek et al., 2013). Lanthanides in TEŠ5-FF are slightly enriched compared to other fine fractions. Actinides, namely Th and U, have similar concentrations in the fine fractions of TEŠ5-FF and TEŠ5-FF1. On the contrary, finer fraction TEŠ5-FF2 shows strong enrichment of both elements.

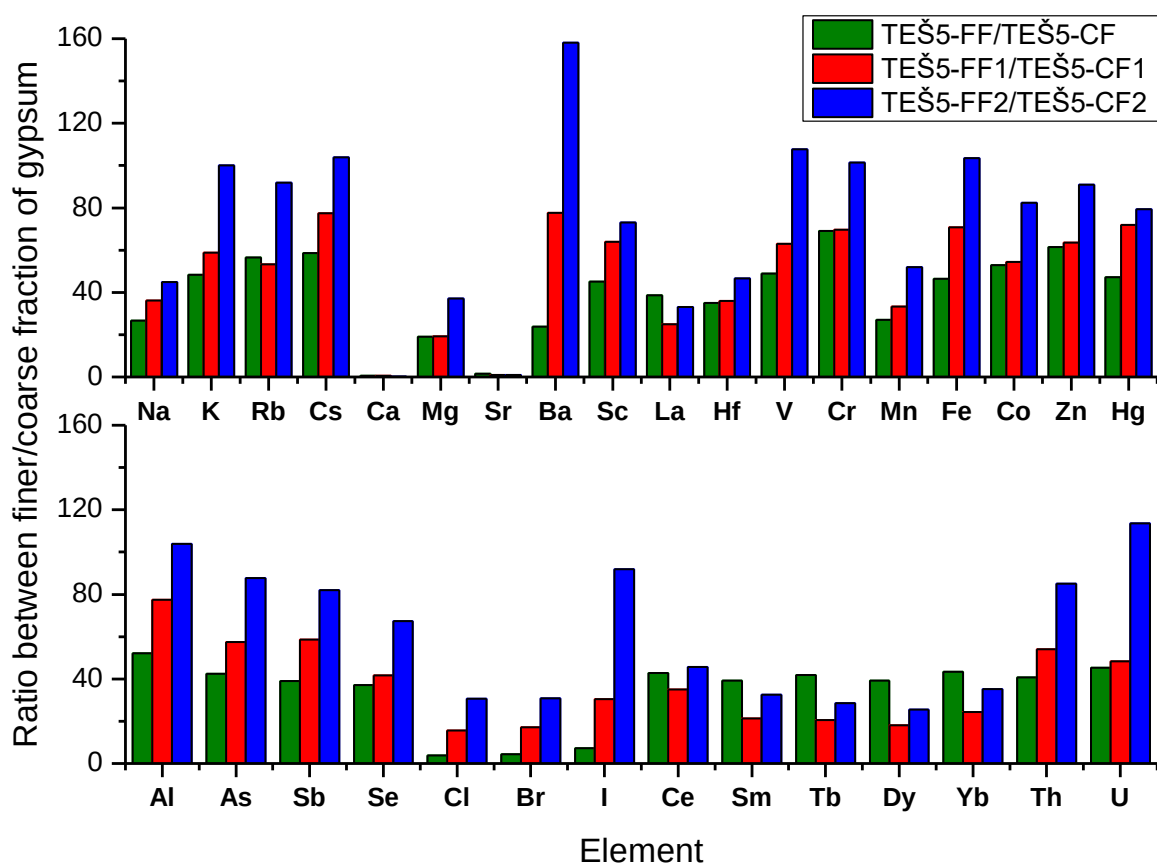


Figure 4.6: Enrichment of elements in the fine fraction compared to the coarse fraction of block 5. Elements are ordered according to the periodic system: alkali, alkaline earth metals, transition and post-transition metals (Al, Ga, In), metalloids (As, Sb), non-metals (S, Se), halogens (Cl, Br, I), lanthanides and actinides.

Table A.2 also includes the data of TMEs measured in slurry water. The concentration of elements (TEŠ5-W1 and TEŠ5-W2) decreases within the following order: Cl, Mg, Ca >> Na, Br, K > I, Mn, Ti > other elements. Different soluble complexes with halogens, SO_4^{2-} and OH^- anions can form in WFGD scrubber (Córdoba et al., 2015). Inorganic pollutants in FGD waters tend to concentrate in the recirculation process, where they could reach equilibrium, and possibly saturate, precipitate, or accumulate in fine fraction afterwards. This is promoted by the operational conditions affecting the wet limestone

FGD-system. However, enrichment of halogens in a fine fraction relating to coarse fractions is not significant, except for iodine in TEŠ5-FF2 (Figure 4.6). High concentrations of those elements in slurry water and gypsum afterwards indicate their accumulation followed by the formation of different insoluble species or adsorption process (highly insoluble Al-Si fraction of limestone, carbonate fraction of limestone that reacts with S to form low soluble sulphate species, elements in gaseous phase that react with limestone components and are retained in gypsum as sulphate or fluoride species, PM elements not dissolved in gypsum slurry water and filtered water) (Córdoba, 2015). Halogens that are well soluble with higher concentrations in slurry water enter the system as volatile compounds, while fly ash components (particulate matter) may be dissolved in the aqueous phase of the absorbent slurry or retained in the solid fraction (gypsum sludge). High levels of TMEs and other pollutants in recirculated water increase the emission of metals by entraining and/or evaporation of droplets as PM from gypsum slurry in the flue gas that escapes the FGD (Córdoba, 2015).

4.1.2.3 Sources of trace and major elements in gypsum

Some properties of limestone such as particle size distribution, porosity, and the impurities of limestone may play a significant role in the efficiency of desulphurization process. These parameters can be considered as key factors of the reactivity of the limestone and thus the formation of gypsum (Córdoba, 2015; Ochoa-González, Díaz-Somoano, & Rosa Martínez-Tarazona, 2013). This has an effect on adsorption and accumulation of TMEs in the gypsum. It is highly recommended to use the limestone with purity higher than 95% due to the impurities that may supply with less pure calcite (e.g. F, Mn, Al, Si) (Córdoba, 2015). However, also limestone with 95% purity involves impurities.

As seen in Figure 4.6, most of the elements in the fine fraction are enriched relative to the coarse fraction. Coarse fraction of TEŠ5-CF1 was chosen for comparison with limestone since it contains almost 100% of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ according to the calculations in Table 4.1. The composition of coarse fraction resembles limestone which is an important source of elements in the system.

Most of the elements represented in Figure 4.7 show higher concentrations in limestone (red bar) compared to the coarse fraction, TEŠ5-CF1 (black bar). It follows that most elements in coarse fraction originate from the limestone (non-soluble species). On the other hand, halogens, Hg and Se show the opposite trend since they are not entering the system with limestone (Figure 4.7). Elements coming with the small particles alongside with flue gases are of minor importance in coarse fraction where bigger crystals of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ are a predominant matrix. As already mentioned, reactivity is dependent on the particle size and coarse fraction with bigger particles showing less affinity to accumulate TMEs.

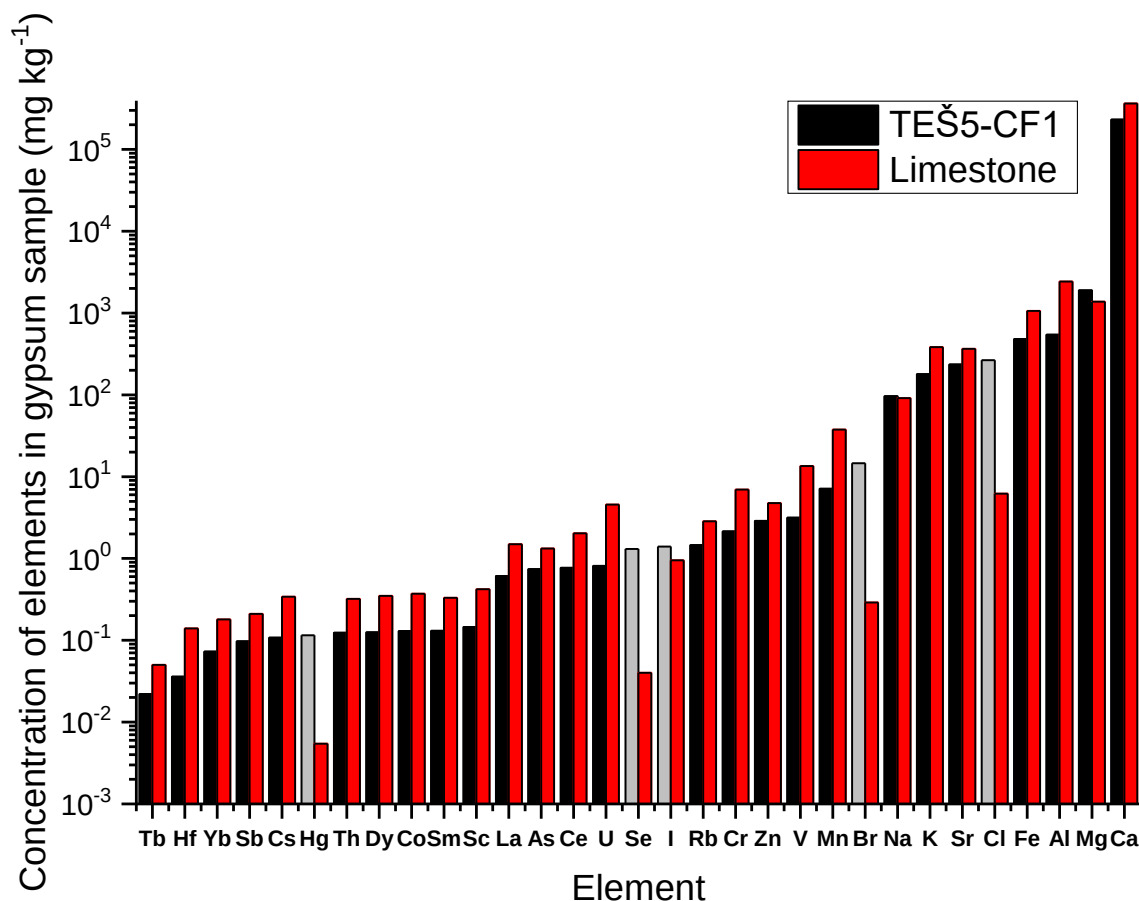


Figure 4.7: Concentrations of elements in limestone as a source of elements and in coarse fraction of gypsum (TEŠ5-CF1) are present in the same graph indicating similarities in composition. Grey bars highlight the elements followed by coal combustion.

To support the above statements associations between concentrations of TMEs in lignite, fly ash, coarse and fine fractions of gypsum and limestone are presented in Figure 4.8.

Trendlines for fine/coarse fractions and fly ash show enrichment/depletion of TMEs regarding lignite while the trendline for limestone versus coal shows their relative contribution of elements into the system. Slopes for fine and coarse gypsum fractions are similar which reflects the same origin of TMEs with enrichment in fine fraction mainly related to particle size effect. The trendline for fly ash and a fine fraction of gypsum coincide with slightly different slopes caused by significant contribution of some elements into the fine gypsum from limestone (Ca, Sr, Mg) and depletion of volatile elements (Hg, Se, Br and Cl) in fly ash. The firmly positioned trendline for coarse fraction and limestone demonstrate a similar composition of coarse fraction as a consequence of limestone introduction (see also Figure 4.7). The coarse gypsum fraction is composed of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ crystals after the reaction between SO_2 and CaCO_3 .

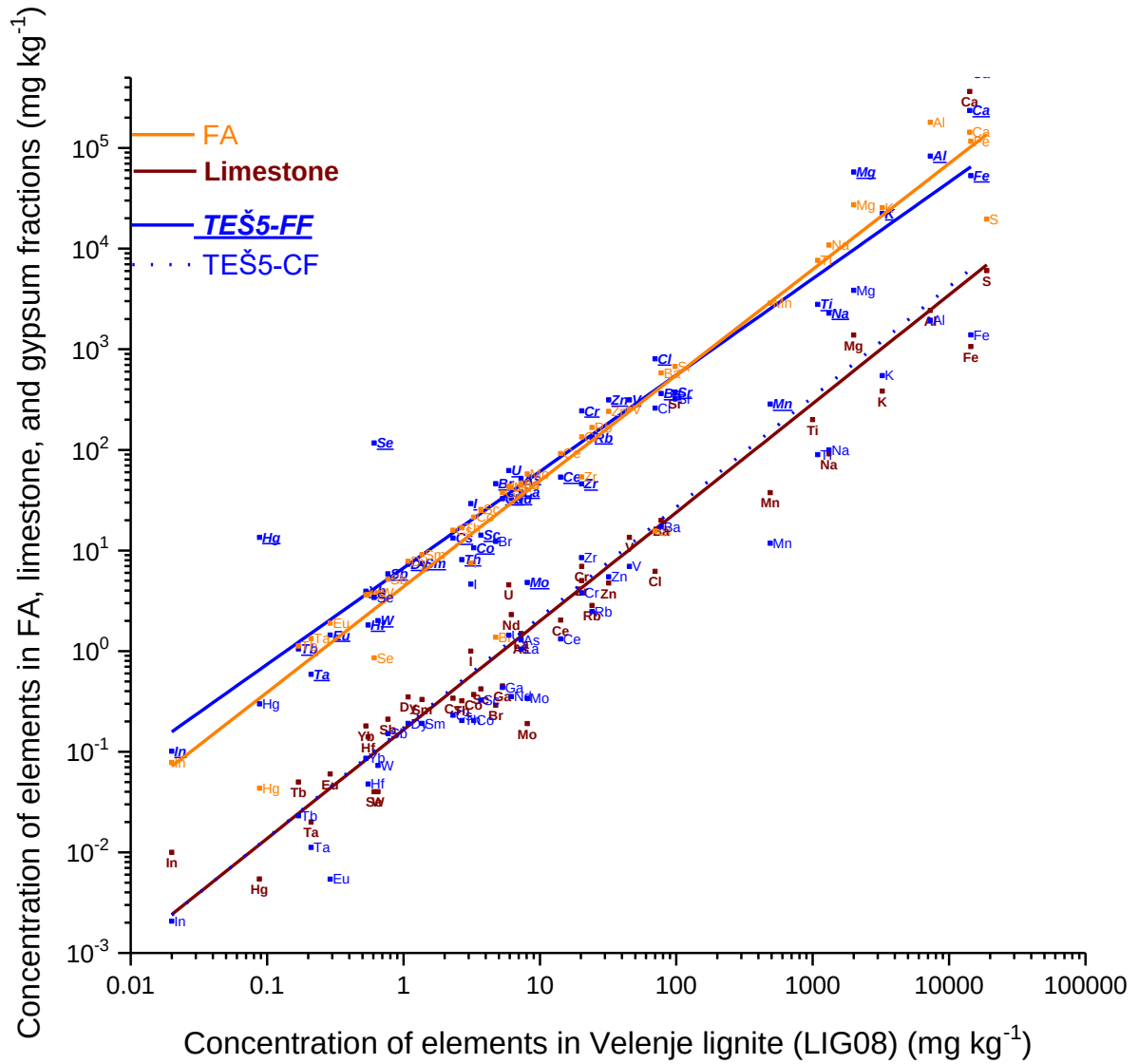


Figure 4.8: Concentration of elements in Velenje lignite versus concentration of elements in FA, limestone, a fine and coarse fraction of gypsum (TEŠ5-FF and TEŠ5-CF).

Deviations from the expected trend lines relative to lignite and limestone contributions of TME in gypsum are due to the solubility effect in WFGD slurry or co-precipitation/adsorption of volatile TMEs. Soluble TMEs are therefore located below the trend line (Mn, Al, Fe, alkali elements) while co-precipitated elements such as Hg and Se are far above the trend lines. In addition to Hg and Se, halogen elements are also typically found above the trendlines due to their volatile nature and good solubility. Concerning the results obtained with calculations of EF_{FA} , EF_{BA} in Chapter 4.1.1.2 and concentration of elements in gypsum samples versus those in coal it is evident that volatile elements depleted in fly ash and slag (see EFs in Figure 4.2) accumulated in gypsum samples.

4.1.2.4 Comparison of fine and coarse fractions versus lignite

To compare trendlines and concentration of elements that are enriched/depleted in all fractions of fine and coarser gypsum, concentrations of elements in different samples are shown in the same graph (Figure 4.9). Similar behaviour for most of the elements is observed, however some distinct differences related to Br, Cl, and I are seen. Concentrations of Cl, Br and I in the fine fractions TEŠ5-FF are close to the trend line itself, following the predicted concentration ratios between fine fraction and lignite samples (Figure 4.9). On the other hand, much higher levels of these elements are present in the other fine fractions of block 5. Similarly, all coarse fractions (TEŠ5-CF, TEŠ5-CF1 and TEŠ5-CF2) show that Br, Cl and I are located significantly higher in relation to the concentrations in coal and according to the other elements present in coarse fraction. Coarse fractions with the majority of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ seem to be an efficient matrix for removal of halogens, whereas high retention is even more apparent in fine fractions indicating greater accumulation with possible binding and reactions with other elements, adsorption onto the minerals or to smaller crystals of gypsum. Concerning the position of the trendlines, it is evident that TEŠ5-FF2 contains higher concentrations of most TMEs. On the contrary, in coarse fractions, there are no such differences among the samples.

Among the most interesting features is high accumulation/retention of Hg and Se in all gypsum fractions regarding coal. Se mainly condenses on fly ash particles while Hg is found as volatile species in flue gas (Otero-Rey et al., 2003). Concentrations of Se and Hg in the particles leaving the ESP are higher in medium to a fine fraction. In the gypsum, Se is suggested to be in oxidation state Se(IV) (Al-Abed et al., 2008). SeO_2 is a predominant species in flue gas that combines with lime in the scrubber to form CaSeO_3 (Huggins, Senior, Chu, Ladwig, & Huffman, 2007). Another explanation for Se accumulation is attributed to its presence in gypsum as calcium selenate dihydrate ($\text{CaSeO}_4 \cdot 2\text{H}_2\text{O}$), which has similar properties as $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (Freyer & Voigt, 2003; Krüger & Abriel, 1991). In the case of Hg, various mercury compounds have been suggested to be present in gypsum, such as Hg-Cl compounds, HgS, HgO, HgSO_4 , etc. (Al-Abed et al., 2008; J.-Y. Lee et al., 2009; X. Liu et al., 2013; Sedlar, et al., 2015; Sui et al., 2015; Z. Zhu et al., 2016). Although Hg and Se form stable Hg-Se compounds, e.g., in biological systems (Khan & Wang, 2009), this has not been proven in WFGD gypsum so far (Córdoba, 2017). Fe and Al (oxides/hydroxides) may also have an essential role in the adsorption of Hg that are formed in the WFGD system (Al-Abed et al., 2008; Beatty et al., 2012; Kairies et al., 2006; Shah, Strezov, Prince, & Nelson, 2008).

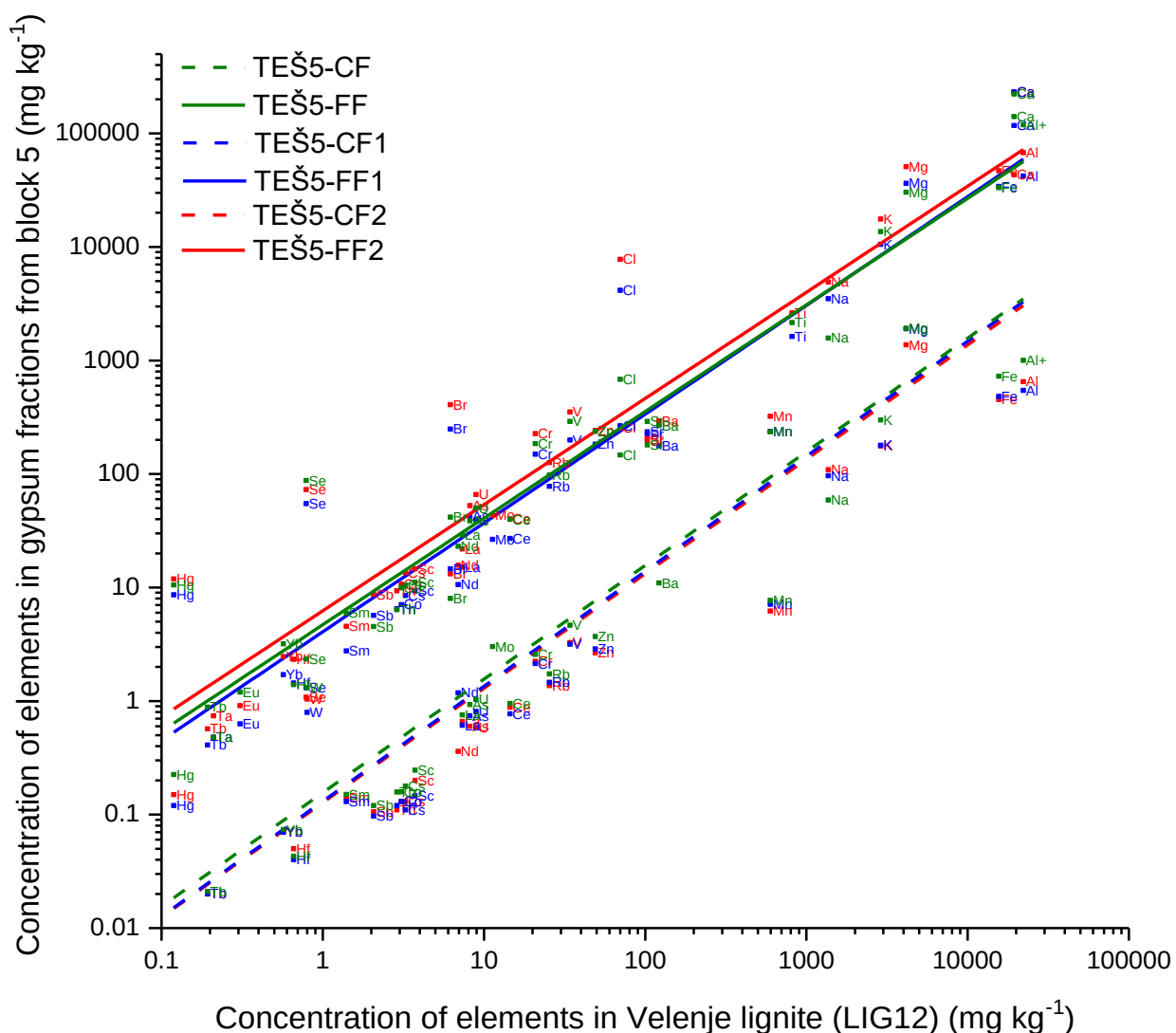


Figure 4.9: Concentration of elements Velenje lignite versus concentration of elements in all six finer and coarse fractions of gypsum (TEŠ5-FF, TEŠ5-CF, TEŠ5-FF1, TEŠ5-CF1, TEŠ5-FF2 and TEŠ5-CF2).

In general, conditions after coal combustion and behaviour/partitioning of elements in APCDs are expected to be constant. However, the sampling procedure itself and separation of gypsum into fine and coarser fraction are important factors affecting partitioning of TMEs in fine and coarser fractions of gypsum samples. Improved (and standardized) separation procedure are needed to obtain comparable results. Also further investigations in obtaining better knowledge about the species formed and to explain reactions present in WFGD boiler. Identification of different species formed during the desulphurization process and better knowledge of the processes in WFGD scrubber would help in the understanding of Hg chemistry and its accumulation in the gypsum samples.

4.1.3 Distribution and accumulation of major and trace elements in Šoštanj thermal power plant – block 6

In this chapter, the properties of three gypsum samples of block 6 were described. Gypsum slurries were taken at the same time from different locations in the WFGD system. Separated gypsum fractions from block 6 are characterised and compared among the samples. Particles size distribution, microstructure images, and thermogravimetric analyses were performed. Also, the results of multielemental analyses for 43 elements in fine and coarse gypsum fractions of block 6 are provided in Table A.4 (Appendix A).

4.1.3.1 Characterization of fine and coarse fractions of gypsum

Figure 4.10 shows the particle size distribution for all separated fractions. The coarse fractions have an identical distribution (DISP-CF, ORIG-CF). All three fine fractions differ from each other (ORIG-FF, DISP-FF and RECY). Additionally, particle size distribution of a slurry sample from the main scrubber (ORIG-slurry) was performed to compare the results with separated fractions. ORIG-slurry significantly differs among other samples, because slurry encompassed both finer and coarse particles. However, the proportion of coarse fraction represents only a minor part due to the rapid settling (sedimentation) of bigger particles although the sample was mixed before analysis.

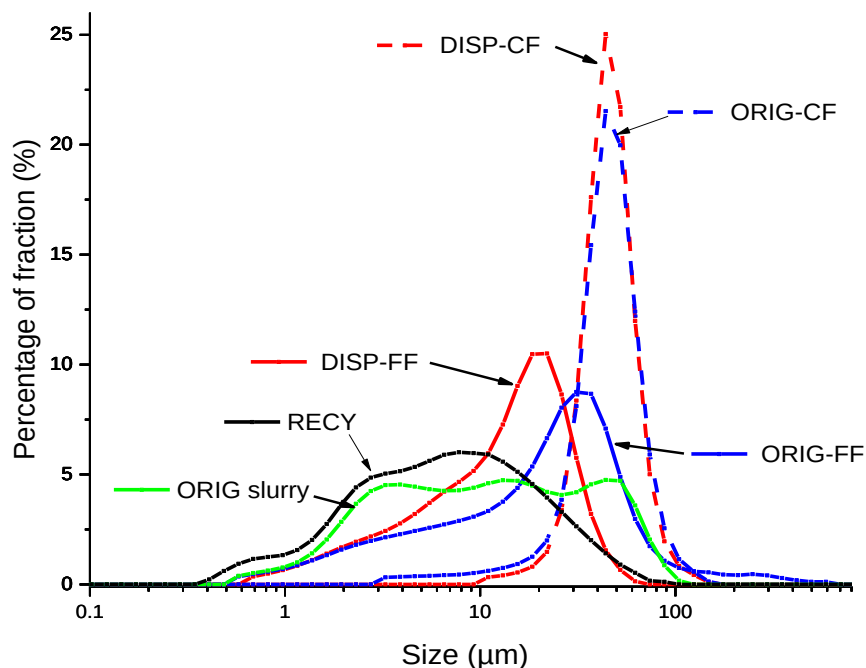


Figure 4.10: Distribution of particles in fine and coarse fractions of gypsum from block 6.

Smaller particles accumulate a higher concentration of TMEs, as it has been already observed in the previous chapter. To connect the particle size distribution with the concentrations of TMEs in the samples, an example for Hg is provided here. RECY - the finest fraction contained the highest concentration of Hg. The Hg concentrations in both coarse fractions were similar (0.22-0.31 mg kg⁻¹), whereas the concentration of Hg in the

finer fractions decreased as follows: RECY (20.6 mg kg^{-1}) > DISP-FF (12.5 mg kg^{-1}) > ORIG-FF (8.94 mg kg^{-1}) (Table A.4), which is consistent with the particle size distribution.

Figure 4.11 shows SEM pictures of various gypsum samples. In the bulk gypsum, coarse fraction prevails, and the fine fraction is barely seen (Figure 4.11a). The coarse fractions are mostly composed of crystals $>40 \mu\text{m}$ size (Figure 4.11b). In the fine fractions (Figure 4.11c), in addition to smaller $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ crystals, other solid compounds were formed under slurry water recirculation process by precipitation and adsorption process (Córdoba et al., 2015). Inclusions of Fe and Al oxy-hydroxides were present in the fine particles of the gypsum (Figure 4.11d; EDS analysis in Figure 4.12).

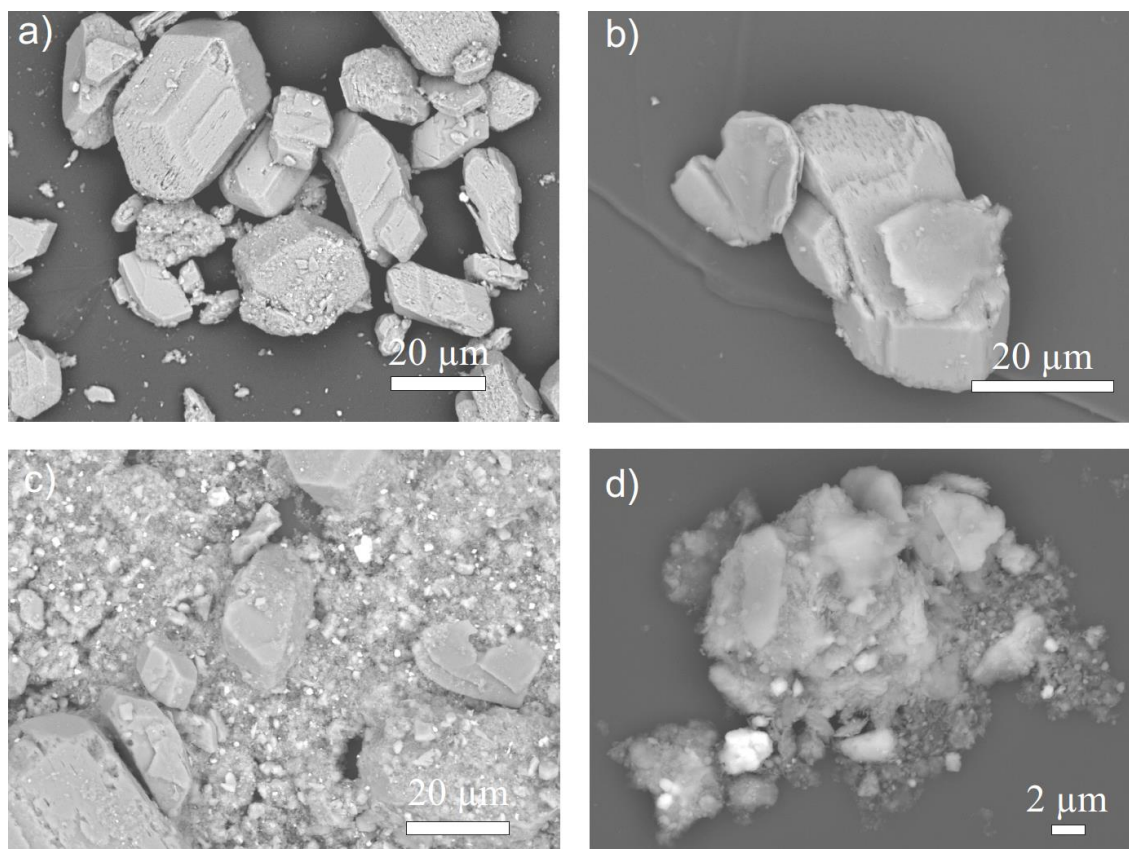


Figure 4.11: Scanning electron microscope (SEM) images of solid particles in gypsum: a) bulk fraction of ORIG gypsum sample, b) crystal of gypsum in a coarse fraction of DISP-FF, c) finer fraction of ORIG-FF gypsum and (d) an example of agglomerate present in the finest fraction of RECY gypsum.

Since SEM figure cannot give us the information about elemental composition, SEM-EDS was applied for observation of the gypsum sample RECY. This methodology enables elemental analysis or chemical characterization of the sample. The advantage of this method is that you can determine the location in the sample which you are interested in and get the information about elemental composition. However, the uncertainty of the method depends on the sample, sample preparation and varies up to 5%. We performed this measurement to confirm the presence of iron/aluminium oxides. However, more measurements are needed as well as using of calibration standards to compare the spectra and to calculate the species possibly present in the sample according to the percent of each element. In general, characterization of the finest particles in the view of speciation is very

important. All this information helps in the understanding of the species responsible for the accumulation of TMEs.

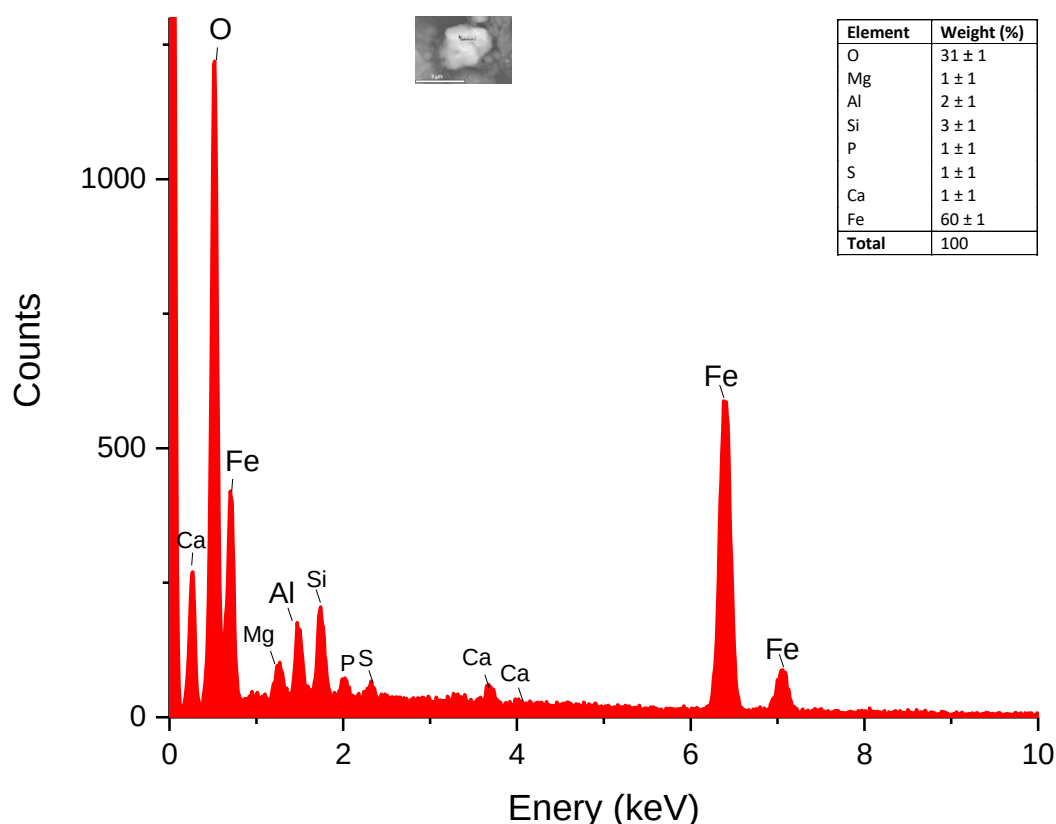
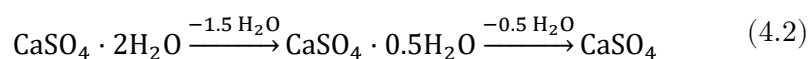


Figure 4.12: SEM-EDS spectrum and elemental quantitative data representative in the gypsum sample RECY.

Figure 4.13 represents the TG-DTA thermograms of two gypsum samples (one coarse and one fine fraction), DISP-CF and RECY, recorded under heating between 25 and 550 °C. Equation 4.2 summarizes the reaction of the removal of H₂O from CaSO₄ · 2H₂O (Borrachero, Payá, Bonilla, & Monzó, 2008; Fatu, 2001):



The temperature interval of interest is between 100 and 220 °C, where the H₂O evolves in two steps (see Figure 4.13 DTA and TG, mass loss) as a consequence of the CaSO₄ · 2H₂O decomposition (dehydration, loss of the hydrated water). DTA maximum is observed at 164 and 183 °C for DISP-CF and 153 and 164 °C at RECY gypsum.

As already mentioned, a sample of coarse fraction mostly consists of CaSO₄ · 2H₂O and graph for DISP-CF gypsum sample representing almost pure gypsum (calculated value from the graph is 97.5%). In Figure 4.13b the situation in the fine fraction of RECY lower water removal indicating less crystalline CaSO₄ · 2H₂O present in the finest fraction (the calculated number is 39.2%). Mass loss (TG) and DTA differ among Figure 4.13a and Figure 4.13b where water from the sample of RECY (Figure 4.13b) starts releasing a little

before than from DISP-CF (Figure 4.13a). This is probably due to the presence of smaller crystals of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. Also, mass loss from the beginning of the DTA curve is seen in the sample of RECY which confirms the presence of other unstable species caused by decomposition and formation of gases that evolve from the sample.

It follows that water removal at higher temperatures represents the strongest decrease in mass loss even in the finest gypsum. Volatile species as a consequence of thermal decomposition start evaporating above 250 °C which is evident in Figure 4.13. In a coarse fraction, this is mainly due to the decomposition of CaSO_4 and unconsumed CaCO_3 , where SO_2 , CO_2 and other gases released. In fine fraction in addition to CaSO_4 decomposition of other decomposition products may form as well.

In case of mercury, interaction with matrix and with water complicate the identification of the mercury species that is initially present in the gypsum sample. Moreover, dehydration and decomposition of the sample change the sample structure (crystal lattice) and Hg that is trapped may release.

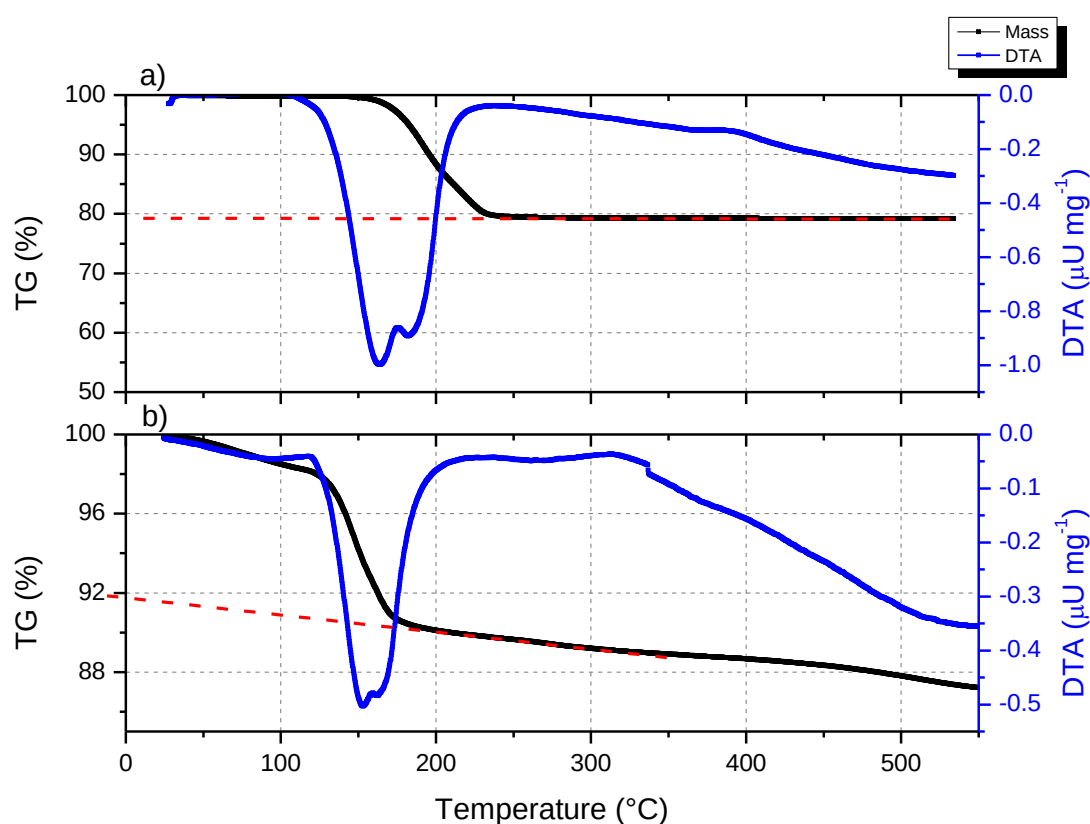


Figure 4.13: TG and DTA analysis for gypsum samples of a) coarse fraction (DISP-CF) and b) fine fraction (RECY) in the temperature interval between room temperature and 550 °C.

4.1.3.2 Partitioning of elements in different size fraction of gypsum

4.1.3.2.1 Enrichment of elements in fine fraction

The results of the multielemental analysis (43 elements) of the fine and coarse fractions are given in Table A.4 in the Appendix A. Most of the elements show positive correlations between the concentrations of Hg and concentrations of other elements (Pearson correlation coefficient and statistical significance are provided in Table A.5). Majority of TMEs

accumulate in the fine fraction rather than in coarse because of the smaller particle sizes. However, negative correlations with the concentration of Hg were shown for Ca, S, Sr and halogens (Br, Cl), except for iodine. Ca, S and Sr are the major elements in coarse fractions, and their concentrations are typically lower in the fine fractions. In the study of Sedlar et al. (2015), halogens were found in much higher concentrations in the fine gypsum fractions compared to the coarse fractions (Sedlar et al., 2015). In this work, high enrichment of Cl and Br in fine fraction compared to the coarse fraction was not observed. Also in the finest fraction of RECY, the halogens are present in concentrations similar to the coarse fraction DISP-CF. One reason could be the presence of SCR which is primarily intended for NO_x removal. Due to the possible formation of various Cl and Br species that may bound to some particles after SCR, these particles may be removed in ESP. It follows that concentrations in the gypsum are lower. Another option is that halogen species in the slurry water do not accumulate in the gypsum but rather circulate in the system. Their concentrations in the slurry water are constant, and when the concentrations exceed the formation of precipitates and adsorption to particles becomes important.

Figure 4.14 shows the Ca:S molar ratios of the different gypsum samples. The Ca:S ratio was nearly unit one in the coarse phases (ORIG-CF and DISP-CF), indicating pure $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, while in ORIG-FF and DISP-FF they were between 1 and 2. In RECY there is a strong deviation from unit one, likely because of the presence of various carbonates (e.g. unconsumed CaCO_3). Moreover, Ca precipitate with molecules and cluster ions other than SO_4^{2-} (Córdoba, 2015).

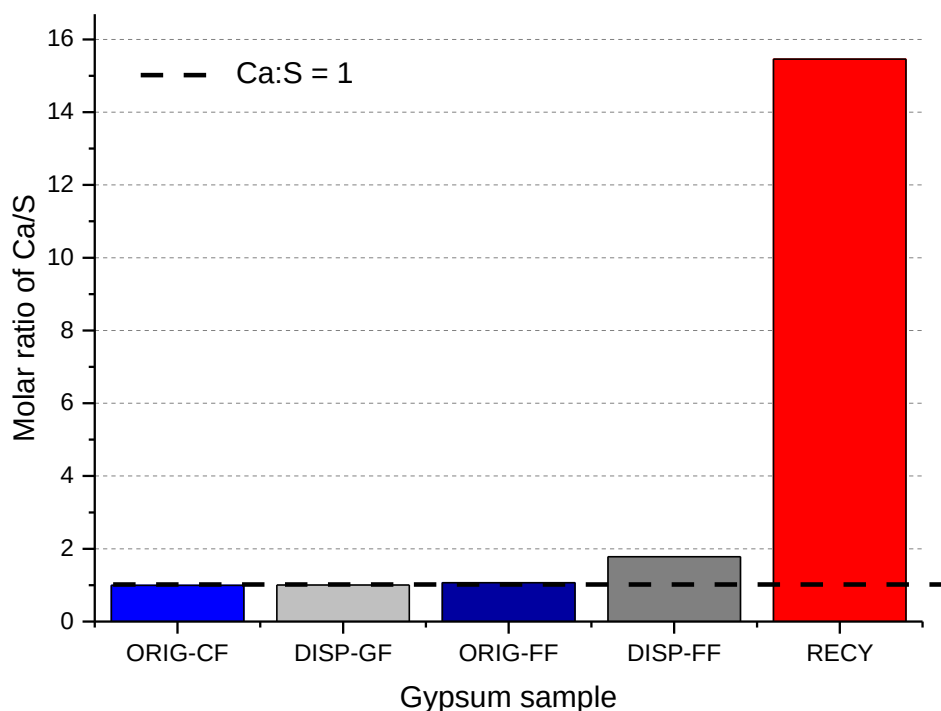


Figure 4.14: The molar ratio between concentrations of Ca and S present in gypsum fractions.

Figure 4.15 shows a significant difference of TMEs concentrations between the ratio of fine to coarse fraction in the samples DISP and ORIG. Gypsum samples intended for further processing before disposal to the landfill (DISP) demonstrate high enrichment for most of the elements in a fine fraction concerning the coarse sample and in comparison with the samples of ORIG. DISP sample is filtered/separated in hydrocyclone and slurry with the smallest particles and soluble species is returned to the scrubber. During the “dewatering process” adsorption and precipitation might be the processes responsible for the accumulation of most of the elements that are present at an elevated concentration in DISP samples regarding ORIG sample. This could also explain a slightly higher ratio for Ca/S in Figure 4.14. The higher Ca/S ratio proposed the formation of other compounds and thus the purity of gypsum decrease.

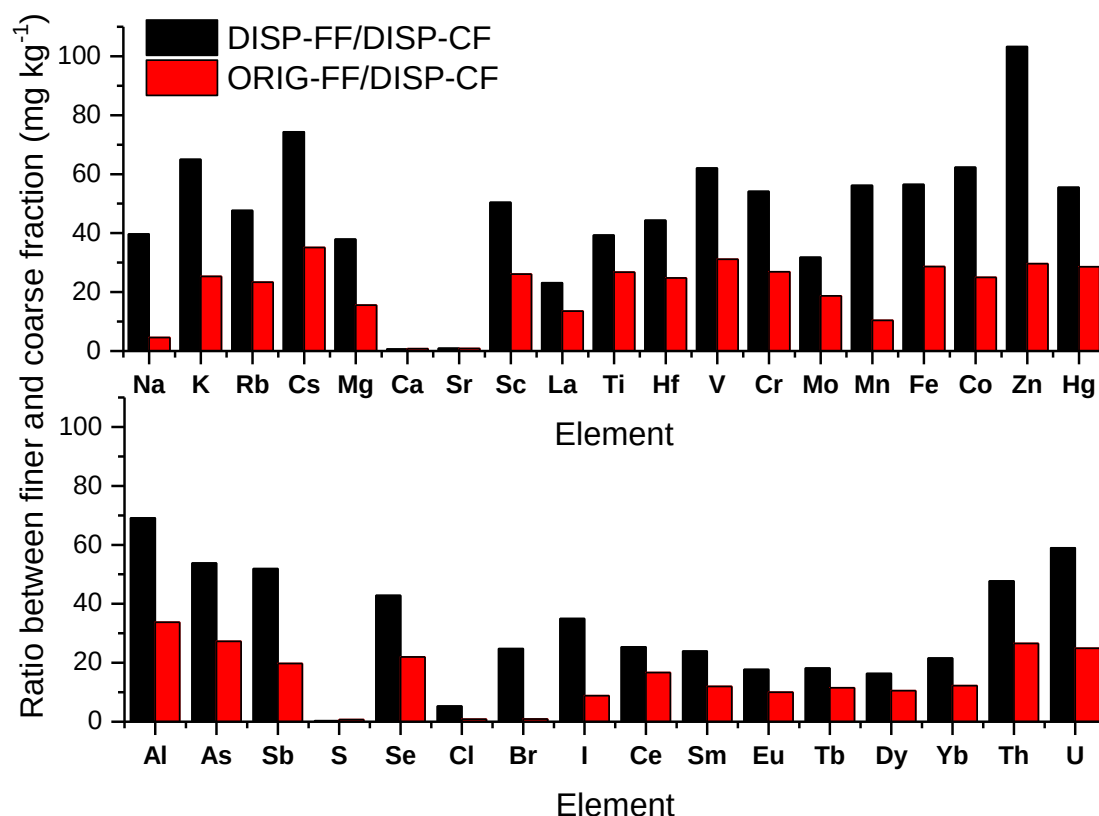


Figure 4.15: Enrichment of elements in the fine fraction compared to the coarse fraction of block 6. Elements are ordered according to the periodic system: alkali, alkaline earth metals, transition metals and post-transition metals (Al, Ga, In), metalloids (As, Sb), non-metals (S, Se), halogens (Cl, Br, I), lanthanides and actinides.

4.1.3.2.2 Comparison of fine and coarse fractions versus lignite

The finer fractions accumulate most of the elements where attention is devoted to Hg and Se. The finest fraction labelled as RECY shows a little different slope of the trendline about the others due to the increased concentration of some elements. Moreover, the smallest particles are responsible for the higher accumulation of some elements (regarding the concentration in coal), such as V, Cr, Zr, U, Ga, Dy, Se, Hg and Ti. On the other side, soluble species such as Br, Cl, Na, Mn and S are depleted in the finest fraction (Figure

4.2 Temperature Programmed Desorption Method

We previously examined the importance of particle size for mercury accumulation in WFGD gypsum from lignite burning Šoštanj TPP and tried to identify possible Hg-species present in the fine fraction of the gypsum (Sedlar et al., 2015; Stergaršek et al., 2008). Because the sensitivity of TPD method using AAS detection is not sufficient to detect the low concentrations of Hg compounds in the solid samples such as coarse gypsum fractions, the mass spectrometer was applied in the present study. We hypothesise that high sensitivity and the ability to measure other volatile species and their fractions would allow the identification of Hg species present in the gypsum samples. Although MS has a lot of advantages versus AAS, it has its limitations that are described in subchapters. The results obtained by TPD method include various gypsum samples from block 4, 5, 6 of Šoštanj TPP and different gypsum samples from China. Since samples were differently prepared, the influences on TPD spectra including sample preparation and age of the sample are presented here. Fe and Al were enriched in the fine gypsum particles compared to the coarser gypsum. Therefore, part of the experiments reported in this dissertation was devoted to studying the desorption/decomposition of different Hg-species mixed with FeOOH, Al(OH)₃ and CaSO₄ · 2H₂O. Part of this chapter is also intended to determine HgCl₂ and HgS in the investigated gypsum samples since these two species are thought to be present in most gypsum samples.

4.2.1 Development and validation of the method for Hg fractionation using quadrupole mass spectrometer (QMS)

TPD approach using CV-AAS detection is well described in the doctoral dissertation of Sedlar (Sedlar, 2014). In the present study, NT-MS was applied at the beginning of the experimental work and then replaced with new set-up (QMS). The desorbed atomic and molecular species were ionized by electron energy of 35 eV (NT-MS) and 70 eV (QMS). These two mass spectrometers have different ion sources for ion generation (both produce ions with electron ionization) and mass analysers for mass separation. NT-MS used magnetic sector for mass ion separation whereas QMS used quadrupole mass filter. NT-MS could not measure more than one ion at the same time (continuous mode), as it is possible with QMS (multiple ion detection mode). Experimental set-up for sample introduction is similar in both cases. Since QMS was used for most of the experiments in this doctoral dissertation, advantages/disadvantages of this instrument are provided in this chapter. Some TPD spectra of gypsum obtained with QMS were compared with NT-MS. NT-MS was also used for experiments with HgCl₂.

4.2.1.1 Method development and optimization

During the development of the method using QMS, we tested and adjusted some parameters (settings) to optimise conditions before starting with the measurements of the actual samples:

- The heating rate of the thermocouple: Three different heating rates (5 °C min⁻¹, 10 °C min⁻¹ and 20 °C min⁻¹) were tested. There were no significant differences in TPD spectra and therefore 10 °C min⁻¹ was chosen for all further experiments. However, linear heating is stable with 5 and 10 °C min⁻¹, while with 20 °C min⁻¹ the heating is not constant and discrepancies (falling/rising) in heating line could be observed.
- Temperature correction factor: Heating quartz cell (where the sample is introduced, Figure 3.2) together with the sample coil and quartz tube were coupled with QMS. Spiral alloy heater has a small introduction hole for sample vessel (heating quartz

cell). The sample should be inserted and positioned at the same place each time, if possible. The sensor of the heating cell is not located in the middle of spiral alloy (where the quartz sample vessel is positioned) but below that, and the following temperature is, therefore, lower than in the sample itself. The correction factor had to be calculated because the temperature obtained in the display (measured temperature) deviated from the real temperature of the sample. Thermocouple type K (Nickel-Chromium) was used to determine temperature correction. To decrease the differences between measured and real temperature, we fixed the position of the sample vessel later (sample was located at the same position (height) in all experiments), and the correction factor was calculated as follows:

$$T_c = 1.42343 \cdot T_m - ((0.000148036) \cdot (T_m)^2) - 14.29032 \quad (5.1)$$

where T_c (°C) represents the corrected temperature and T_m (°C) the measured temperature.

- The amount of the sample: Mass is dependent on the concentration of Hg in the sample. A minimal amount of the sample (less than 1 mg with estimated uncertainty ± 0.2 mg) was weighted in the case of the pure Hg-standard mixture (mixture with $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ or SiO_2), few mg for other Hg compounds mixed with FeOOH or $\text{Al}(\text{OH})_3$, and between 1-15 mg for actual gypsum samples (depends on Hg concentration in the sample). Experiments showed that in the presence of smaller sample weight, the obtained TPD spectra show peak(s) with fewer interferences (peaks are smoother). However, this is not the case in the samples with Hg concentration below 0.5 mg kg^{-1} .
- Powder sample with smaller particles may enter into ionisation cell and might form a barrier for efficient ionization. To prevent this effect a quartz nozzle was inserted between the sample cell and quartz tube. With appropriate heating rate (should not be too fast) and slow achieving of vacuum in pre-chamber (regulating with the rotary vane pump) sample entering into the ionization cell is prevented. This is also dependent on the sample material.
- Sample with higher humidity: Samples containing crystalline water or moist samples should be dried before measuring with QMS. In the case of no sample pre-heating, the presence of water vapour could saturate in the ion source, and ionization is not proper around 100°C . Although the boiling point is determined to be at 100°C , evaporation starts below this temperature. Simultaneous increasing of both Hg isotopes (200 and 202) and the background at m/z 203 confirm the presence of the false peak. This phenomenon is observed in the samples containing small Hg concentrations while at higher concentrations this effect is less pronounced. For that reason, most of the samples (including Hg-compounds mixed with $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) were dried in a heating cell under vacuum at $75\text{--}78^\circ\text{C}$. To see if there was any loss of Hg when the sample was preheated, various Hg-standards and gypsum samples were tested before pre-heating was regularly applied. In most experiments, mercury is detected at room temperature, but the proportion of Hg releasing in relation to the main Hg evaporation (main TPD peak) is negligible. Therefore, preheating has been routinely applied in further experiments with gypsum. An example of false peaks (artefact) in the presence of crystalline water is presented in Figure 4.17.

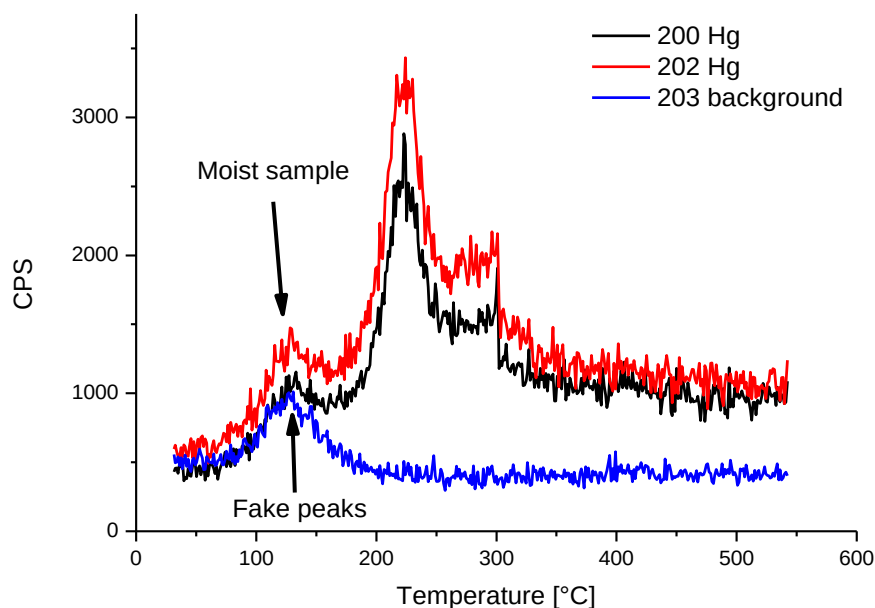


Figure 4.17: TPD spectra of two different isotopes of Hg (m/z 200 and 202) and background (m/z 203).

- Washing of the sample: For studying desorption/decomposition profile with QMS, it is recommended that samples are not treated before analysis to get the real TPD spectra. Some species in the samples may interfere with the spectra. Therefore, it is desirable that samples are water free (previously dried) and washed. The washing procedure usually does not significantly change Hg releasing profile but decreases the background. Therefore, interpretation of the peaks is easier, and the maxima of the peaks are more accurate. For this reason, a washing step was included as an efficient way of reducing background interferences. The presence of hydrocarbon and their fragments also interfere with the measured ionic species. More about the washing effect on TPD spectra is presented in the following sections describing the results obtained from samples of block 4, 5 and 6 of Šoštanj TPP.
- Heating of the system: Introduction part (cell) and tubes connecting rotary pump and MS have been covered with the heating tape. After each measurement (especially when using samples with Hg concentration $> 10 \text{ mg kg}^{-1}$) all these parts are heated to remove Hg that might potentially adsorb to the walls. This step is also essential for decreasing the background.
- Quartz tube introduction into the ionization cell (cross beam ion source with electron ionization, EI): Long quartz tube was inserted toward an ion source without touching the hole that leads into the cross beam ion source. Between quartz tube and ion source, the distance was $< 1 \text{ mm}$ supposing there was no ion lossless. We observed that if the quartz cell touches the collision cell, baseline (background) significantly increases and samples with low Hg concentration are unable to detect.

4.2.1.2 Mercury detection by QMS

Mercury has 7 stable isotopes with different natural abundances. Since the highest proportions have Hg isotopes 200 (23.10%) and 202 (29.86%), these two ions are normally used for measuring.

- Two Hg isotopes were measured simultaneously, m/z 200 and 202. Sometimes the background is very high, and isotope ^{200}Hg shows different releasing peak (TPD spectrum) than ^{202}Hg . Therefore, the whole m/z spectrum in the range between 194 and 207 was recorded (scan mode). If all seven Hg isotopes show an appropriate ratio between peaks, then Hg is confirmed to be present in the sample (Figure 4.18). All isotopes are seen except ^{196}Hg (its natural abundance is only about 0.15%).

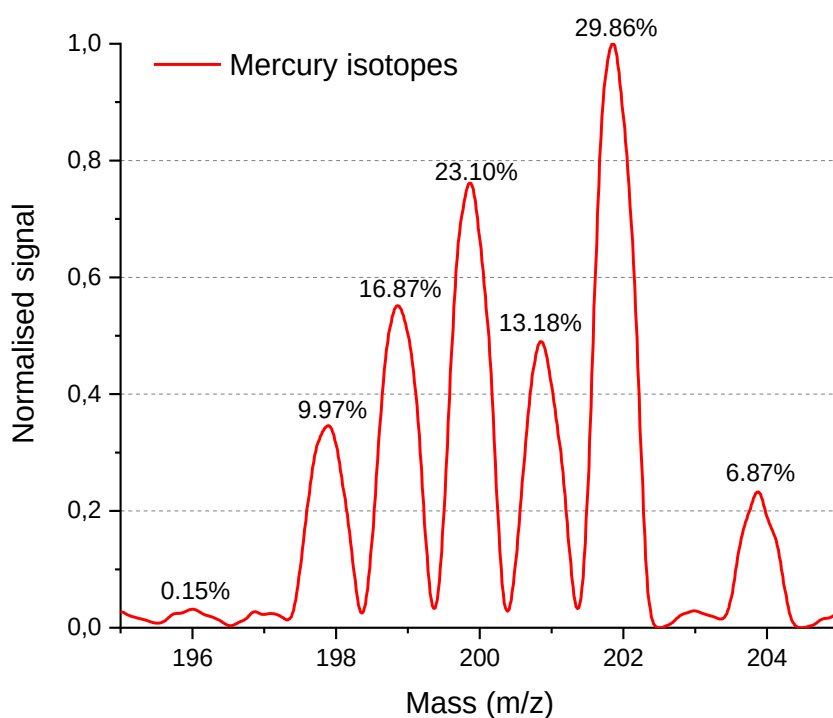


Figure 4.18: Typical mass spectra of seven different isotopes of Hg where ^{196}Hg is barely seen. Natural abundances (atom % in the environment) are written in percentage above the signal peaks.

Figure 4.19 does not represent typical pattern for Hg isotopes (scan mode). Two options are possible in such cases; mercury is not present in the sample, or background is much higher relative to the Hg. However, in this case, Hg is not present because intensity at m/z 200 is very low.

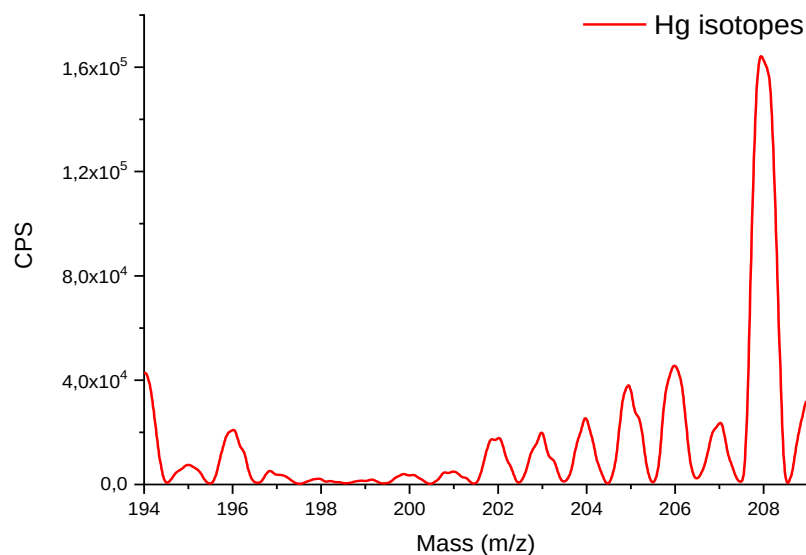


Figure 4.19: Mass spectra recorded in the m/z range 194-209. Typical mass spectrum of seven different isotopes is absent.

In the next example (Figure 4.20) the influence of background on Hg isotopes could be seen. This is emphasised especially at m/z 202. Here, Hg could be present in the sample. To confirm the presence of Hg in such a case, more Hg scans need to be recorded and compare the scans at room temperature and at elevated temperatures to see if Hg starts evaporating from the sample.

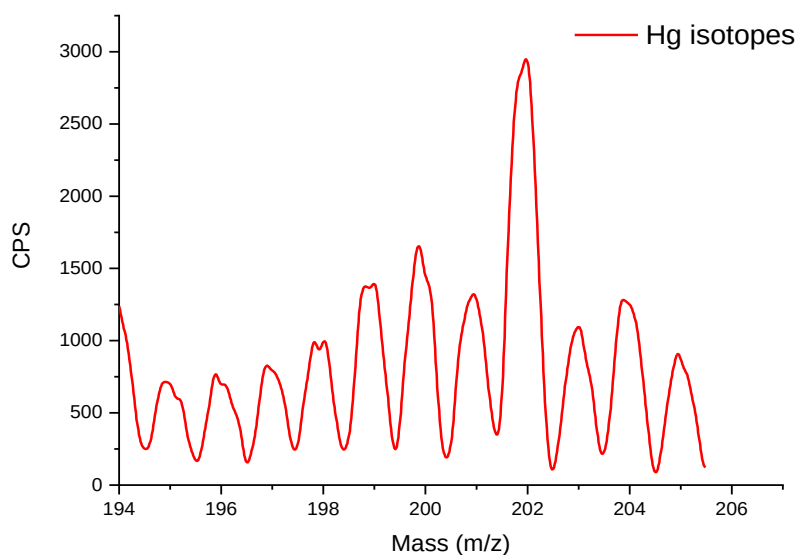


Figure 4.20: Mass spectra recorded in the m/z range 194-207. The ratio of Hg isotopes is under background.

- According to Figure 4.20 ^{200}Hg isotope was typically chosen for graphical presentation of TPD spectra due to its smaller background influence compared to the ^{202}Hg . To test the effect of the background, m/z 203 was measured simultaneously with two mercury isotopes (200 and 202). Background optimisation is an essential step in obtaining reliable results, especially at low mercury concentrations. The background is then subtracted from the main line of ^{200}Hg or ^{202}Hg (Figure 4.21).

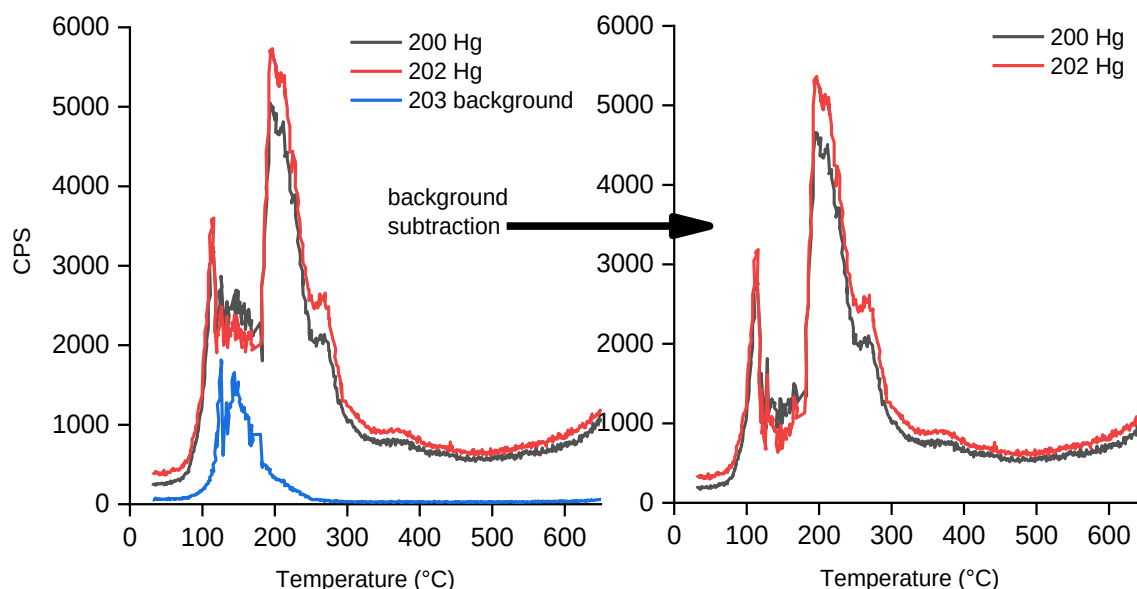


Figure 4.21: Background subtraction.

Sometimes the peak at m/z 203 is higher than at m/z 200 and 202. In Figure 4.22 at temperatures between 150 and 200 °C Hg peak is expected but due to the high background (m/z 203), this peak may be an artefact since all three peaks show a similar releasing profile. Similar trend is observed with the peaks at higher temperatures (Figure 4.22), where the background peak (m/z 203) is the most intensive and overlaps both Hg peaks.

In the presence of organic matter or complex matrices, the background might increase significantly. Additionally, the proportion (intensity) between Hg isotopes differs a lot, and this indicates that Hg is not present or is present in a very low amount (could not be detected). Scanning of mercury isotopes (the pattern similar to the one in Figure 4.19) confirm the absence of mercury in the sample and thus the formation of peaks that do not represent Hg releasing.

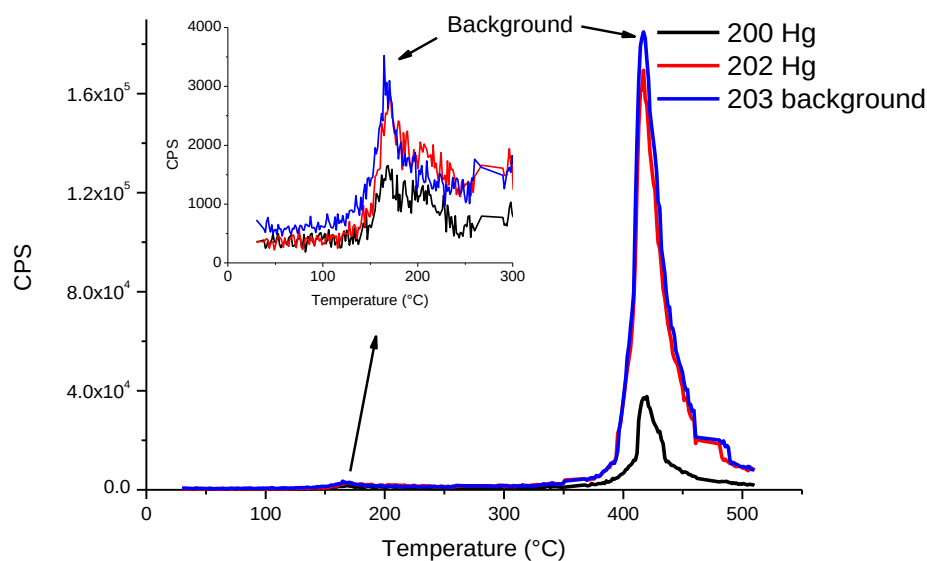


Figure 4.22: TPD spectra measure at m/z 200 and 202 and background m/z 203.

4.2.1.3 Sensitivity of the QMS

For TPD experiments, QMS is not intended to determine Hg concentration in the samples (quantitative Hg measurements) but rather to observe different releasing temperatures at which Hg or mercury compounds evaporate (decompose, desorb or sublimate). The concentration of Hg is measured with other instruments. The total amount of mercury in WFGD gypsum (a mixture of the fine and coarse fraction) is typically low ($<1 \text{ mg} \cdot \text{kg}^{-1}$) and even lower in the coarse fraction ($<0.2 \text{ } \mu\text{g} \cdot \text{g}^{-1}$). Fortunately, the much higher sensitivity of the QMS enables a reliable release profile in samples containing as little as $10 \text{ ng} \cdot \text{g}^{-1}$ of Hg.

- QMS is much more sensitive than CV-AAS (detection with Lumex device; RA-915+ mercury analyser with Zeeman background correction). In case of QMS (or NT-MS), typically less than 10 mg of the sample is needed to obtain thermograms with visible, separated peaks. Regarding the CV-AAS up to 0.5 g of a sample is required when the concentration of Hg in the sample is very low ($<0.2 \text{ mg} \cdot \text{kg}^{-1}$). The limit of quantification in QMS is about 0.05 ng of Hg present in the sample concerning the Lumex where at least 20 ng is needed to get the thermograms of sufficient peak visibility (meaning that maximum of the temperature could be easily determined from the spectra). TPD spectra with the amount of Hg less than 0.05 ng could be obtained by QMS, but the background effect prevails (Figure 4.23), and the spectrum is not clear. Detection of mercury (TPD spectra, thermograms) depends not only on Hg concentration in the sample but also on the sample matrices which can affect overlapping of the Hg peaks with the background of unknown species in the sample.

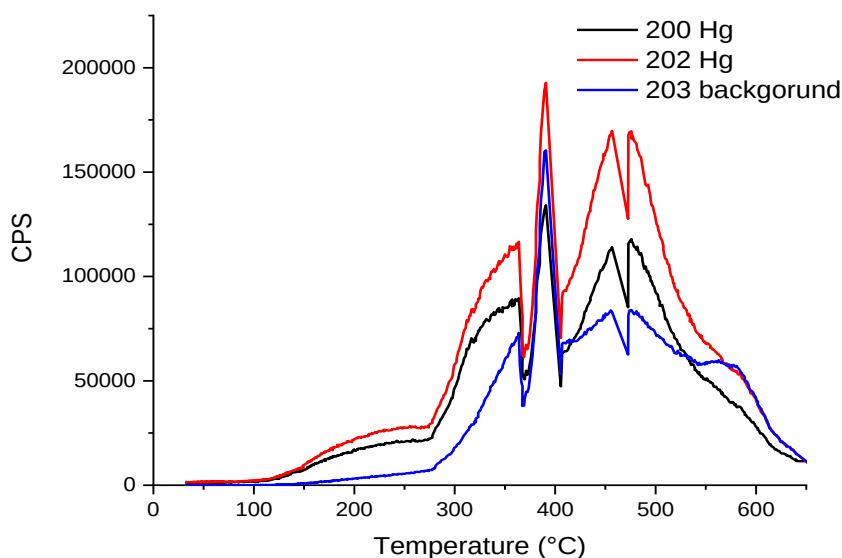


Figure 4.23: Sample contains 0.02 ng of Hg.

- Manipulation of the sample, such as washing or sample pre-heating, significantly improves the sensitivity. In the case of mercury species that tend to change (transform) under different environmental conditions, any handling may change the original identity. Therefore, doubt remains about the authenticity of the mercury species in the sample after sample manipulation.

Measuring of other ions (volatile compounds): Up to ten volatile species could be measured in the same experiment. Ion current is measured for each volatile species. Volatile species that released at higher concentrations should not exceed ion current of 10^{-5} A. For volatile compounds with elevated concentrations it is better to use Faraday cup detector than secondary electron multiplier (SEM). One needs to be aware that vacuum pressure should be better than 10^{-5} mBar (maximum operation pressure) during the whole measurement to get reproducible thermograms. If the vacuum is worse than 10^{-5} mBar, this could damage the instrument (SEM, ionization filament).

- Thermal decomposition of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is an example of observing other volatile compounds as a consequence of sample decomposition. The decomposition of crystalline water from the matrix shows a very intensive peak. In this case, the vacuum inside the instrument gets worse and also the ion current (intensity of the peak) confirms this (intensity of H_2O almost reaches the upper limit (threshold), 10^{-5} A). Water is one of the most critical gases. However, the same precaution also applies to other gases (e.g. SO_2 , CO_2).

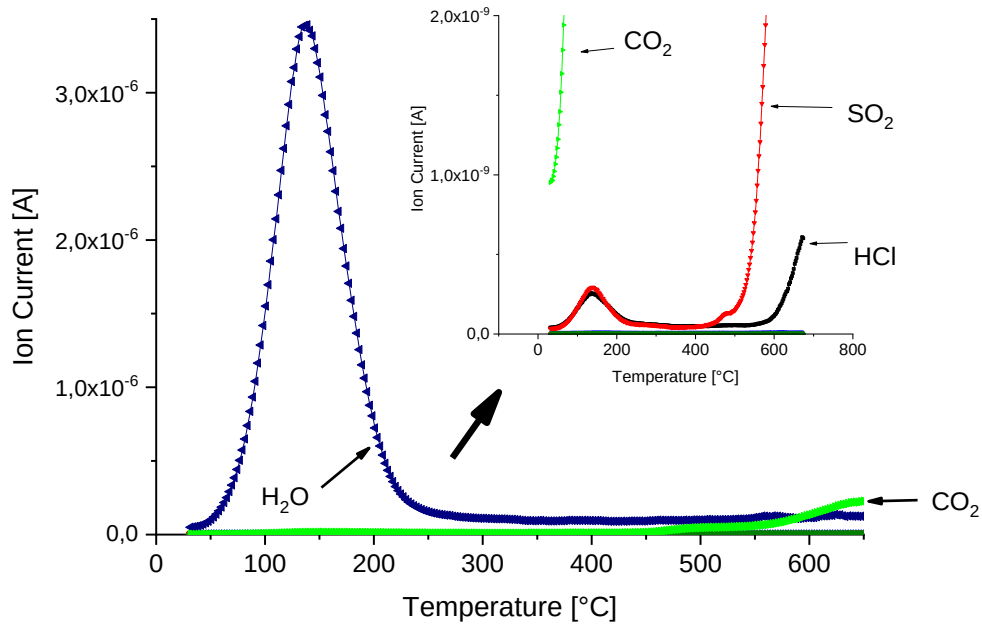
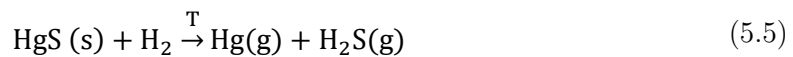
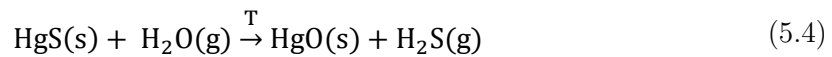
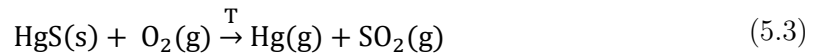


Figure 4.24: TPD spectra of H_2O , CO_2 and SO_2 released from the pure $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (SEM continuous mode).

- During sample heating, the sample start to decompose and different volatile species evaporate (as seen in Figure 4.24). But decomposition fragment could help with identification and prediction of the decomposition reactions. This is only possible for pure Hg compounds, not with the actual sample. In the actual samples, reactions cannot be assumed due to the much higher concentration of other volatile compounds rather than mercury. An example where we can predict decomposition reactions is HgS mixed with powder $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (Figure 4.25). Different reactions are suggested to happen during the decomposition of HgS according to the literature (Leckey & Nulf, 1994; Wu et al., 2011):



The first reaction suggests decomposition into Hg and sulphur. This reaction is favourable in the absence of O_2 . In the presence of O_2 reaction 5.3 is more likely. In the mass spectrometer under high vacuum, it is believed that a very small amount of oxygen is always present. However, the amount of O_2 is still much higher compared to the Hg present in the sample (or in the mercury standard). A small amount of SO_2^+ is detected and coincides with the peak of Hg^+ ions. The intensity of SO_2^+ depends on the presence of

O₂. Formation of intermediate [HgSO₃] is proposed in the study of Wu et al. (2011). Step reaction follows by the decomposition of [HgSO₃] into HgO and SO₂. HgO is further decomposed into Hg(0) and O₂ (reaction not showed) (Wu et al., 2011). The presence of H₂S⁺ ions is not expected and might form as a consequence of hydrolysis (Eq. 5.4). Here, the formation of HgO is suggested instead of Hg releasing. HgO decomposed into Hg(0) and O₂. HgS⁺ ion was not detected although sublimation of HgS is suggested in the literature (Lide, 2009). HgS decomposition is also proposed via reaction with H₂, which is also present in a small amount in a vacuum. Reaction in Eq. 5.5 was proposed at temperatures above 340 °C in a flow of hydrogen where dissociative sublimation (into Hg and S) and reduction of HgS proceeds (Baláž & Godočiková, 2001). However, due to the presence of a small amount of H₂ in the QMS system, this reaction cannot be excluded.

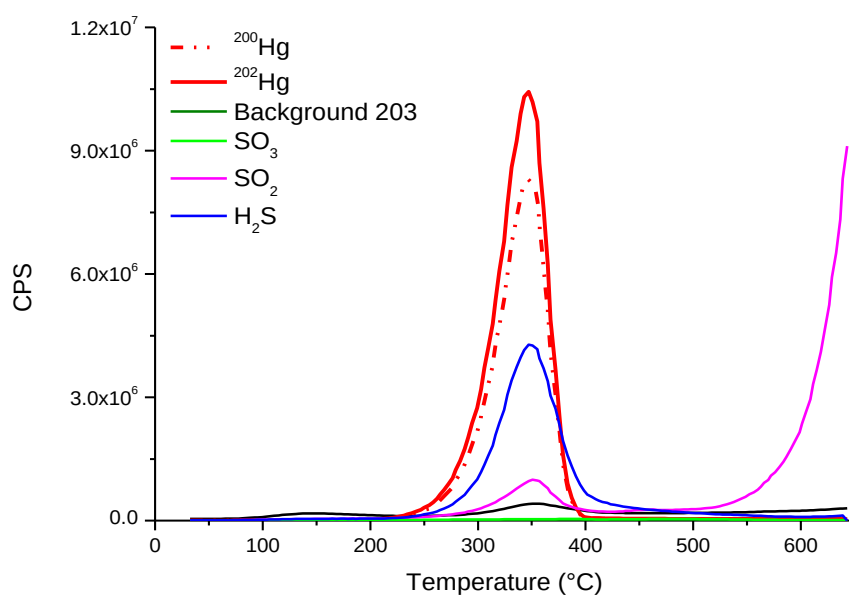


Figure 4.25: TPD spectra of various ions observed by decomposition of HgS mixed with dry CaSO₄ · 2H₂O.

4.2.2 Gypsum samples from Šoštanj thermal power plant

Different gypsum samples from Šoštanj TPP were analysed to determine the thermal stability of mercury/mercury compounds present in the sample and try to identify those compounds. All samples were separated into fine and coarse fractions as described in Chapter 3.3.3.1. TPD spectra were recorded in these samples (block 4, 5 and 6 from Šoštanj TPP). We compared the results with two different mass spectrometers, NT-MS and QMS. Also, the influence of sample preparation (washing effect, pre-heating of the gypsum, aging of the samples) on TPD spectra has been tested.

4.2.2.1 Samples from block 4

50 L of gypsum slurry was sampled from the WFGD scrubber of block 4 and two different aliquots of gypsum slurry sample were taken from barrel (Figure 4.26). One aliquot had normal particle size distribution (mixed slurry taken immediately after shaking the barrel; sample labelled as TEŠ4-MSN) while the other contains small amount of coarse fraction (finer slurry sample at the top was taken after sedimentation; sample labelled as TEŠ4-FS).

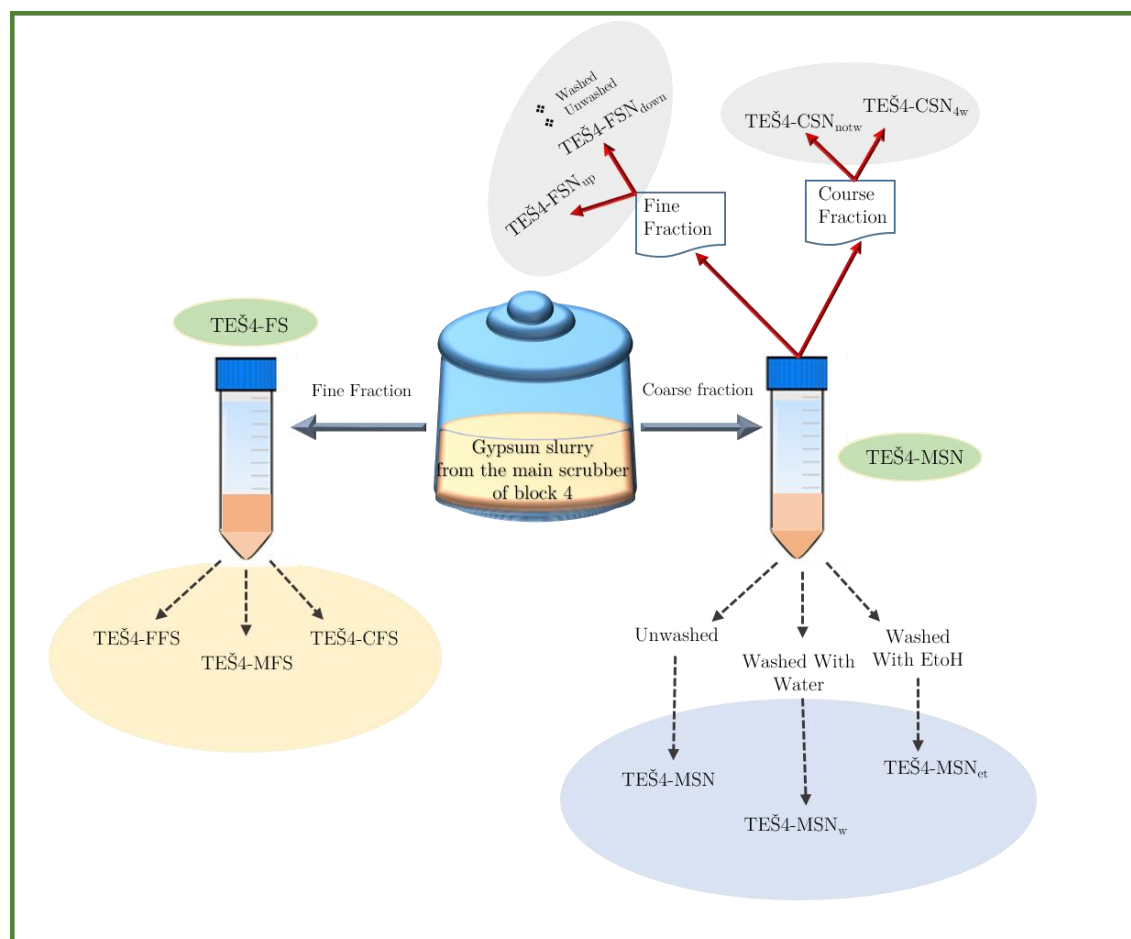


Figure 4.26: Scheme represents the preparation of different samples taken from the main sample of gypsum slurry which has been sampled from block 4.

These two aliquots were separated into different fractions (coarse and fine fractions) among which some were washed and others not. Separated fractions of aliquot that contains mostly fine fraction (TEŠ4-FS) are labelled as TEŠ4-FFS (fine fraction), TEŠ4-MFS (mixed

fraction), TEŠ4-CFS (coarse fraction). Different sub-aliquots were taken and prepared from aliquot with normal particle size distribution (TEŠ4-MSN); TEŠ4-MSN_{notw}, TEŠ4-MSN_w, TEŠ4-MSN_{et}, TEŠ4-CSN_{notw}, TEŠ4-CSN_{4w}, TEŠ4-FSN_{up}, TEŠ4-FSN_{down} and TEŠ4-FSN_{downnotw}. Separation based on sedimentation and the colour of the different gypsum fractions.

The total Hg concentrations and TPD spectra are provided to compare concentrations and variations among different gypsum samples and to see the differences between the washing procedures. The concentrations of each separated fraction are provided in Table 4.2. The results of thermograms are shown in Figures 4.28–4.31. Each measurement in Table 4.2 shows the concentration of Hg in various gypsum samples of block 4 that were used for TPD spectra characterisation. Additionally, sample weight used for each TPD measurement is written in the last column.

The concentration of mercury and particle size distribution in gypsum samples:

Table 4.2: The concentration of total Hg present in different gypsum samples from block 4 of Šoštanj TPP. Samples in the table are labelled the same as in TPD graphs.

Gypsum samples	Concentration (mg kg ⁻¹)	Mass (mg)
Finer fraction of block 4 (washed) - TEŠ4-FFS	4.05 ± 0.02	2.5
Mixed fraction of block 4 (fine + less coarse fraction, washed) - TEŠ4-MFS	1.09 ± 0.02	6.2
Coarse fraction of block 4 (washed) - TEŠ4-CFS	0.310 ± 0.003	11.7
Sample of mixed fraction (coarse + fine fraction of block 4, not washed) - TEŠ4-MSN _{notw}	0.644 ± 0.001	5.2
Sample of mixed fraction (coarse + fine fraction of block 4, washed with water) - TEŠ4-MSN _w	0.421 ± 0.007	5.8
Sample of mixed fraction (coarse + fine fraction of block 4, washed with ethanol) - TEŠ4-MSN _{et}	0.305 ± 0.008	5.1
Coarse fraction (not washed) taken from mixed fraction - TEŠ4-CSN _w	0.12 ± 0.01	11.6
Coarse fraction (highly washed) taken from mixed fraction - TEŠ4-CSN _{4w}	0.057 ± 0.001	10.7
FFF fine upper lighter fraction - TEŠ4-FSN _{up}	3.07 ± 0.02	2.4
FFF fine bottom dark fraction - TEŠ4-FSN _{down}	1.72 ± 0.01	2.6
FFF fine bottom dark fraction (not washed) – TEŠ4-FSN _{downnotw}	1.61 ± 0.13	11.7

*All samples were measured with DMA.

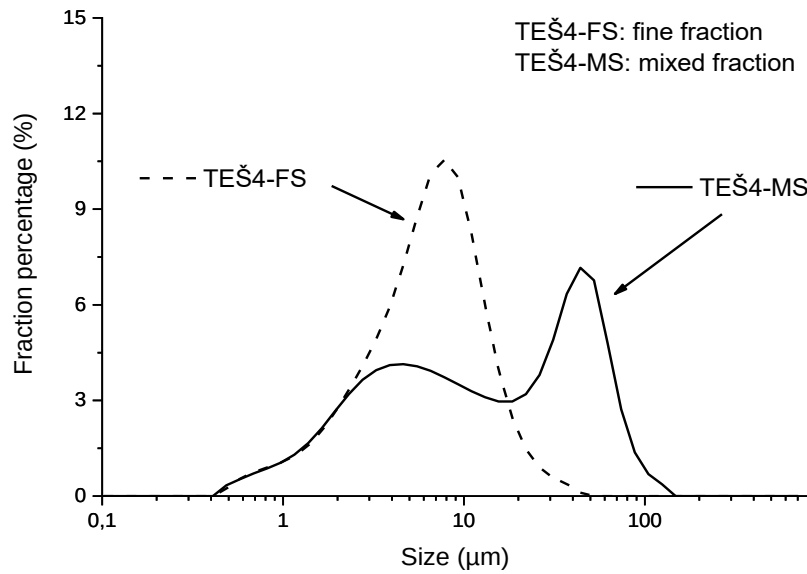


Figure 4.27: Particle size distribution of two gypsum samples from block 4, TEŠ4-MS and TEŠ4-FS.

Figure 4.10 shows the influence of particle size on Hg concentration where smaller particles accumulate more Hg (samples taken from block 6). In block 4, particle size distribution has not been obtained for all samples but only for TEŠ4-MFS and TEŠ4-FFS (Figure 4.27). Mixed fraction (TEŠ4-MFS) represents the sample aliquot that contains more fine fraction than is normally present in mixed gypsum (contains less than 50% of the coarse fraction). Bulk gypsum usually consists around 90% of the coarse fraction. Particle size distribution in TEŠ4-MFS is a consequence of the sampling procedure. The distribution in fine fraction (TEŠ4-FFS) is similar to the sample of RECY (Figure 4.10). The majority of particles size lies in the range between 5-10 μm. TEŠ4-FFS was prepared from TEŠ4-FS, and it contains the highest concentration of Hg among the samples prepared from the gypsum slurry samples of block 4. However, the concentration of Hg in fraction TEŠ4-FFS (Table 4.2) is five times lower compared to the sample RECY from block 6 (Table A.4). It follows that sample preparation represents an important step in the determination of total mercury concentration. Although smaller particles accumulate more Hg, its final concentration is still dependent on other factors present in TPP.

Table 4.2 shows a higher concentration of Hg in all fine fractions. However, concentrations in fine fractions differ among the samples for more than two times ($\text{TEŠ4-FFS} > \text{TEŠ4-FSN}_{\text{up}} > \text{TEŠ4-FSN}_{\text{down}} > \text{TEŠ4-FSN}_{\text{downnotw}}$). This is the consequence of sample preparation (Figure 4.26) where sample with the highest concentration (4.05 mg kg^{-1}) was prepared from different aliquot than other three samples. TEŠ4-FFS accumulates more Hg as a consequence of smaller particles compared to the samples $\text{TEŠ4-FSN}_{\text{up}}$, $\text{TEŠ4-FSN}_{\text{down}}$. Although these two samples represent fine fractions, the presence of bigger particles causes "dilution effect" and thus the concentration of mercury is lower (Table 4.2). However, Hg concentration in $\text{TEŠ4-FSN}_{\text{up}}$ is higher than $\text{TEŠ4-FSN}_{\text{down}}$. To test the washing effect, half of the $\text{TEŠ4-FSN}_{\text{down}}$ was washed, and the rest represents an unwashed sample $\text{TEŠ4-FSN}_{\text{downnotw}}$. There are not big differences in concentration between these two samples (washed and unwashed). This could be attributed to the species present in the gypsum that shows affinity to Hg. Both fractions ($\text{TEŠ4-FSN}_{\text{up}}$ and $\text{TEŠ4-FSN}_{\text{down}}$) differ in colour which is probably the result of a different composition of those two fractions.

Unfortunately, multielemental analysis has not been made for samples of block 4. Coarser fractions obtained from TEŠ4-MSN, labelled as TEŠ4-CSN_{notw} and TEŠ4-CSN_{4w}, show the lower concentration of Hg compared to the coarse fraction of TEŠ4-CFS. TEŠ4-CFS represents the residue of fine slurry particles that means that although it represents a coarse fraction, the particles are probably smaller than in normal coarse fraction taken from the mixed slurry.

TPD spectra: TPD spectra show one peak in most of the samples. The peak shape and peak height depend on the particle size – the presence of coarse fraction, and the amount of Hg in the sample. All TPD spectra are divided into four figures: Figure 4.28 represents fractions prepared from sample aliquot containing less coarse fraction (TEŠ4-FS), Figure 4.29 shows samples prepared from aliquot of normal particle size distribution (TEŠ4-MSN) where a different washing procedure was applied to see if there are any differences between the peaks, Figure 4.30 compares two coarse fractions, washed and unwashed prepared from the same aliquot (TEŠ4-MSN, normal particle size distribution), and the last Figure 4.31 represents different finer fractions also prepared from aliquot TEŠ4-MSN.

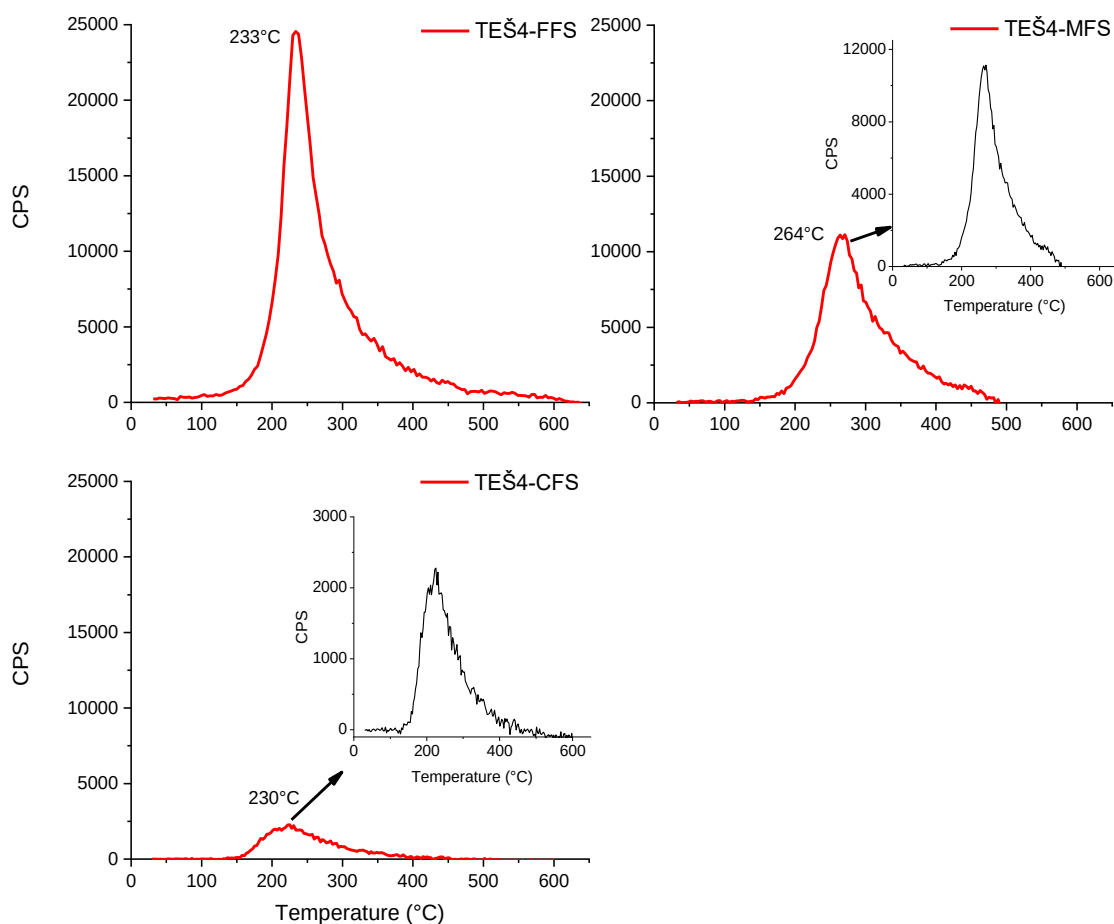


Figure 4.28: TPD spectra of finer (TEŠ4-FFS), mixed (TEŠ4-MFS) and coarse fraction (TEŠ4-CFS) are shown. Samples are prepared from TEŠ4-FS. All samples were washed before analysis.

TPD spectra in Figure 4.28 show one peak in all fractions. The shapes are similar while the temperature of peak maximum varies in the range of 247 ± 17 °C. As already mentioned, fine, mixed and coarse fractions originated from mixed gypsum slurry that contains less coarse particles (TEŠ4-FS). The same mercury compound(s) are suggested to be present in those samples.

Unwashed samples show different peaks compared to the washed gypsum. Thermograms of mixed fraction treated (rinse) with water, ethanol and without washing are presented in Figure 4.29. Water was used to see if removal of a soluble part in the sample effect on TPD spectra and if rinsing with the water removes soluble Hg from the samples. Ethanol was taken for removal of the organic soluble part since organic matter may disturb the TPD spectra. However, when using ethanol or water for rinsing, the concentrations of Hg in the samples is slightly lower (Table 4.2).

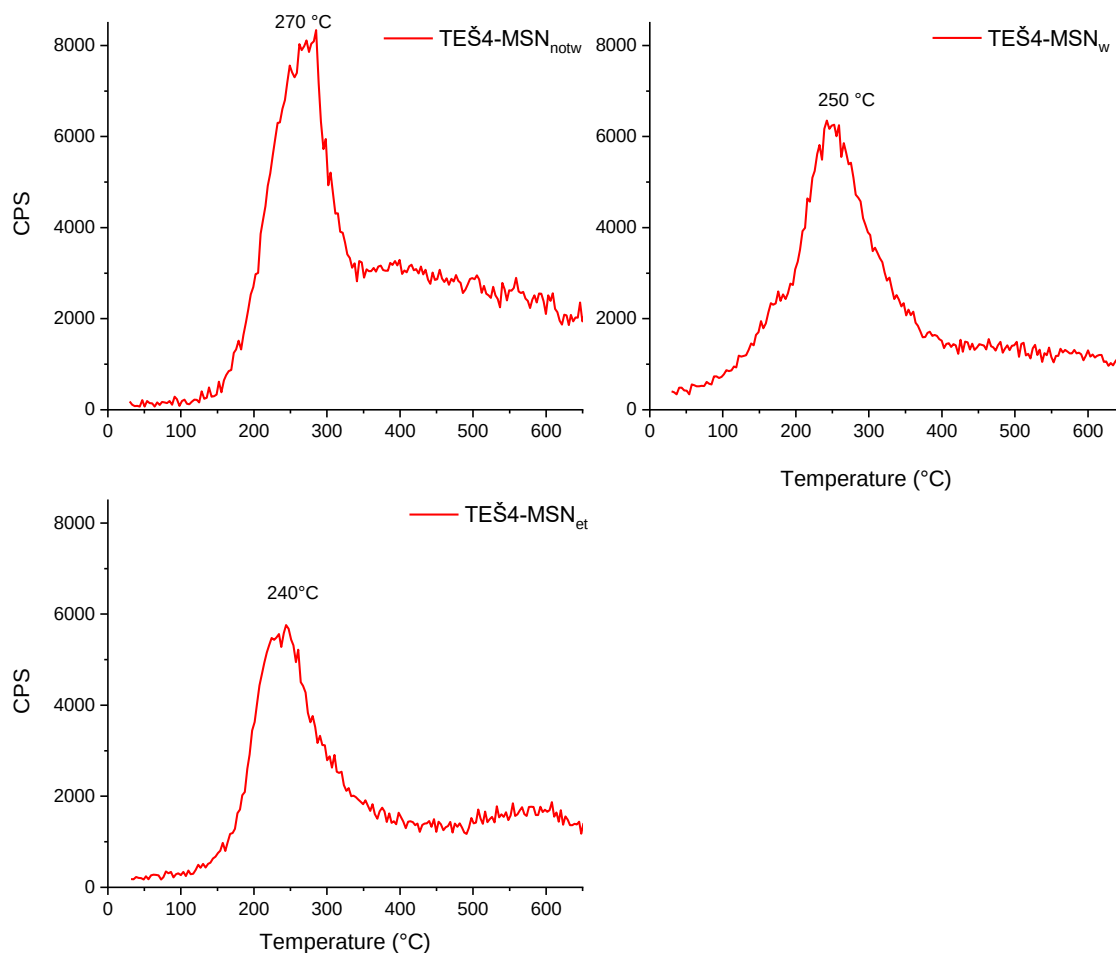


Figure 4.29: TPD spectra of gypsum slurry (randomly sampled) washed with water, ethanol or without washing.

Bigger particles (coarse fraction) broaden the peak shapes but releasing pattern for all three samples is similar. Unwashed sample (TEŠ4-MSN_{notw}) shows the influence of background, but the background is also observed in the TPD spectra of washed samples, TEŠ4-MSN_w and TEŠ4-MSN_{et}. In the unwashed sample Hg released (peak maximum) at 270 °C which is a little higher temperature than in washed samples (240 and 250 °C). In

TPD spectra of unwashed samples, more peaks may occur, and the peaks are not smooth. However, peaks are not smooth also in case of washed samples (TEŠ4-MSN_{et} and TEŠ4-MSN_w). In general, spectra do not differ so much, and procedure such as washing could only reduce the background. However, concentration in washed samples is lower meaning that part of Hg is lost during the washing procedure. This probably represents soluble Hg species, and Hg adsorbed on a surface that can easily be removed.

TPD spectra of two different coarse fractions prepared from TEŠ4-MSN are shown in Figure 4.30. Highly washed coarse fraction (rinsed four times), TEŠ4-CSN_{4w}, has a similar shape than a coarse fraction obtained from TEŠ4-FS (TEŠ4-CFS, Figure 4.28), but the peak intensity and Hg concentration are much lower compared to TEŠ4-FS. Unwashed coarse fraction has a higher concentration than highly washed gypsum (Table 4.2), but the influence of background is observed. The peak is wider with many humps compared to TPD spectrum of TEŠ4-CSN_{4w}. The peak of TEŠ4-CSN_{4w} is very noisy due to low Hg concentration. It is possible that soluble Hg-compounds (if present in the gypsum samples) wash out from the sample during rinsing of the gypsum. To see if Hg is released with washing, we measured the concentration of Hg in the washing solution. Hg concentration of around 2.5 ng mL⁻¹ was obtained in the "leached solution". In the study of Stergaršek et al., Hg concentration < 1 ng mL⁻¹ was measured in WFGD water from block 4 (Table A.1). Gypsum slurry water contains a small amount of Hg due to the conditions in WFGD scrubber that retain mercury in a stable form (as bound to particles). However, we did not perform the measurements in the gypsum slurry (water residual) from the main scrubber to compare the data of slurry water and rinsed water solution.

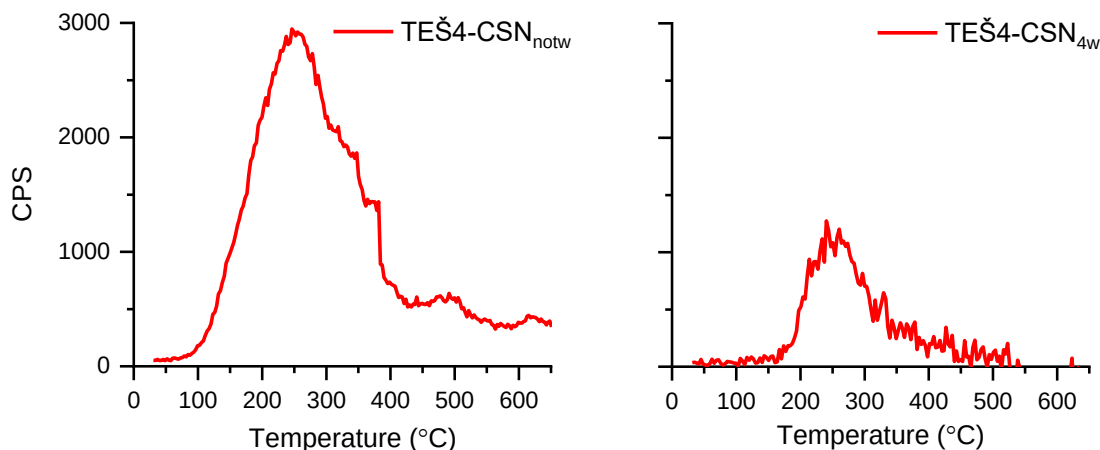


Figure 4.30: TPD spectra of unwashed and washed samples taken from mixed fraction TEŠ4-MSN.

Figure 4.31 shows the thermograms of two finer fractions (TEŠ4-FSN_{up} and TEŠ4-FSN_{down}) prepared by separation of the fine fraction taken from TEŠ4-MSN. One narrow peak is seen for TEŠ4-FSN_{up} (upper lighter fraction), while for TEŠ4-FSN_{down} (dark bottom fraction) the intensity of the peak (peak height) is much lower and consequently the peak shape is broader. A higher proportion of coarse fraction in this sample follows by lower Hg concentration (Table 4.2). Also, one unwashed sample of the fine bottom fraction was tested (TEŠ4-FSN_{downnotw}). A significantly different peak was observed. Similar as in Figure 4.29, unwashed samples show a broader peak with a peak maximum at little higher temperatures. However, it is hard to determine the peak maximum due to the peak shape. It seems that different species (impurities) in fine fraction have the stronger influence to

the peak shape compared to coarse or bulk fractions where this is not so obvious. A unwashed sample of TEŠ4-FS_{up} has not been prepared due to the small amount of sample.

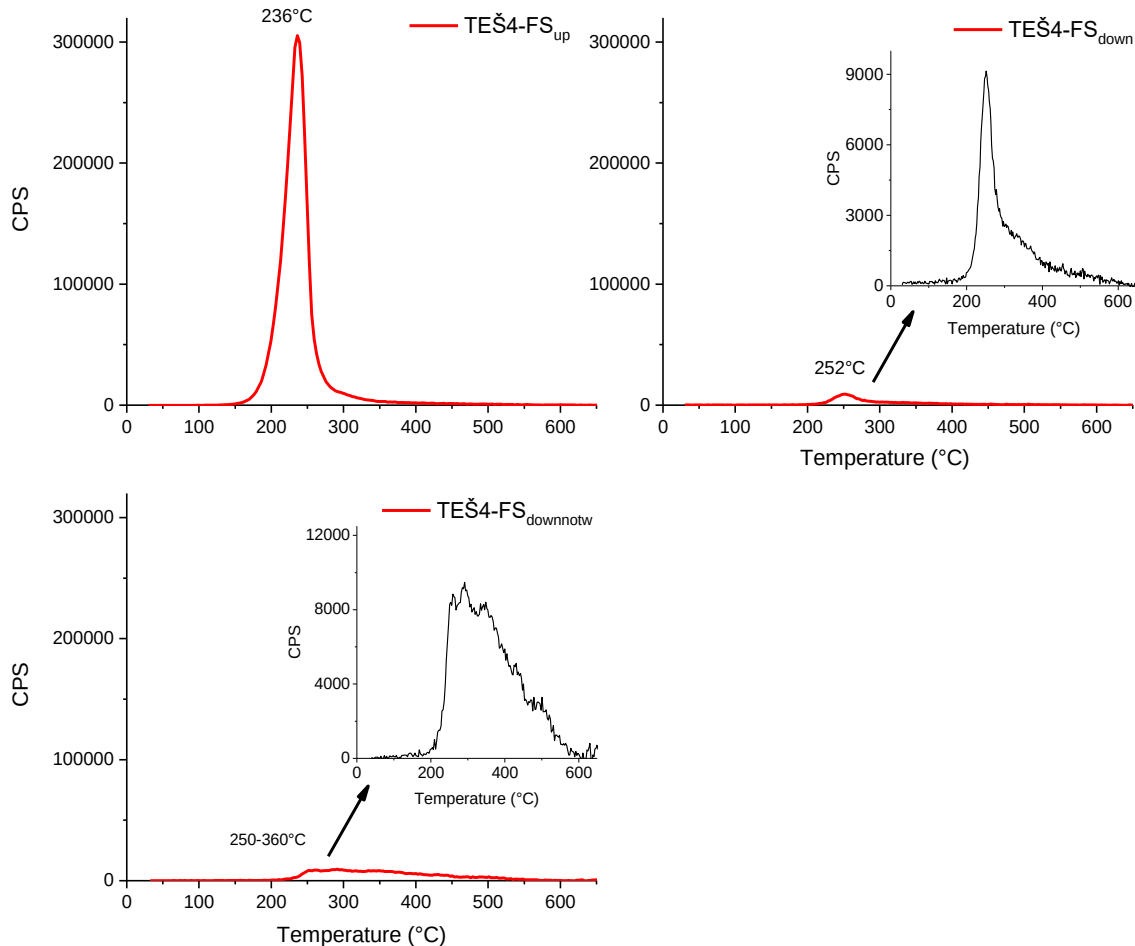


Figure 4.31: TPD spectra of fine fraction separated into FFF upper fraction and FFF bottom fraction. The unwashed sample is shown for comparison.

Discussion: It is suggested that the washing procedure (rinsing of the sample) leached a small part of soluble mercury species or weakly adsorbed mercury/mercury species. The literature states no obvious differences in Hg concentrations between the washed and unwashed materials taken from the same facilities. However, watering promoted Hg release from all FGD materials to the air after some time with more Hg release from those samples that have been previously washed. This could be explained by the reduction of oxidized Hg (Gustin & Ladwig, 2010). In the doctoral dissertation of Sedlar, it was found out that humidity has a significant effect on Hg releasing from the samples shown by the different TPD profile (peak shape) for the moist (wet) and dry sample. By using QMS, all samples were pre-dried before measuring since unreal peaks were formed in the presence of water (moist sample), see Chapter 4.2.1. Humidity affects Hg releasing but also other impurities in the sample matrix play an important role as found in the TPD spectra of unwashed gypsum. If we compare the washed, and unwashed samples, higher background, broader peaks, differences in the peak shapes and slightly higher temperature of Hg releasing from the sample are typical in unwashed samples. Therefore unwashed samples prevent detail

observation of Hg releasing peak in our study. Washing is an efficient way to the decrease measurement background. However, according to the results demonstrated in Figure 4.28, it should be emphasised that some Hg could release during the sampling preparation. More studies are needed to see the effect of water on the releasing of Hg from gypsum samples from Šoštanj TPP. Moreover, more leaching tests should be performed to obtain the information about the soluble and weakly adsorbed part of Hg in the gypsum.

4.2.2.2 Samples from block 5

The properties of samples from block 5 are described in Chapter 4.1.2. The composition of gypsum and the concentrations of TMEs differs among the samples. Gypsum slurry samples were sampled three times where each slurry was separated into fine and coarse fraction (Figure 4.32). Within coarser fractions, there are not so many differences as in fine fractions (concentrations in coarse fractions are between $0.1\text{--}0.2\text{ mg kg}^{-1}$). Fine fractions contain about 10 mg kg^{-1} of Hg ($\text{TEŠ5-FF2} = 11.9\text{ mg kg}^{-1} > \text{TEŠ5-FF} = 10.6\text{ mg kg}^{-1} > \text{TEŠ5-FF1} = 8.6\text{ mg kg}^{-1}$).

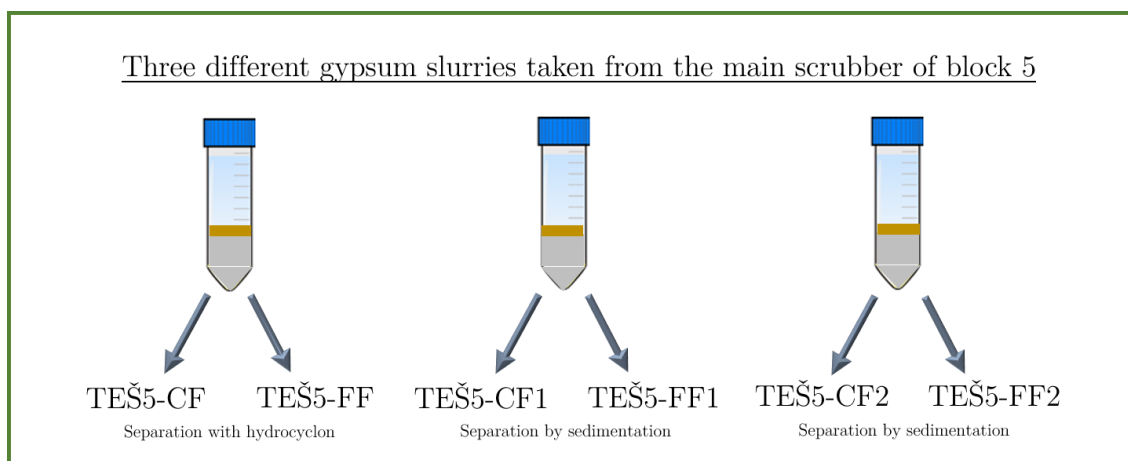


Figure 4.32: Three different gypsum slurry samples were obtained from block 5 and separated into finer and coarse fractions.

TPD spectra of gypsum samples obtained from block 5 are shown in Figures 4.33–4.35. Gypsum slurry samples were taken at three different sampling times and separated with two different procedures as described in Chapter 3.3.3.1. All samples were analysed with NT-MS where sample pre-heating has not been applied, and with QMS where samples were heated before TPD analysis. Some differences among the thermograms have been observed. Samples were not washed before TPD analysis.

Experiments with NT-MS: The coarser fractions (TEŠ5-CF, TEŠ5-CF1 and TEŠ5-CF2) are similar, and the strong sharp peak is observed around $90\text{ }^{\circ}\text{C}$. In the fine fractions, the position and intensities of the peaks differ among the samples. Three different peaks are seen in the samples of TEŠ5-FF1 and TEŠ5-FF2: at around $90\text{ }^{\circ}\text{C}$ (similar than in coarse fraction), between 140 and $200\text{ }^{\circ}\text{C}$ and the last peak is observed in the range between $300\text{--}360\text{ }^{\circ}\text{C}$. In the fine fractions of TEŠ5-FF1 and TEŠ5-FF2, the peak above $300\text{ }^{\circ}\text{C}$ is the most intensive. As seen in Figure 4.33, TEŠ5-FF shows a completely different TPD spectrum concerning TEŠ5-FF1 and TEŠ5-FF2. TEŠ5-FF shows only two peaks instead of three; strong peak at $144\text{ }^{\circ}\text{C}$ and peak at $356\text{ }^{\circ}\text{C}$, which is barely seen. The peak at about $90\text{ }^{\circ}\text{C}$ is absent.

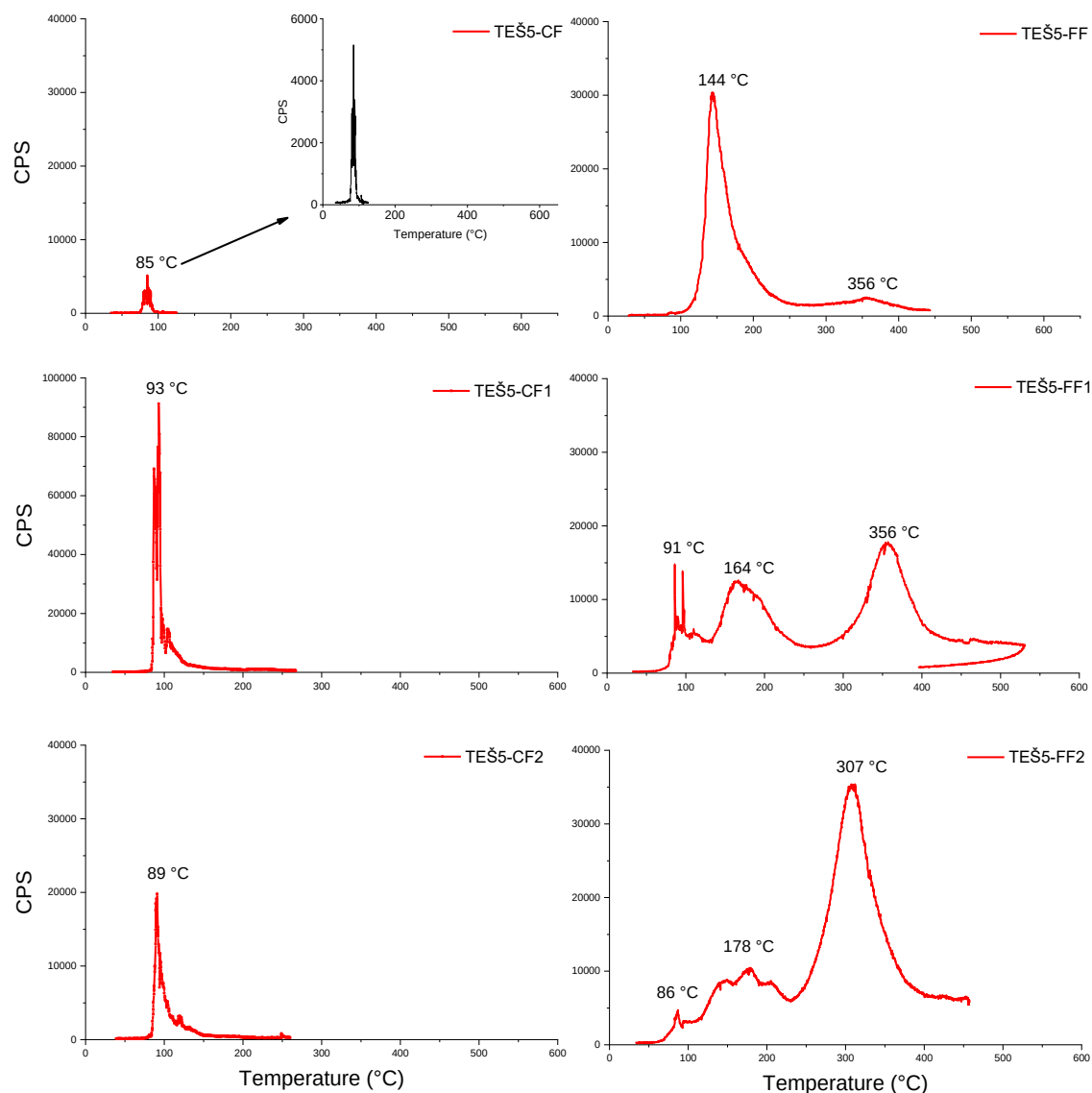


Figure 4.33: TPD spectra of separated WFGD samples from block 5 of Šoštanj TPP (finer and coarser fractions) sampled in a) May 2013, TEŠ5-CF and TEŠ5-FF b) in December 2013, TEŠ5-FF1 and TEŠ5-CF1 and c) in January 2014, TEŠ5-FF2 and TEŠ5-CF2. Samples were measured with NT-MS.

Experiment with QMS: TPD spectra obtained by QMS (Figures 4.34 and 4.35) significantly differ from those observed with NT-MS (Figure 4.33). It has to be taken into account that all samples were pre-heated before TPD analysis. More about pre-heating is written in Chapter 4.2.1. Only gypsum sample TEŠ5-FF (Figure 4.35) shows TPD spectrum that is similar with both mass spectrometers. Peak maximum obtained by QMS (Figure 4.35) represents the temperature at about 50 °C higher than with NT-MS (Figure 4.33), while the second peak differs for 100 °C. Both spectra for TEŠ5-FF (obtained by QMS or NT-MS) show intense first peak and small second peak. Other TPD spectra of samples TEŠ5-FF1, TEŠ5-FF2, TEŠ5-CF1 and TEŠ5-CF2 (Figure 4.34) show completely different Hg releasing concerning those obtained by NT-MS, especially for coarse fractions.

None of the coarse fractions show the peak at 100 °C, but rather at higher temperatures in the range between 240 and 260 °C. In both coarse fractions, the additional smaller peak is seen above 300 °C. The broader peak of TEŠ5-CF1 might be the consequence of sample preparation since samples were not washed before analysis. Finer fractions show at least two peaks, similar than with NT-MS. However, the maxima of the peaks differ between the samples. TEŠ5-FF shows two maxima at 192 and 455 °C, similar to TEŠ5-FF1 with the peaks at 243 and 510 °C. Finer fractions of TEŠ5-FF2 represent three peaks at 271, 352 and 500 °C. Coarser fractions TEŠ5-CF1 and TEŠ5-CF2 differ from each other, but the maxima and the shape of the peaks resemble the TPD spectra measured in the fine fractions. However, the first peak at about 100 °C was not observed in any of the samples.

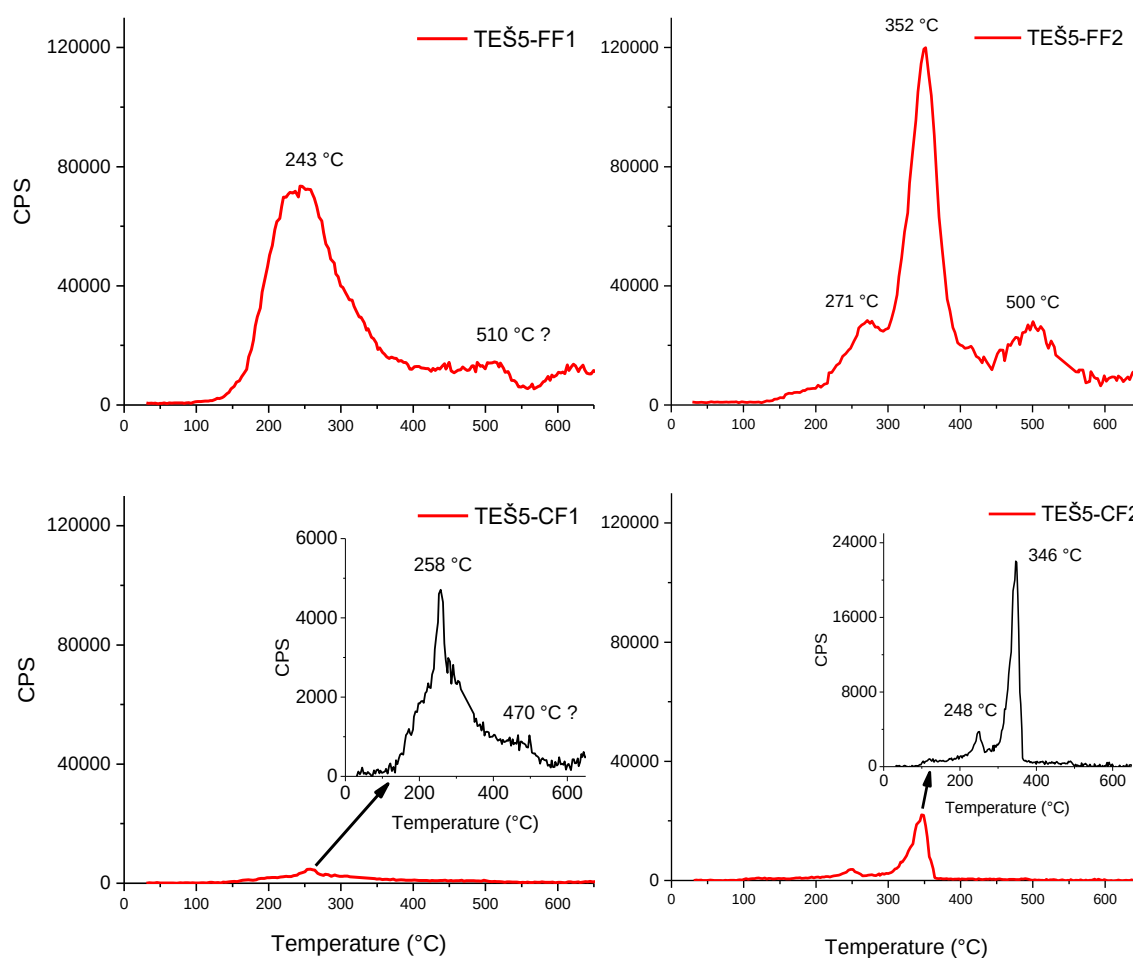


Figure 4.34: TPD spectra of separated WFGD samples from block 5 of Šoštanj TPP (finer and coarser fractions, TEŠ5-FF1, TEŠ5-CF1, TEŠ5-FF2 and TEŠ5-CF2). Samples were measured with QMS.

Since well-seen peaks were observed in coarse fractions by QMS, we cannot explain the absence of those peaks using NT-MS.

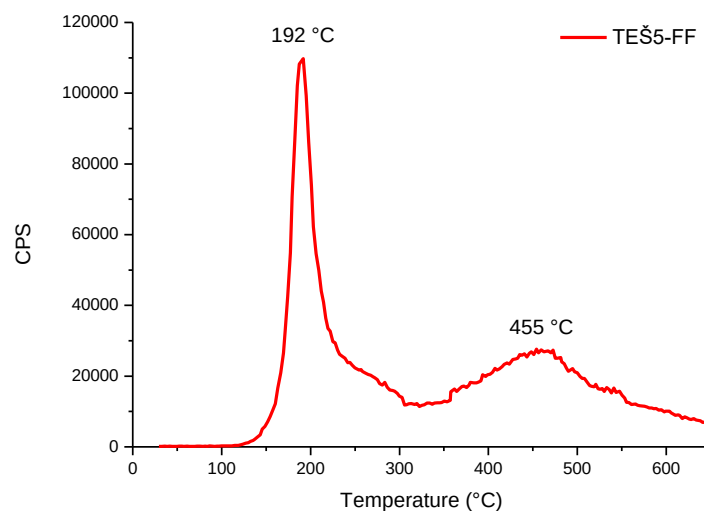


Figure 4.35: TPD spectra of a fine fraction of the sample from block 5 of Šoštanj TPP (TEŠ5-FF).

Discussion: All samples were taken from the main tank of block 5, and differences among the samples (composition of the gypsum sample) probably resemble the operation conditions of the power block, sampling procedure (collecting of the sample), the presence of different species and conditions in WFGD scrubber. The importance of sampling and separation procedure into fine and coarse fractions is well described in Chapter 4.2.1.

TPD analysis show differences in spectra between the two mass spectrometers and among the samples. It has to be emphasized that temperature correction was not applied with NT-MS and therefore the resulted temperature should be slightly higher as presented in Figure 4.33. Differences between NT-MS and QMS are mainly observed in coarse fractions at around 90 °C. The main reason is probably pre-heating of the samples. With slow pre-heating we can lose some mercury, but on the other side humidity (most of the water present in the samples) that may affect the measuring process (ionization) has gone. However, if only Hg(0) is present in the gypsum sample (adsorbed on the surface or incorporated in the matrix) some part of mercury may evaporate at the pre-heating temperature (75-78 °C), dependent on how strong it is adsorbed to the surface (physical, weak adsorption). Also TPD spectra of finer fractions show differences. Multielemental analyses vary among TEŠ5-FF, TEŠ5-FF1 and TEŠ5-FF2 where elevated concentrations for most of the elements are found in fine fraction TEŠ5-FF2. TEŠ5-FF show composition of elements similar to the sample TEŠ5-FF1, but the TPD spectrum differ. Considering halogens, TEŠ5-FF shows much lower concentrations of Br, Cl and I compared to the TEŠ5-FF1 and TEŠ5-FF2. Hg-halogenides are suggested to be present in the gypsum samples (Sedlar et al., 2015). In our previous study more than one peak was observed in TPD spectrum of pure mercury compounds of HgCl₂ and Hg₂Cl₂ mixed with CaSO₄ · 2H₂O. Moreover, with spiking pure compounds into the gypsum sample, only Hg-Cl compounds fitted with the sample peak. If Hg-Cl is present in the gypsum samples from block 5, the differences in TPD spectra between TEŠ5-FF and TEŠ5-FF1 or TEŠ5-FF2 may be related to the concentration of chlorine present in the sample. However, additional studies should be done to confirm this.

4.2.2.3 Samples from block 6

The results for two types of samples are provided in this chapter: i) gypsum slurry samples (ORIG, DISP and RECY) taken from two different sampling points of block 6 that were washed and pre-dried before analysis, and ii) samples prepared from gypsum slurry taken from the main scrubber (ORIG_S) that were not washed. ORIG_S slurry sample was separated into five different fractions (ORIG_S-FFF, ORIG_S-FFF + ORIG_S-FF, ORIG_S-FF, ORIG_S-FF_{brown} and ORIG_S-CF). Samples of ORIG, DISP and RECY were separated into coarse and fine fractions, except the sample of RECY (Figure 4.36). TPD spectra for ORIG, DISP and RECY were obtained by both mass spectrometers, while only QMS was used for ORIG_S. Samples were preheated when measured with QMS, but not with NT-MS.

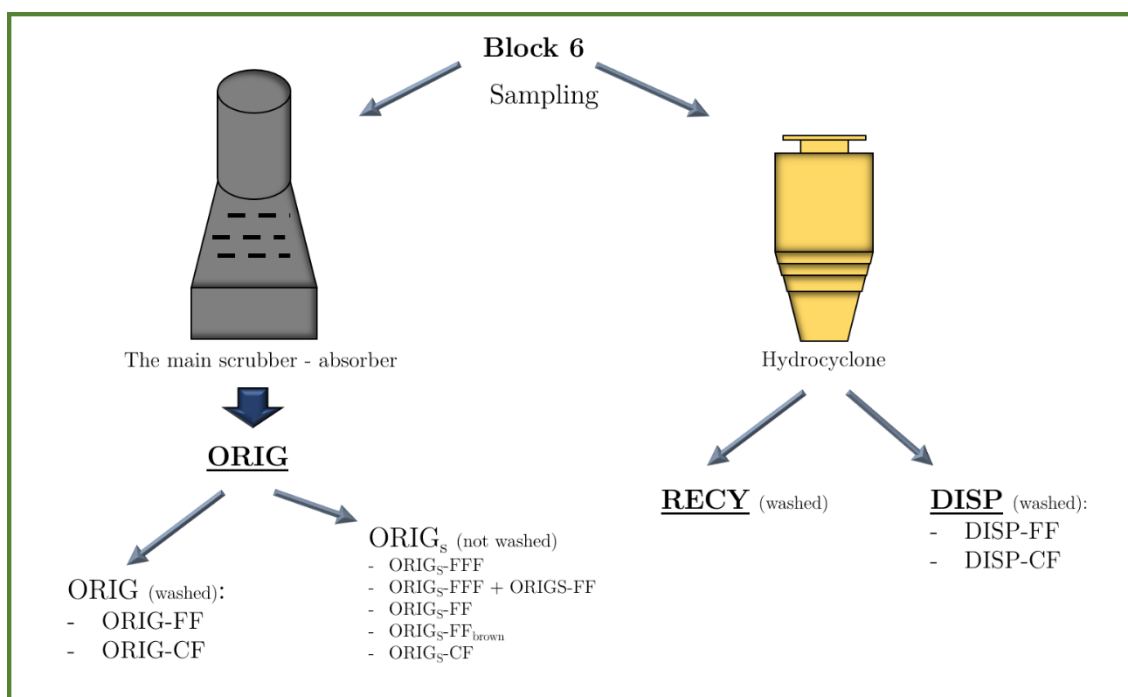


Figure 4.36: Scheme of gypsum slurry samples obtained from two different sampling points of block 6. Samples were separated into various gypsum fractions.

The same samples as described in the next Subchapter 4.2.2.3.1 were taken to see the effect of aging to the Hg TPD spectra in these samples. Within this experiment, we also observed the influence of pre-heating and washing to the Hg spectra. In the last part of this chapter (Subchapter 4.2.2.3.4), we were focused on the releasing of other volatile compounds from the sample RECY to study the decomposition of Hg-compounds in gypsum samples.

4.2.2.3.1 TPD spectra of washed samples

Experiments with NT-MS: Five different gypsum samples (RECY, DISP-FF, DISP-CF, ORIG-FF and ORIG-CF) were analysed with NT-MS. Thermograms of fine fractions (DISP-FF, ORIG-FF and RECY) released between 200 and 220 °C (Figure 4.37). The peak shapes are similar and differ in intensities which are consistent to the concentrations of mercury present in these samples (RECY > DISP-FF > ORIG-FF). Coarse fractions show Hg peak at about 100 °C, similar than in block 5 (Figure 4.33). The second small peak follows at around 200 °C and is barely seen. On the other side, fine fractions show strong Hg peak at around 200 °C. Small first peak is observed in the samples ORIG-FF and DISP-

FF. All TPD spectra are put on the same scale for comparison. Sample pre-heating was not applied here.

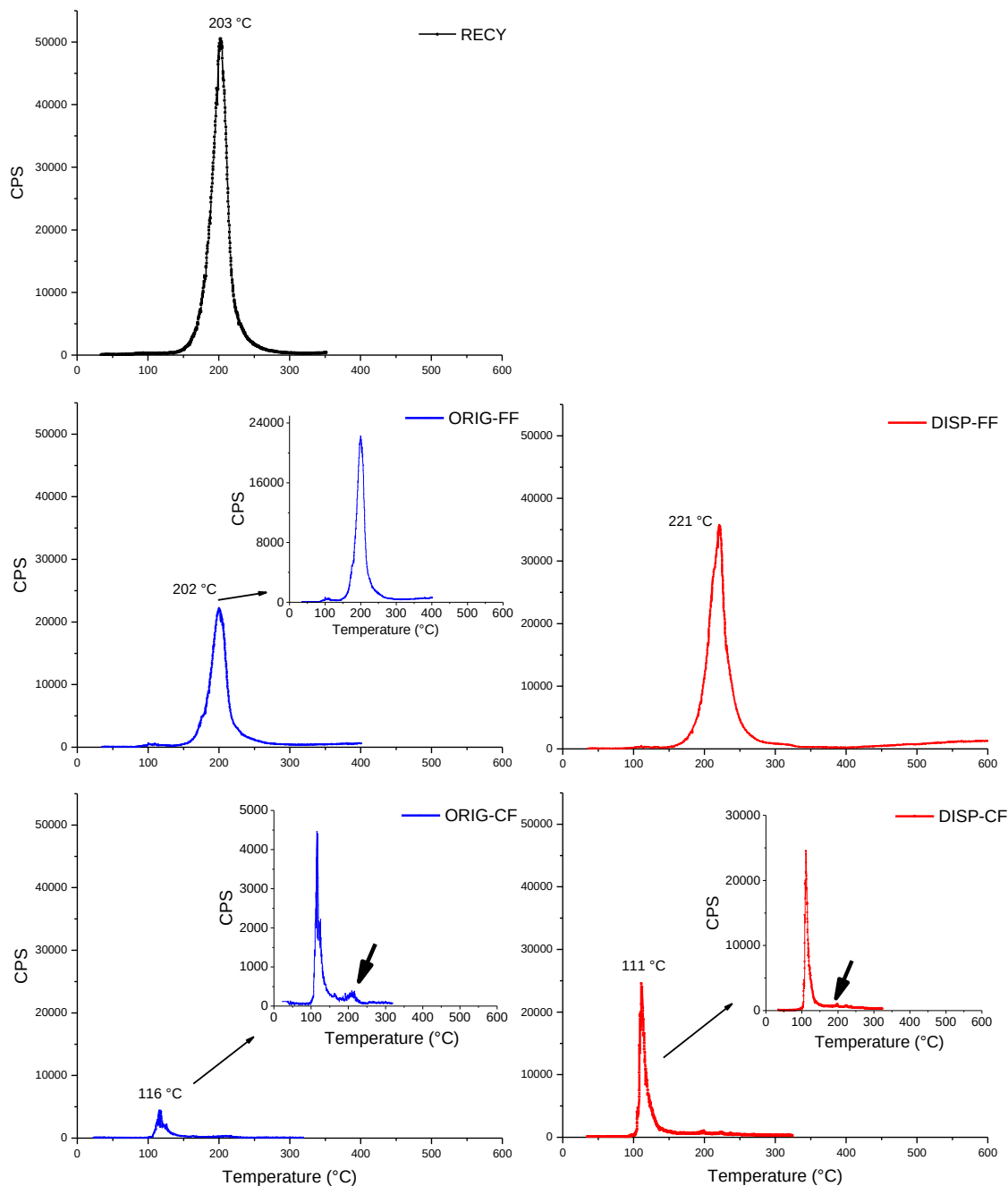


Figure 4.37: TPD spectra of five separated WFGD samples of Šoštanj TPP (finer and coarser fractions).

Experiments with QMS: In the experiment with QMS, pre-heating was used before TPD analysis. The same samples (ORIG-FF, ORIG-CF, RECY, DISP-FF and DISP-CF) as with NT-MS were measured with QMS. Additionally, bulk washed sample ORIG was analysed. Figure 4.38 shows TPD spectra of all six samples put on the same scale for comparison among the samples. A single peak is observed in each sample with the maximum positioned in a range between $(259 \pm 7) ^\circ\text{C}$. The mixed fraction of ORIG (bulk)

shows medium intensity as a consequence of "dilution" of a fine fraction with the coarse one, the latter representing the majority (by weight) of WFGD material. Significantly lower Hg peaks are observed for both coarse fractions. This is consistent with the particles size where bigger gypsum particles accumulate less Hg.

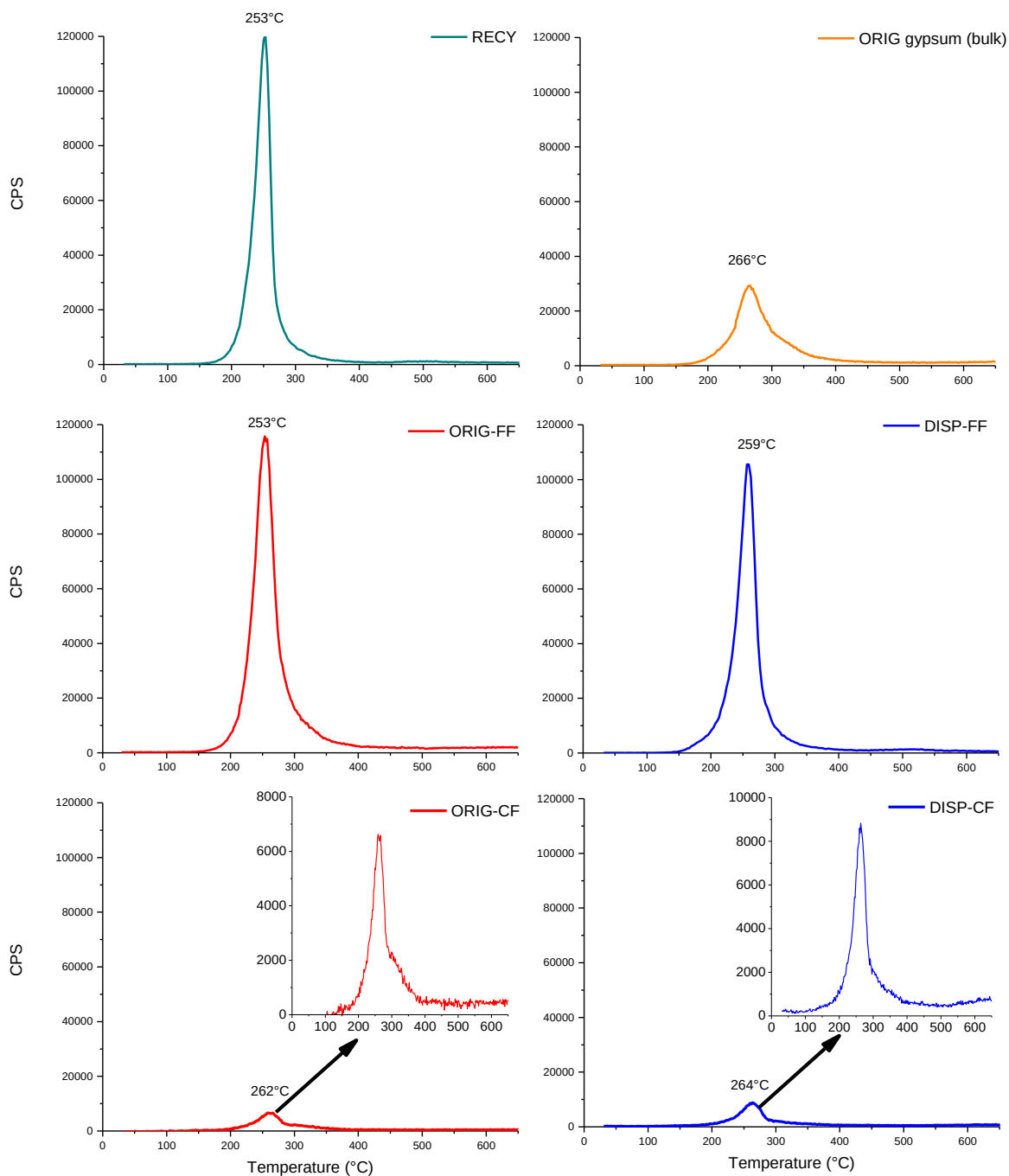


Figure 4.38: TPD spectra of five separated WFGD samples of Šoštanj TPP (finer and coarser fractions) and one mixed fraction containing both fractions (bulk fraction).

According to the Chapter 4.1.3, RECY contains far less $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ than other samples. The peak shapes and the positions on temperature scale are similar in all fractions indicating single decomposition process of Hg compound. The peak at 100 °C is not seen as it was observed with NT-MS. The absence of the peak at 100 °C could be the

consequence of sample pre-heating. Without preheating, all gypsum samples except RECY showed a small, barely seen a peak at 100 °C (not shown).

Discussion: Strong peak below 100 °C in coarse fractions is observed by NT-MS. It is thought to represent Hg(0). It follows that bigger particles may retain mostly adsorbed Hg(0) and very few other mercury species since the second peak is very small. On the other hand, using QMS we got different TPD spectra with strong second peak, but small first peak at 100 °C. The same results were obtained when sample preheating has been applied.

We found the importance of sample pre-heating at 75-78 °C to remove the surplus of humidity. Coarse gypsum fraction is mostly composed of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ where more than 20% of the whole mass represents water. Water starts decomposing around 100 °C (Figure 4.13). In samples containing water or not dried samples unreal peak appeared at around 100 °C (Figure 4.17). Not only Hg but also other volatile species show increased intensity (small peak) at a temperature around 100 °C (Figure 4.17). This was confirmed by QMS, where more ions could be observed simultaneously (all releasing spectra show peaks at the same temperature). The phenomenon is more significant when "water" (humidity) is present in a higher proportion such as crystalline water (e.g. $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ or coarse gypsum samples) or when the sample is not dried before analysis. However, with the dry samples contain no crystalline water sample pre-heating is not necessary.

During thermal heating, the crystalline water in $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ starts to decompose/crack and evaporates close to 100 °C (see Chapter 4.1.3). Normal heating without cracking would probably cause releasing of Hg at higher temperatures, but due to the small explosions and possible changes in the structure, Hg evaporates and shows plenty of sharp peaks around 100 °C that disturb TPD spectrum. Part of the released Hg could represent Hg(0) captured in the crystal of the gypsum. With heating up to 75-78 °C (pre-heating of the sample), decomposition and releasing of water is not so intensive since most of the water evaporates at lower temperatures and the small amount released during thermal heating when recording the TPD spectra. Moreover, water vapour hinders normal ionization and with preheating it cannot enter the ionization cell. Using preheating, the obtained TPD spectra show the smooth, flat peak(s) instead of the irregular peak with many small or intensive sharp peaks.

According to the explanation above, the peaks obtained in all coarse fractions are supposed to be unreal and only minor proportion represents Hg(0). Unfortunately, NT-MS does not allow us to observe two ions (isotopes) simultaneously, so we cannot observe this at the time of experiments as with QMS.

4.2.2.3.2 TPD spectra of unwashed samples

In the next experiment (Figure 4.39), we took an aliquot of ORIG gypsum slurry labelled as ORIG_s and separated it into five different fractions according to the sedimentation and different colours (the finest fraction ORIG_s-FFF-dark brown, ORIG_s-FFF + ORIG_s-FF, fine fraction ORIG_s-FF-light brown, ORIG_s-FF_{brown}-brown with dark brown inclusions that differ from the fine and the finest fraction, and coarse fraction of ORIG_s-CF). Darker gypsum represents a finer fraction, while coarse fraction has the same white-light brown colour in all coarse samples. The purpose of this test was to see if there are any differences in TPD spectra within the separated fractions obtained from the same sample (ORIG_s), and if there are differences compared to the washed samples of ORIG (previous Subchapter 4.2.2.3.1).

The total Hg concentrations in all five fractions were measured and the results are provided in Table 4.3. The highest concentration was obtained in the finest fraction, ORIG_s-FFF. Interestingly, brown precipitate ORIG_s-FF_{brown}, which was darker than other parts of the sample shows much higher Hg concentration than fine fraction FF (ORIG_s-FF). Unfortunately, multielemental analysis has not been obtained for those samples to compare the concentration of other elements present as well. However, these results confirm greater accumulation of Hg to some species (elements) in a fine fraction as already seen from previous experiments.

Table 4.3: The concentration of total Hg present in different size fraction of gypsum from block 6 of Šoštanj TPP. Samples are labelled the same as in TPD graphs in Figure 4.39.

Gypsum samples (block 6, ORIG _s)	Concentration (mg kg ⁻¹)	Mass (mg)
ORIG _s -FFF	32.2	2.1
ORIG _s -FFF + ORIG _s -FF	9.2	2.5
ORIG _s -FF	1.2	6.8
ORIG _s -FF _{brown}	21.2	2.5
ORIG _s -CF	0.2	9.1

TPD spectra of different fractions of ORIG_s from the main scrubber of block 6 are shown in Figure 4.39. Similar releasing of Hg is observed in all cases with only one peak to be released at (260 ± 13) °C. Although samples were not washed, peaks are smooth and did not become broader because they have not been washed.

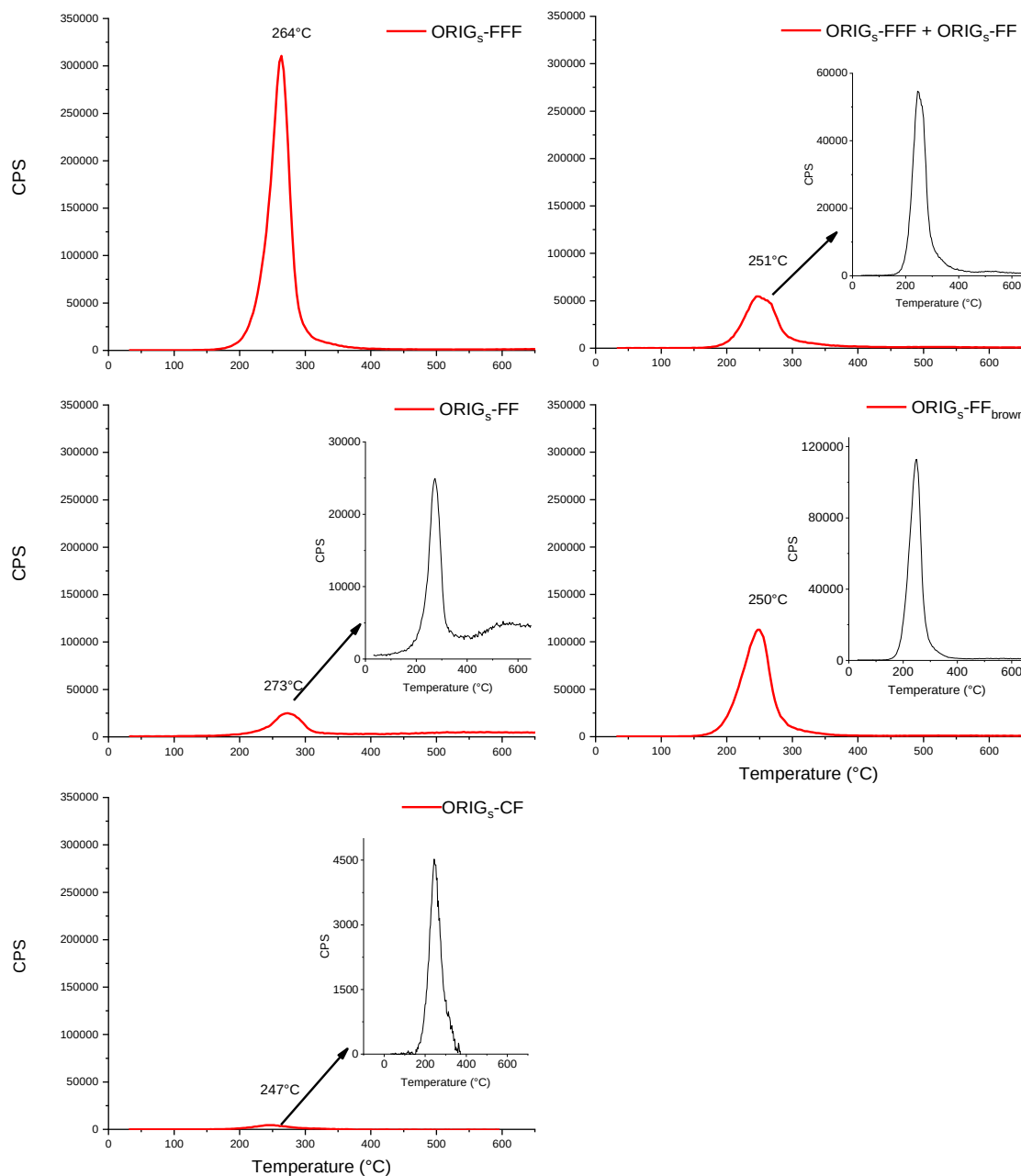


Figure 4.39: TPD spectra WFGD samples of Šoštanj TPP separated into various finer and coarser fractions from ORIG sample.

4.2.2.3.3 TPD spectra of aged samples

In this experiment, we evaluate the influence of sample aging in the view of changes of TPD spectra after 18-24 months since the first set of TPD analysis has been performed. Moreover, we compare the influence of sample pre-heating and washing in those samples after this period. The results were obtained with QMS and the spectra are provided in Figures 4.40–4.43.

The most obvious changes occur in the coarse fraction from block 6. To compare the effect of washing and heating in those samples, we took washed and unwashed coarse fractions which were heated or not heated before TPD analysis (Figure 4.40). All TPD

spectra for coarse fractions of ORIG-CF differ with the TPD spectrum shown in Figure 4.38. TPD spectrum of ORIG-CF in Figure 4.38 shows one narrow peak without any sample pre-peak. On the contrary, peaks of coarse fractions in Figure 4.40 show one or more peaks. Significant differences are observed between heated and not heated coarse fractions. Heated samples of ORIG-CF are similar if the sample is washed before analysis or not. However, the peak is broader with a shoulder before the main peak probably due to the reduction of Hg. Samples without preheating show at least two peaks where TPD spectra of the main peak also differ, especially in case of the unwashed sample.

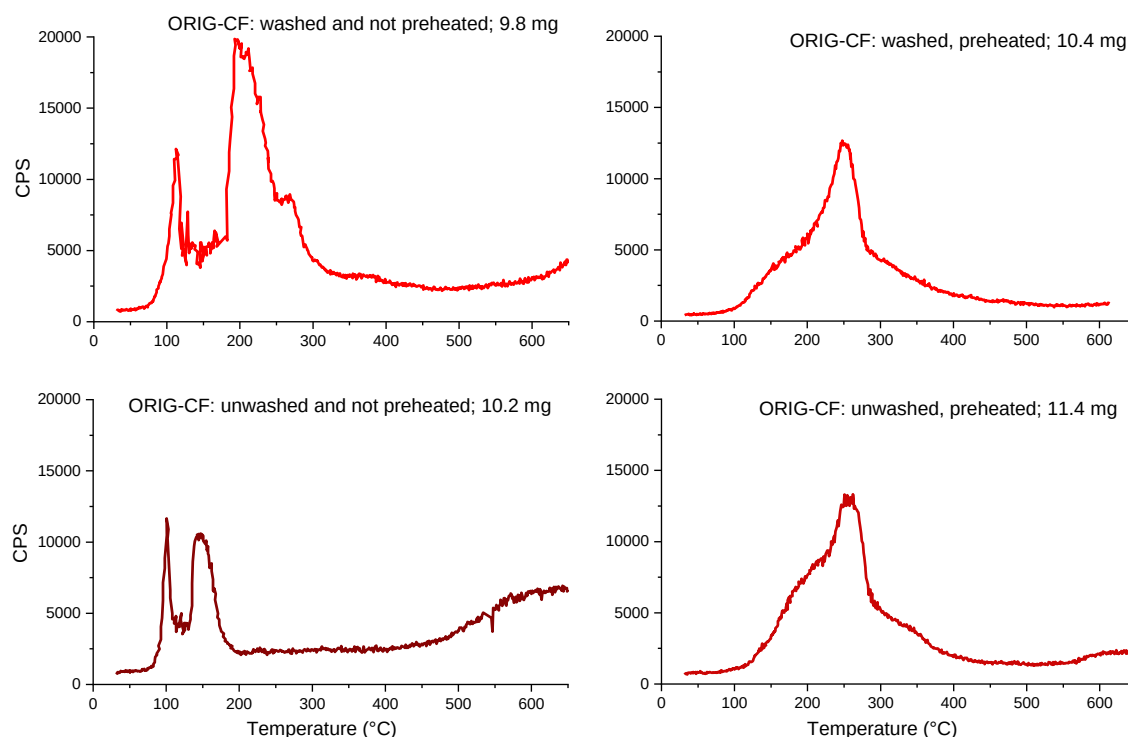


Figure 4.40: TPD spectra of aged washed and unwashed coarse fractions of ORIG-CF with and without sample preheating.

The strong peak at around 100 °C possibly represents Hg(0), which releases much more intensively as in the case when preheating is applied. Due to structural changes (fast decomposition of crystal water; see explanation in Chapter 4.2.2.3.1) this causes deviation in TPD spectra as found in both coarse samples without preheating. Therefore preheating is useful since water evaporates slowly, but part of Hg may be lost, and we cannot observe the peak at 100 °C. However, the strong peak representing Hg(0) has not been observed in the first measurements (Figure 4.38), even without preheating. After two years, some Hg in the sample may reduce and Hg(0) is weakly adsorbed to the surface which then released and the peak for Hg(0) is detected at around 100 °C.

Washed and unwashed samples of finer fraction from block 6 (ORIG-FF) that were preheated show one peak where the peak of the unwashed sample is broader (Figure 4.41). Additional peaks occurred in case of no preheating. Similar as with coarse fraction, releasing of Hg at around 100 °C probably represents Hg(0) due to the Hg transformations (Hg reduction). In washed sample two peaks occurred while in unwashed (and not preheated)

the TPD spectra completely change. The presence of a higher amount of water vapours is not recommended in the mass spectrometer, and this may change the TPD spectra.

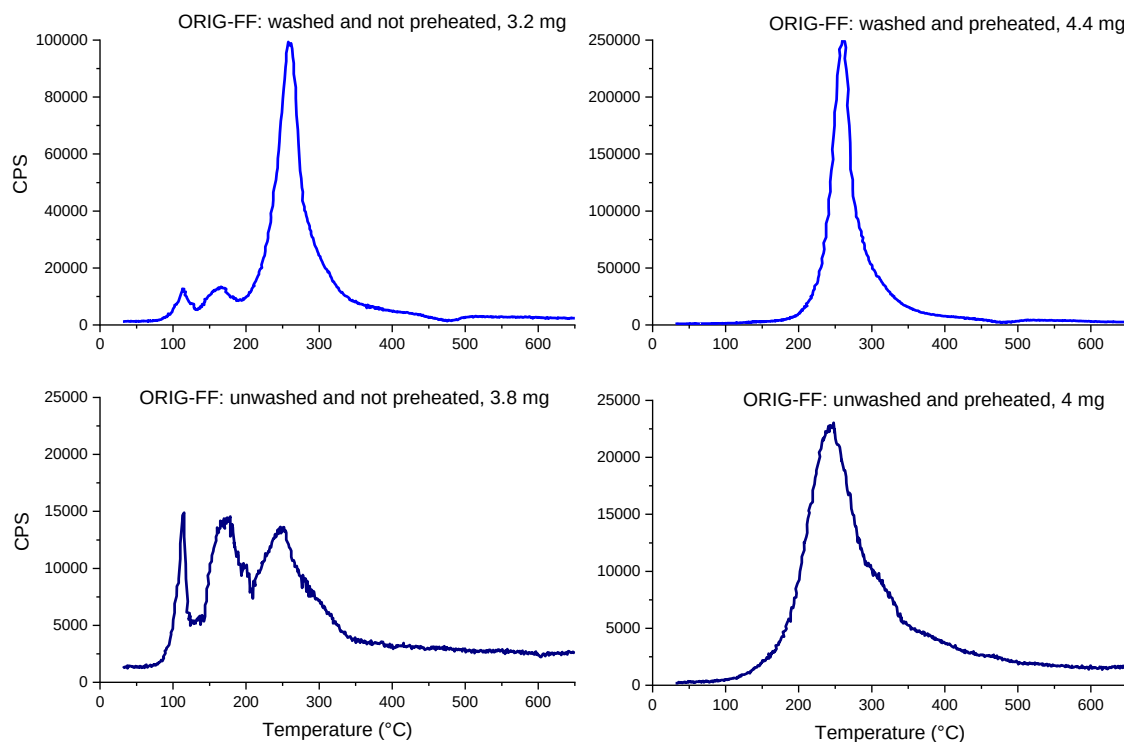


Figure 4.41: TPD spectra of aged washed or unwashed fine fractions of ORIG-FF with and without sample preheating.

In case of DISP and RECY only washed samples were tested. Coarse fractions, DISP-CF, show slightly different TPD spectra as in coarse fraction ORIG-CF (Figure 4.38). In Figure 4.42, the preheated sample shows two peaks which resemble reduction of Hg-species into Hg(0) or transformation into less stable Hg-compounds. DISP-CF without preheating indicate releasing of Hg(0) at 100 °C similar to the sample of ORIG-CF. The main Hg peak in a coarse fraction above 200 °C also differs by shape in comparison to the heated sample. A preheated and not preheated samples of DISP-FF shows a similar main peak. Similar to ORIG-FF, additional peaks occur in the sample without preheating. However, the main peak in DISP-FF (washed and not preheated) does not change a lot compared to ORIG-FF (washed and not preheated).

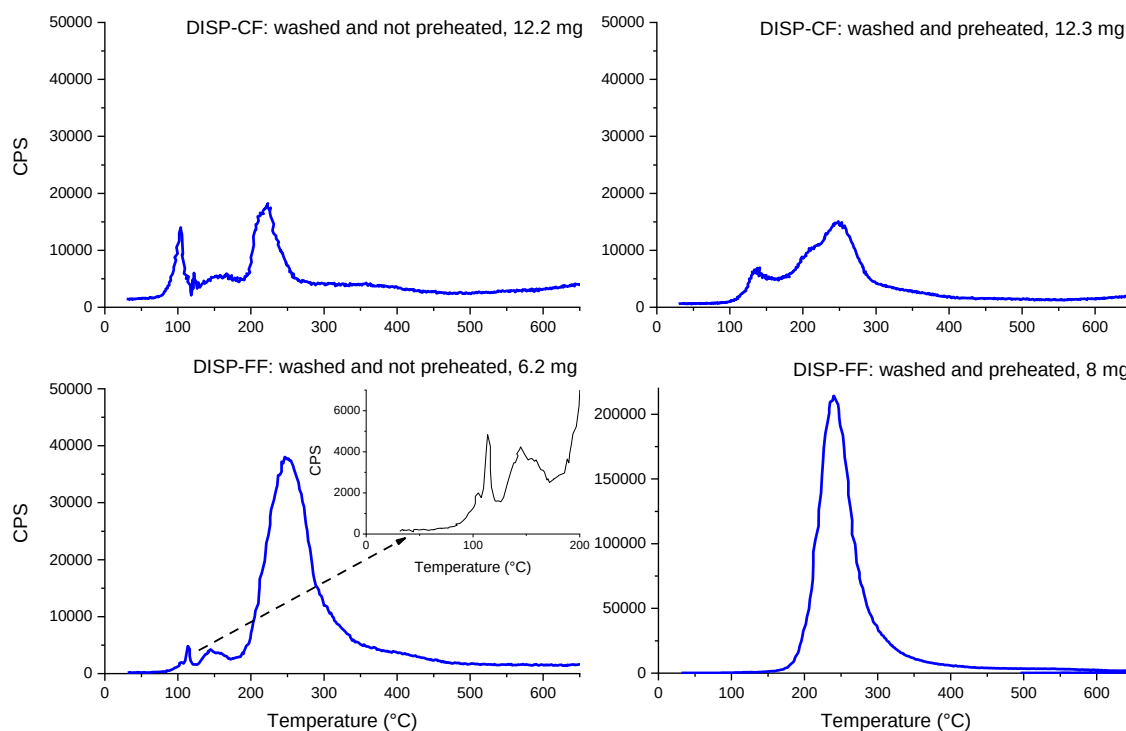


Figure 4.42: TPD spectra of aged washed fine and coarse fractions of DISP with or without sample preheating.

Figure 4.43 represents heated and not preheated sample of RECY. The small peak at 100 °C probably indicates Hg(0). Peak at around 150 °C may represent reduced or less stable Hg species or Hg(0) that is more strongly adsorbed to the surface. This peak is present in sample DISP-FF (washed, not preheated) as well. However, this first peak(s) is negligible in comparison to the main peak, and usually cannot be observed (if the data are not enlarged) in TPD spectra due to the intensity of the main peak (higher concentration of Hg in the sample).

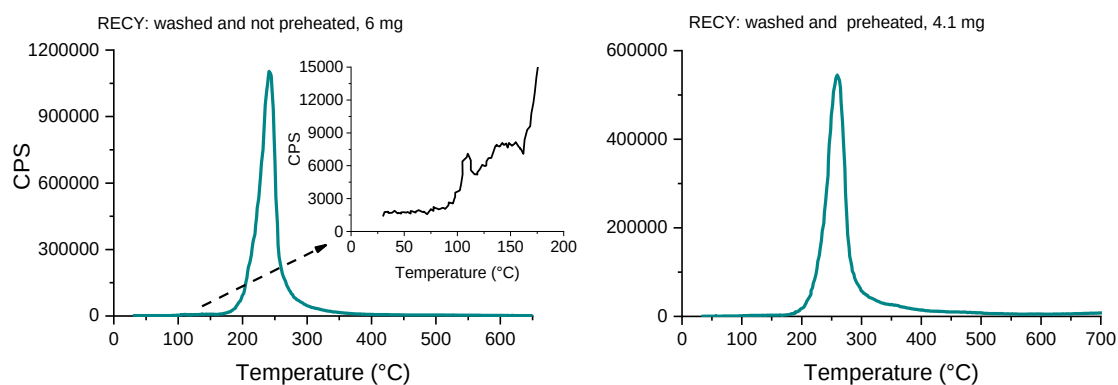


Figure 4.43: TPD spectra of aged washed sample RECY with or without sample preheating.

Discussion: All coarse fractions show different TPD peaks compared to the first measurement in Figure 4.38. It follows that sample aging affects the Hg species present in coarse fractions as observed in TPD spectra (Figures 4.40–4.43). Additional peaks are also present in fine fraction, but this phenomenon is not as strong as in coarse fractions. The changing of the samples over time depends on the sample matrices. In fine fraction mercury is bound stronger than in coarse fraction due to the non-changing of chemical and physical properties over time. Better stability of Hg species is reflected with higher accumulation of Hg in those fractions and no peak changes after period of time. On the other side, coarse fractions are subject to the process of conversion that are present on the sample surfaces. UV, humidity and temperature have a strong influence on Hg reduction. However, samples may also contain species that favours reduction of Hg. UV and temperature are excluded here, due to the storage in the dark and at the same temperature all the time. Therefore, humidity may cause reduction. Although coarse fraction is dry, it still contains crystalline water which may cause and accelerate transformations of Hg-species. In finer fractions, this is not so obvious due to the presence of other species that stabilize Hg species. Some reduction and thus the presence of Hg(0) has also been observed. However, we did not observe this in our first measuring campaign even when samples were not preheated.

Chemical and physical properties of the samples change over time, and Hg transformations on the surface of these samples have to be taken into account. Weak physical adsorption may retain reduced Hg(0). It follows that gypsum eventually changes and this is of key important for its permanent storage, disposing to the landfill or reusing in the production of new products.

4.2.2.3.4 Observation of other volatile compounds

Mercury represents only a small proportion in gypsum samples and identification of mercury species by observing other volatile compounds is difficult. For example in Figure 4.24, volatile compounds such as CO₂, H₂O, HCl that released from the sample show high intensity. Intensity of Hg peak is negligible in this case. However, the peak of HgS mixed with CaSO₄ · 2H₂O in Figure 4.25 resembles the TPD spectra released from gypsum of block 6. Therefore we observed TPD spectra of H₂S and SO₂ in the sample of RECY which contains the highest Hg concentration among the samples in block 6. Literature indicates decomposition of HgS (metacinnabar) or HgS_x (mercury polysulphide) into Hg(0) and S₂ (Q. Wang et al., 2018). Since S₂ and SO₂ have the same m/z, decomposition into S₂ cannot be excluded.

Figure 4.44 shows simultaneously observed TPD spectra of mercury, H₂S and SO₂. Four different experiments with different sample masses indicate a similar releasing pattern for SO₂ and H₂S with different intensities. This is dependent on the conditions in the mass spectrometer (background at particular m/z) and sample preparation. A sample of RECY in the experiment "a)" was not preheated and peak at around 100 °C is observed for both SO₂ and H₂S. This is a consequence of water evaporation which influences all observed volatile species. The small peak for H₂S is observed at the same position where Hg is released. Similar as with SO₂. According to Figure 4.25, H₂S and SO₂ are the decomposition fragment which is supposed to be involved in decomposition of HgS (cinnabar) present in the sample. In Figure 4.44, the intensities of H₂S and SO₂ released from RECY gypsum are much higher compared to Hg whereas in Figure 4.25 pure HgS was mixed with CaSO₄ · 2H₂O, and thus Hg releasing prevails relative to SO₂ and H₂S. Therefore, the presence of HgS is suggested in the sample of RECY.

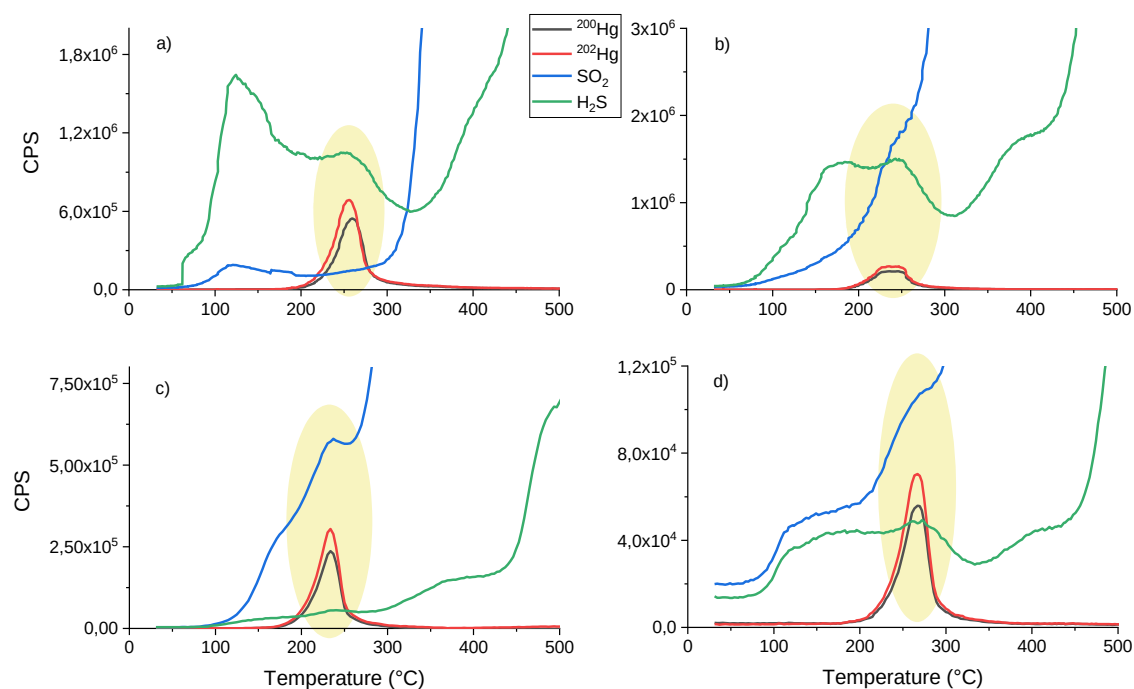


Figure 4.44: TPD spectra of H_2S , SO_2 and mercury isotopes 200 and 202.

4.2.2.4 Comparison between the gypsum samples from Šoštanj TPP - summary

These results give us important insight into the TPD spectra from different gypsum samples of the same TPP, burning the same coal. Most of the results for block 5 and 6 were obtained by two different mass spectrometers for comparison which sometimes gives different TPD spectra due to the sample preparation. Comparison between block 4, 5 and 6 indicates different concentrations of Hg in the samples. Not all results of total Hg are directly compared. Samples from block 4 and 5 are taken only from the main scrubber, while in block 6 samples were also obtained from hydrocyclone. The concentrations of Hg present in the samples from block 6 are similar to block 5, whereas block 4 contains far less Hg in all samples investigated. Since TPD spectra in block 4 and 6 are very similar, this could be the consequence of APCDs. Samples from block 5 contain elevated concentrations of halogens compared to the block 6. TPD spectra also differ among samples. Block 4 and 6 show similar thermograms with one peak, whereas spectra from block 5 are completely different and indicate at least two peaks. The presence of an elevated concentration of halogens such as chlorine and bromine could reflect the differences in TPD spectra. Halogens may influence the shape, position and the number of peaks with the formation of different Hg-halogen species. However, also some other metals such as Fe, Al, Ti, Mn that accumulate in elevated concentrations in gypsum (especially in the fine fractions) may have an important role in accumulation in adsorption/oxidation of Hg.

Identification of mercury compounds from TPD spectra is difficult. Although QMS enable us observation of more than one ion simultaneously, this cannot always solve the problem with Hg speciation in the samples. Hg is present only as a minor element in the gypsum and observation of decomposition reaction and identification of mercury compounds present in the sample is only an approximation. However, TPD method is a good approach for the determination of stability of mercury/mercury compounds in the samples. In the samples containing a low concentration of Hg, we could not get any

additional information on decomposition/desorption of mercury compounds by observing the other volatile species which form as a consequence of thermal decomposition. In general, artificially prepared mercury standards are normally used where pure mercury compounds are mixed with different substrates. According to the position of the TPD spectra of mercury standard and actual sample, we try to identify mercury compounds in the solid samples. This type of identification is better described in the next chapter (Chapter 4.2.3).

Chapter 4.2.2 also provides an important insight into sample preparation. Unwashed samples sometimes show different TPD spectra compared to the washed. This was observed in samples from block 4, but not in block 6. Samples from block 5 were not washed, and this might be the reason for more, broader peaks. As it was seen from the thermograms, unwashed samples broaden the peak and the peak is not smooth. Sample pre-heating is useful for decreasing the background in gypsum samples. However, with this manipulation, we can lose some mercury that could be adsorbed to the surface and/or released at a temperature below 100 °C. Regarding this, it is important to mention the age of the sample. After some time, TPD spectra may change due to the reduction of Hg compounds in the sample (Hg transformations in the sample matrix). With sample preheating, the first peak cannot be observed. Mercury transformation is more probably present in the samples containing less stable Hg-compounds (e.g. HgCl_2 , graph not showed). In case of Hg-Cl standards, different shapes and positions of Hg thermograms were obtained in our previous study using AAS detection (Sedlar, 2014). Moreover, similar changing happened with samples from block 5 which were analysed after some time. Since Hg-Cl were the Hg species suggested in those sample, we predict that those species are unstable in gypsum samples and transformed or reduced in Hg(0) or other less stable Hg-species which appeared as a peak(s) at lower temperatures. Hg-Cl compounds are classified as a water-soluble fraction when using SEP and gradually decreasing of Hg was found with aging time in the study of Diao et al. Moreover, more Hg(0) was found in the different fractions of SEP. The results indicated that the aging process could result in the change of mercury fractions in gypsum (Diao et al., 2018). However, not only less stable Hg-species, but also sample matrix (e.g. coarse fraction containing mainly $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and particle size distribution in the samples are very important. Gypsum contains a variety of different species among which some could reduce Hg. As already mentioned, mercury could release as Hg(0) and/or stay weakly adsorbed on the surface. In the present study, this has been confirmed by the formation of pre-peak that did not occur at first analysis. It follows that sample aging indicates Hg reduction (transformation) in gypsum samples, where the amount of reduced Hg is dependent on sample composition and particle size. This is more obvious within the sample with a low concentration of Hg (coarse fraction of gypsum) whereas at elevated concentration this is less profound. QMS detect a small amount of mercury even at room temperature (in the aged samples) which indicates constant evaporation from the sample. This has been more obvious in not preheated samples.

4.2.3 Preparation of mercury standards

Identification of mercury compounds in gypsum is complicated due to the matrices which could differ among the samples. The composition of gypsum is a consequence of many factors such as sampling and sample preparation, type of coal and Hg concentrations there, presence and efficiency of various APCDs, the presence of TMEs, etc. The chemistry present in the WFGD slurry is responsible for the formation of different Hg-species. However, Hg species in WFGD scrubber are in solution where conditions are different than later in moist gypsum. Stability of mercury in the gypsum depends on the mercury species present as well as interaction with the surface and incorporation into different matrices present in the sample. Moreover, during dewatering, drying and heating of the gypsum samples, Hg species might change, and real identity is questionable. This makes identification of mercury compounds by TPD method in the gypsum samples even more difficult.

In the previous chapter, we showed the TPD spectra of gypsum samples from Šoštanj TPP. Decomposition fragments suggest the presence of HgS in the sample, however, due to the differences between the spectra and because we did not test all other possible volatile compounds that may resemble the presence of other Hg species, we cannot confirm this. Therefore, we performed additional experiments. Different mercury standards were prepared, and we compare their spectra with those from actual samples. HgS and HgCl₂ are two Hg-species most likely to be present in the gypsum according to other researchers. In the previous study of Sedlar et al. we identify HgCl₂ as the possible Hg-species present in the gypsum from block 5 (Sedlar et al., 2015). Therefore, in the present doctoral dissertation, we try to identify HgCl₂⁺ ions (pure compounds or mixed with the substrate) by using NT-MS. The presence of HgCl₂⁺ ions would make further identification in actual gypsum sample much easier. However, theoretical calculations show various factors affecting the decomposition of HgCl₂ in the mass spectrometer and thus inability to detect HgCl₂⁺ ion. In the next step, we prepared different mercury compounds mixed with different substrates and compared TPD spectra of those Hg-mixtures. Also, mercury compounds were dissolved in different water solution, dried and precipitates were analysed with TPD method to see the differences between dry preparations. We studied the effect of Fe and Al on TPD spectra as it has already been known that Fe and Al species have a catalytic role or adsorb mercury species and thus change the position of the peak in TPD spectra. There is also a lack of knowledge about the possible reactions between Hg and different compounds present in the gypsum sample that may occur at elevated temperature. In this chapter, all experiments except detection of HgCl₂ ions were performed with QMS.

4.2.3.1 Detection of HgCl₂ molecule by mass spectrometer

HCl and Cl₂ are highly present in the flue gas of coal combustion, and HgCl₂ is likely to be present in flue gas (Galbreath et al., 2000; Pavlish et al., 2003). It is volatile and highly soluble, and as such, it is expected to be present in WFGD slurry. Various chlorine complexes of [HgCl_x]^{y-}, precipitated Hg₂Cl₂ and other complexes/precipitates with Hg could form as well. In general, conditions and a variety of different species that are included in Hg oxidation-reduction and binding processes in WFGD slurry influence the formation of the final Hg-species. The presence of HgCl₂ (and other halogens such as HgBr₂ and HgI₂) in various samples has been identified previously using either atmospheric pressure chemical ionization mass spectrometry, APCI-MS ("soft ionization" technique) (Deeds et al., 2015) or gas chromatography-mass spectrometer, GC-MS (Babko et al., 2001; Jones, Lyman, Jaffe, Allen, & O'Neil, 2016) but not as desorbed (volatile) species in untreated

solid samples using TPD approach. Therefore, the possibility of direct identification of HgCl_2 by MS was investigated in the present subchapter.

In principle, the use of mass spectrometer enable us to detect any molecular species involved during the desorption process. However, in this work, we were preferably interested in the shape and temperature of the maxima of TPD curves to answer whether or not their shapes could be used for mercury speciation. For this reason, we were mainly concerned with mercury-containing ions and their precursors. Since HgO , HgS , HgSe , Hg_2SO_4 and HgSO_4 are thermally unstable compounds, only atomic Hg (Hg^+ ion) could be expected as desorption species. According to the literature data, HgCl_2 should be stable upon heating and ions such as HgCl_2^+ , HgCl^+ might be found in mass spectra. There are some studies describing ionisation and fragmentation of Hg-halogenides (Jones et al., 2016; Kiser, Dillard, & Dugger, 1968; Kokkonen, Löytynoja, Hautala, Jänkälä, & Huttula., 2015; Matsumoto, Sasaki, & Takeuchi, 1972). However, the mass spectrum of HgCl_2 is known in the database of mass spectra (Figure 4.45; NIST Chemistry Webbook, 2014). In the ion source of MS, HgCl_2 is ionized into HgCl_2^+ , HgCl^+ and Hg^+ and their relative abundances are 100:5:60, respectively. Hg^+ ions are formed due to the dissociative ionization according to the following equation:

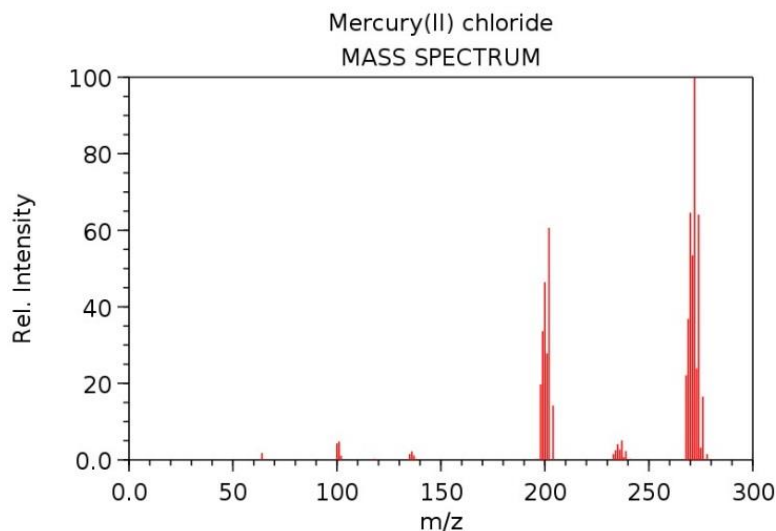
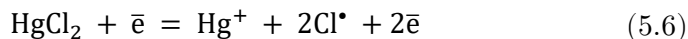


Figure 4.45: Mass spectrum of HgCl_2 obtained from NIST database.

In the first experiment, we mixed HgCl_2 with SiO_2 . Figure 4.46 shows that mass spectrum obtained by desorption of HgCl_2 from silica does not correspond to the expected from NIST. NIST spectrum proposes more HgCl_2^+ than Hg^+ ion detects in the mass spectrum. However, the great majority (100/1) of ions in desorption spectra were observed to be Hg^+ , indicating mostly dissociative desorption process. In the experiments where HgCl_2 was mixed with $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ mass spectrum shows no HgCl_2^+ peaks at 140 °C, but only the presence of Hg^+ ion (Figure 4.47). Moreover, no HgCl_2^+ ion was observed even at a lower temperature.

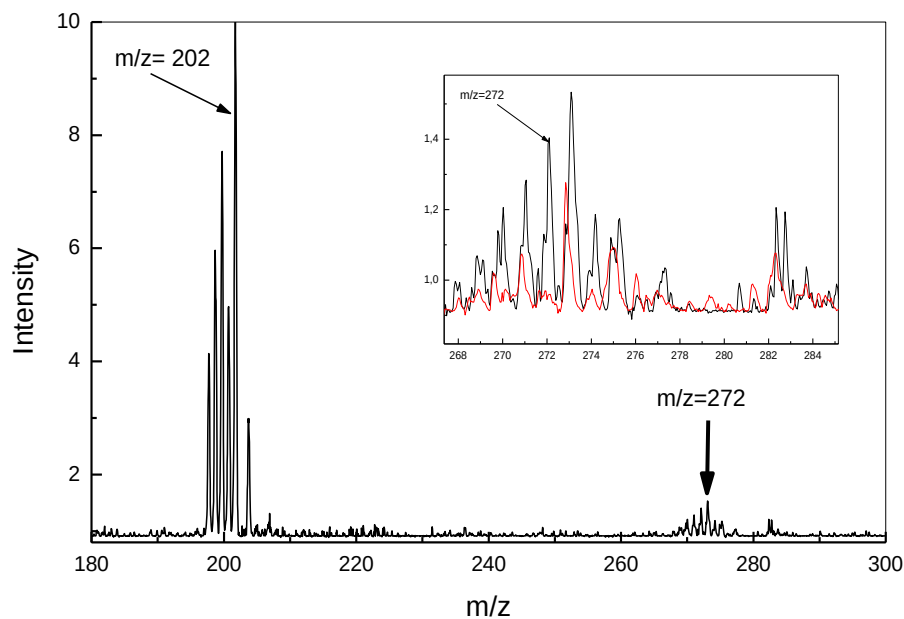


Figure 4.46: Mass spectrum of Hg vapours obtained during TPD experiment of dry SiO_2 mixed with HgCl_2 (100 mg kg^{-1} mixture) at 70°C . Very weak peaks at m/z 272 represent HgCl_2^+ ions.

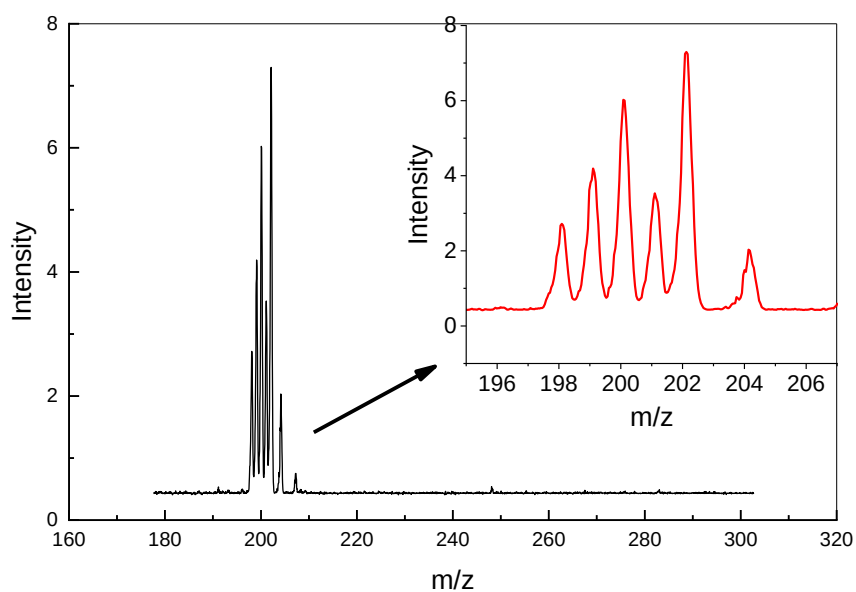


Figure 4.47: Mass spectrum of Hg vapours obtained during TPD experiment of dry $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ mixed with HgCl_2 (0.9 g kg^{-1} mixture) at 140°C . No peaks of HgCl_2^+ ions are seen at m/z around 270.

In a rather comprehensive work of Wu (Wu et al., 2011), when studying the desorption of various Hg compounds from different matrices, it was found that HgCl_2 predominately desorbs as atomic $\text{Hg}(0)$, for which the authors could give no reasonable explanation given that HgCl_2 is thermodynamically stable (Kozin & Hansen, 2013). In the mass spectrometer, certain reactions govern the formation of $\text{Hg}(0)$ (dissociative desorption of HgCl_2 from a seemingly inert material) during thermal desorption of HgCl_2 at low pressures (vacuum $>10^{-5}$ Pa). Additionally, in the presence of water, the hydrolysis of HgCl_2 cannot be ruled out. To understand this better, additional experiments were performed using high purity HgCl_2 (not mixed with the substrate).

Pure HgCl_2 : Figure 4.48 shows a spectrum of ultra-pure HgCl_2 obtained by NT-MS. At 20 °C, the equilibrium pressure of the HgCl_2 vapour over bulk HgCl_2 was $5 \cdot 10^{-3}$ Pa (IVTANTHERMO database). It is apparent that the spectrum does not correspond to the NIST entry. The excess of Hg^+ ions most likely derives from elemental mercury, $\text{Hg}(0)$, which is present as a contaminant in the HgCl_2 reagent and the presence of $\text{Hg}(0)$ as a contaminant in the pure reagent can be explained, in addition to possible hydrolysis, by the photodecomposition of HgCl_2 . To test HgCl_2 stability, the same measurement was repeated with a long-standing (old) HgCl_2 reagent, revealing an even more profound deviation from the NIST data (not shown). The deviation of the HgCl_2 spectrum (Figure 4.48) from the NIST data was less intense than seen in Figure 4.46. Thermogram was obtained probably because of the use of a new ultra-purity HgCl_2 reagent and a pressure of $5 \cdot 10^{-3}$ Pa (Iorish, Belov, & Gurvich, 2005).

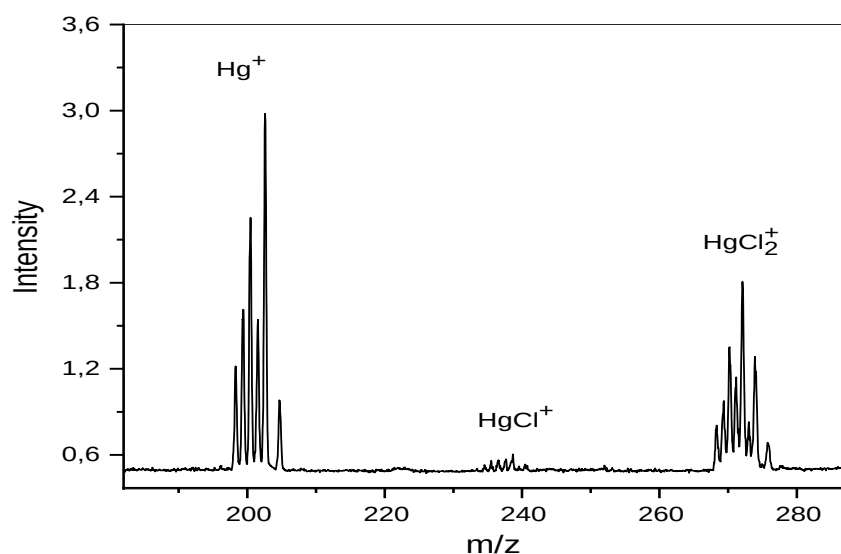


Figure 4.48: Mass Spectra of HgCl_2 vapours in equilibrium with condensed HgCl_2 at 20 °C.

Theoretical calculations: The possible hydrolysis of HgCl_2 within the MS has been investigated using thermochemical calculations in the IVTANTHERMO program incorporated into the Glusko database (Iorish et al., 2005). For this purpose, the HgCl_2 :Hg equilibrium ratio is computed as a function of total pressure, temperature and the H_2O : HgCl_2 mole ratio (Figure 4.49). Analyses confirm that the hydrolysis of HgCl_2 is promoted at low pressure, elevated temperatures and a water content relative to HgCl_2 . Evidently, the HgCl_2 :Hg ratio in the vapour phase is temperature-pressure-concentration dependent.

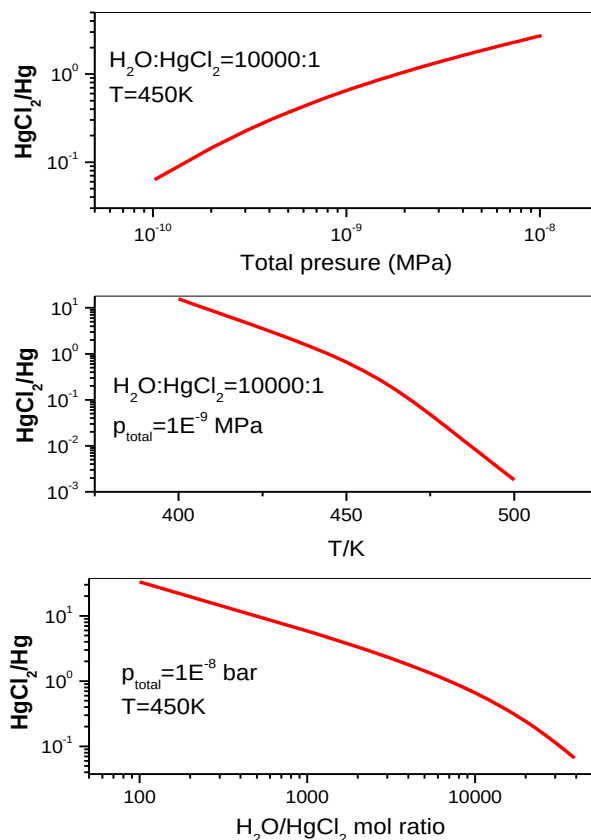


Figure 4.49: The calculated equilibrium ratio of HgCl_2/Hg dependency on pressure, temperature and molar $\text{H}_2\text{O}/\text{HgCl}_2$ vapour ratio.

For a better understanding of HgCl_2 hydrolysis, Figure 4.50 shows the dependency of $\text{HgCl}_2:\text{Hg}$ versus the pressure at constant temperature. The amount of Hg decreases in higher pressure whereas HgCl_2 shows a different behaviour. Considering thermodynamic calculations, the stability of HgCl_2 at atmospheric pressure is more favourable than in vacuum conditions. However, the presence of water is significant and shows almost no changing in the amount of HgCl_2 even at low pressure at a lower amount of water. HCl is shown to confirm the hydrolysis of HgCl_2 by the same decomposition pattern as Hg.

The ratio of $\text{HgCl}_2:\text{Hg}$ in the vapour phase is temperature-pressure-concentration dependant. Taking this into account, it becomes easy to explain the observations of other researchers (Sedlar et al., 2015; Uddin et al., 2009; Wu et al., 2011) who studied the desorption of HgCl_2 from various sorbents, such as SiO_2 and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, using MS. When the concentration of adsorbed HgCl_2 is high, for example, when using pure HgCl_2 , it is reasonable to expect HgCl_2^+ ions in the mass spectrum, but in the presence of low amounts of HgCl_2 relative to the amount of water, they decompose entirely into $\text{Hg}(0)$.

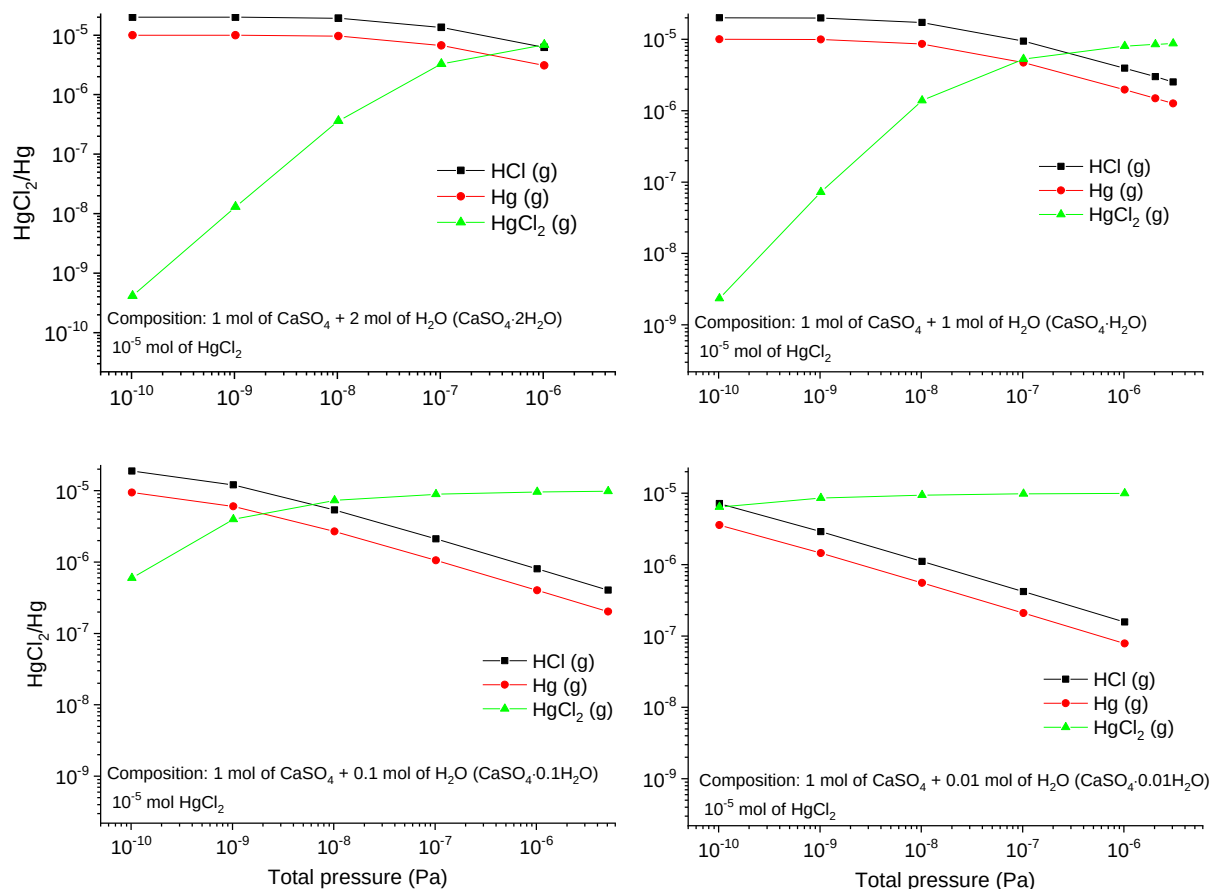


Figure 4.50: The calculated equilibrium ratio of HgCl_2/Hg dependent on the pressure at constant HgCl_2 concentration and different water content.

The concentration of mercury in the WFGD gypsum is low (around 1 mg kg^{-1} or lower in the bulk samples) relative to the pure Hg compound, meaning that the presence of HgCl_2 (by observing HgCl_2^+ ions) using MS was unlikely, especially if the water was co-released. Gypsum also loses water when heated. Although care should be taken when using thermodynamic calculations based on chemical equilibrium to explain kinetically governed processes, such as thermal desorption-decomposition, in the present case, the calculations agree with experimental observations (Sedlar et al., 2015; Uddin et al., 2009; Wu et al., 2011).

Mass spectrum of HgCl_2 in gypsum of TEŠ5-FF: The only gypsum sample in which we were able to detect HgCl_2^+ was TEŠ5-FF (Figure 4.51). HgCl_2 was not detected during the thermal heating process of this sample but after the heating was finished (at room temperature). There was a small amount of fine white powder sample dispersed on the walls of the quartz sample vessel, and it seems that acts as a condensation medium for HgCl_2 (see sample vessel in Figure 3.1). An alternative explanation proposes the formation of HgCl_2 from Hg and chlorine that evaporates as a decomposition of various halogenides present in the gypsum. Although the sample is heated in the vacuum, “cold surfaces” may cause condensation (and adsorption) on the particles. Figure 4.51 represents the only

spectrum where HgCl_2^+ ion has a higher intensity than Hg^+ and resembles the original NIST spectrum. Since we were not able to obtain the spectrum similar to the NIST's one from the pure Hg-compounds, we hypothesise that " HgCl_2 " formed after heating or evaporated as pure Hg-compound may accumulate onto quartz tube after a couple of measurements and not as a consequence of only one completed measurement.

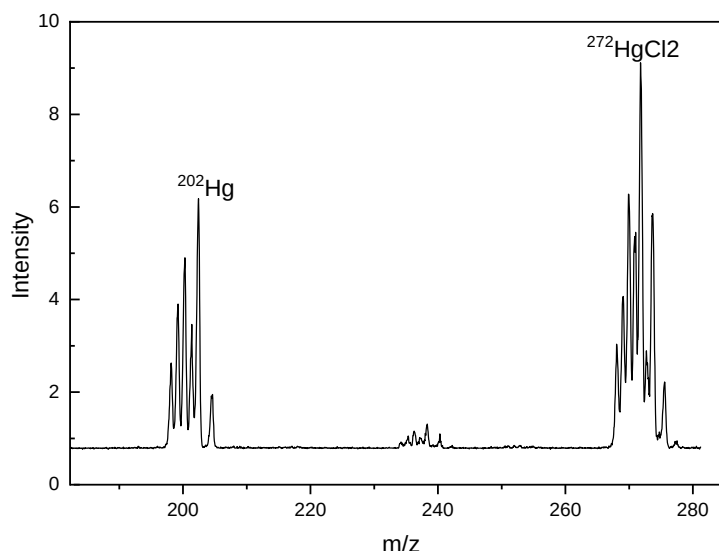


Figure 4.51: Mass spectrum of HgCl_2 measured in the ash of gypsum sample accumulated on the walls ("cold surface") during the measurements.

4.2.3.2 Differences between HgCl_2 and Hg_2Cl_2 adsorbed to the surface or bounded in crystalline $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$

The data about the identification of HgCl_2 shows that it only exists at low temperatures and high concentrations, typically as a pure Hg compound. In the presence of different dry (powder) substrates, it is expected that dissimilarities in releasing of Hg-compounds are the consequence of energy (higher temperature) necessary to break weak Van der Waals force due to the physical adsorption. According to the literature, most of the HgCl_2 decompose when is in contact with the substrate (Ozaki et al., 2008; Uddin et al., 2009; Wu et al., 2011). To evaluate the effect of substrates on TPD spectra and variances between $\text{HgCl}_2/\text{Hg}_2\text{Cl}_2$ species prepared by dry and wet mixing, three different substrates ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, SiO_2 and FeOOH) were chosen (Figures 4.52 and 4.53; releasing temperatures are provided in Table 4.4). In case of dry mixtures, Hg is adsorbed to the surface (e.g., to the $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), while in solution Hg compounds ionized and/or they could be incorporated and bounded by the crystal structure of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in the drying of the sample. Significant differences are seen between the Hg releasing profiles. Hg mixed with powder $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ released at about 70-90 °C lower temperatures than from the inside of the crystal. Only one peak was obtained when Hg-Cl species were added to the saturated solution of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. However, in the latter case, it was not possible to differentiate between HgCl_2 and Hg_2Cl_2 due to the similar releasing temperatures and the peak shape. In water solution formation of the same Hg-species is proposed for both Hg-species. Decomposition (desorption) of HgCl_2 shows the position of Hg peaks at similar

temperatures for FeOOH and SiO₂, whereas with powder CaSO₄ · 2H₂O it is shifted to a lower temperature (Figure 4.52).

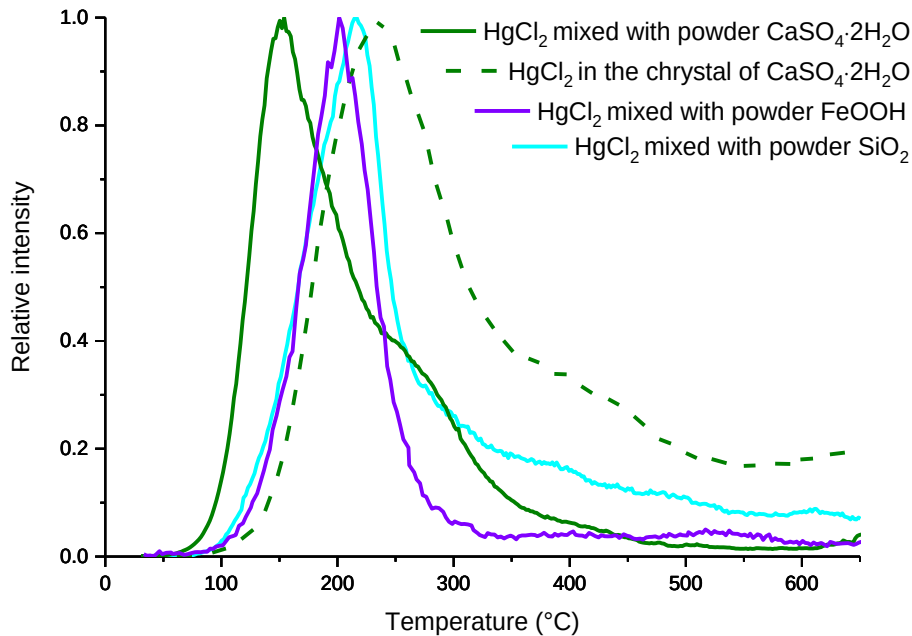
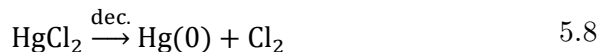
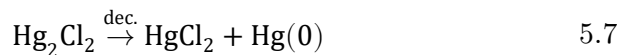


Figure 4.52: TPD spectra of dry mixtures and precipitate from wet mixture show differences between HgCl₂ released when Hg is adsorbed to the CaSO₄ · 2H₂O, SiO₂, FeOOH or mixed in a solution of CaSO₄ · 2H₂O (Hg located in the crystal).

On the contrary, dry mixture of Hg₂Cl₂-FeOOH indicates two-step decomposition. Mixture with powder CaSO₄ · 2H₂O proposes step decomposition as well, but it is not as profound as with FeOOH. This decomposition path is consistent with other researchers (Lopez-Anton et al., 2010; Raposo et al., 2003) according to the following reactions (eqs. 5.7 and 5.8):



However, single peak observed with the mixture of Hg₂Cl₂-SiO₂ indicating decomposition of Hg₂Cl₂ into HgCl₂ and Hg(0). This could happen in previous preparation steps as a consequence of light exposure, mechanical forces and humidity effect. Interaction with matrix is also important. The higher temperature of maxima peak demonstrates the stronger interaction between SiO₂ and FeOOH than with CaSO₄ · 2H₂O. Moreover, in the previous Subchapter 4.2.3.1, the influence of water has been proposed as a factor affecting the decomposition of HgCl₂. According to the theoretical calculations and TPD spectra (Figures 4.52 and 4.53), crystal water present in dry powder of CaSO₄ · 2H₂O caused similar decomposition and desorption process of both Hg-Cl species showing by the same temperature of the Hg releasing peak. Two-step decomposition in case of Hg₂Cl₂ is therefore questionable.

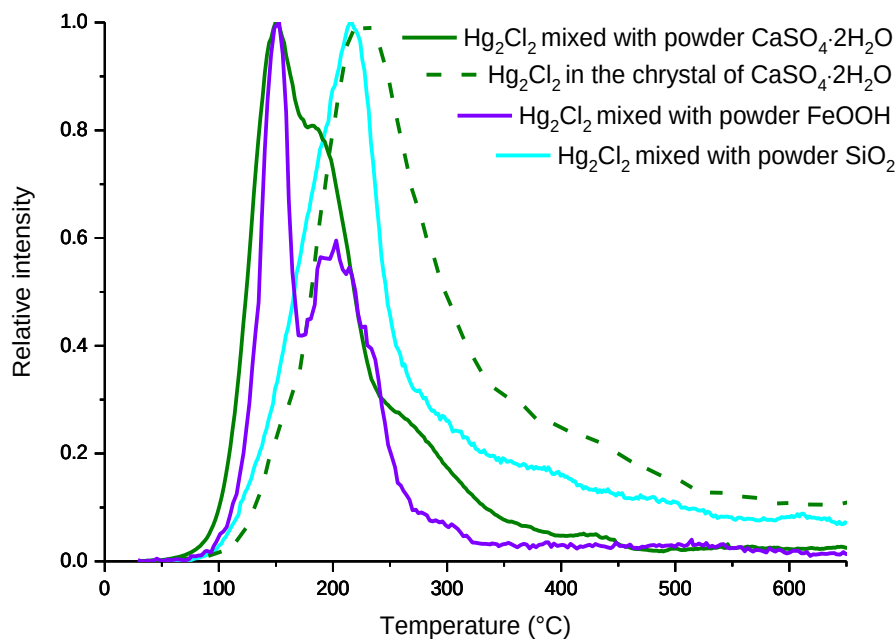


Figure 4.53: TPD spectra show differences between Hg_2Cl_2 released when Hg is adsorbed to the $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, SiO_2 , FeOOH or in a solution of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (Hg located in the crystal).

Table 4.4: Temperature at which peaks attain its maximum (maximum temperature) for Hg-Cl species mixed/added in solution with different substrates such as SiO_2 , $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and FeOOH .

Hg-compounds + substrate	Temperature (°C)
HgCl_2 mixed with powder $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	152
Hg_2Cl_2 mixed with powder $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	151, (181)
HgCl_2 mixed in the crystal with powder $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	237
Hg_2Cl_2 mixed in the crystal with powder $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	227
HgCl_2 mixed with powder SiO_2	216
Hg_2Cl_2 mixed with powder SiO_2	216
HgCl_2 mixed with powder FeOOH	201
Hg_2Cl_2 mixed with powder FeOOH	153, 203

4.2.3.3 Hg-compounds mixed with dry $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$

$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is one of the dominant components in the gypsum samples. In addition to Hg-Cl species, we prepared additional Hg-mixtures. Previous Subchapter (4.2.2) showed the TPD spectra of samples from block 4, 5 and 6. In this doctoral dissertation, we are mainly focused on identification of the mercury species present in block 6. However, TPD spectra prepared by mixing of pure mercury compound with the substrate such as $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ could be applicable for identification of mercury compounds in other gypsum samples as well.

To determine which of the mercury species decompose at 260 °C in the samples of block 6 (Figure 4.38), the resultant spectra were compared with seven dry mercury standards mixed with pure $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (Figure 4.54; releasing temperatures are written in the Appendix Table A.6). Standard mixtures (HgS , HgCl_2 , Hg_2Cl_2 , $\text{HgO}(\text{red})$, $\text{HgO}(\text{yellow})$, Hg_2SO_4 and HgSO_4) show smooth peaks at defined temperatures. $\text{HgO}(\text{red})$, $\text{HgO}(\text{yellow})$ and Hg_2SO_4 show two peaks (one bigger and one smaller). Similarly, HgSO_4 show more peaks where first two peaks are very small. HgS show one narrow peak whereas HgCl_2 and Hg_2Cl_2 have broadened peak with small shoulders. All compounds released as a consequence of decomposition/desorption of pure Hg-compound from the surface of the substrate. However, the substrate may affect the final position of the TPD spectrum.

None of the mercury compounds mixed with dry $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ matched the actual gypsum samples in Figure 4.38. There are two possible reasons for this; i) none of the compounds is present in the gypsum or ii) the chemical composition of the gypsum changes the desorption temperature of Hg compounds. Another concern is that the system was "calibrated" using pure crystal mercury compounds mixed with crystalline $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, and does not reflect the conditions in the gypsum of the WFGD system. Also, HgS as an Hg-species that may be present in the gypsum of block 6 according to the decomposition fragments SO_2 and H_2S does not fit with the decomposition temperature of the peak of pure HgS in Figure 4.54. To identify Hg peak(s), wet mercury standards were prepared in the next step.

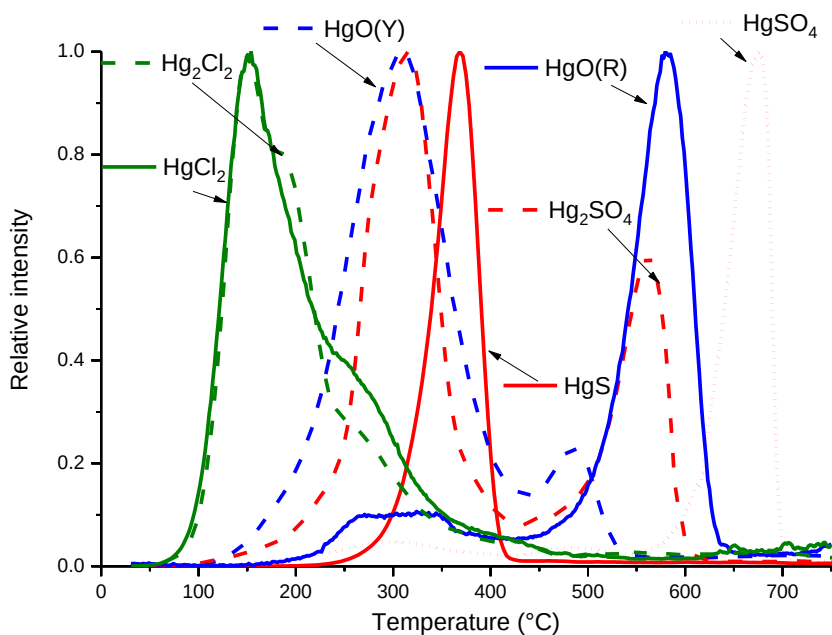


Figure 4.54: TPD spectra of reference standards prepared by dry mixing of various Hg-species with pure $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

4.2.3.4 Hg-compounds in a solution of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$

In the samples prepared by dry mixing of Hg compounds with $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, a desorption/decomposition process takes place from the surface of the crystals dispersed in the matrix ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), and diffusion is unlimited, meaning that there is less interaction with the matrix. This produces narrower peaks at different positions on the temperature scale (Figure 4.54). In slurries, however, Hg exists in its ionic state and can form complexes

or become attached to different particles. Consequently, it is unreasonable to expect identical decomposition spectra in both cases.

Therefore, a simple experiment was performed using mercury compounds (HgS , HgSO_4 , Hg_2SO_4 , HgO(Y) , HgCl_2 , Hg_2Cl_2) dissolved in a saturated solution of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. The solution was dried, and the TPD spectra for the remaining solid samples (solid precipitate) were recorded in Figure 4.55. From the resulting family of TPD curves using $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (Figure 4.55) regardless of which Hg compound was used in the “wet” preparation of mercury compounds, all Hg-species decomposed at a similar temperature (maximum at 243 ± 13 °C), unlike in the case of dry mixing (Figure 4.54). The family of curves represents the desorption/decomposition processes of Hg compounds from the bulk of the $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ crystals. Evaporation processes are hindered by the diffusion of Hg through the crystal bulk and by the kinetics of the possible reactions taking place between the bulk $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and Hg compounds during heating. The resulting TPD spectra all exhibit broad unsymmetrical peaks with humps, and the presence of several shoulders indicate various decomposition reactions between the gypsum matrix and Hg compounds.

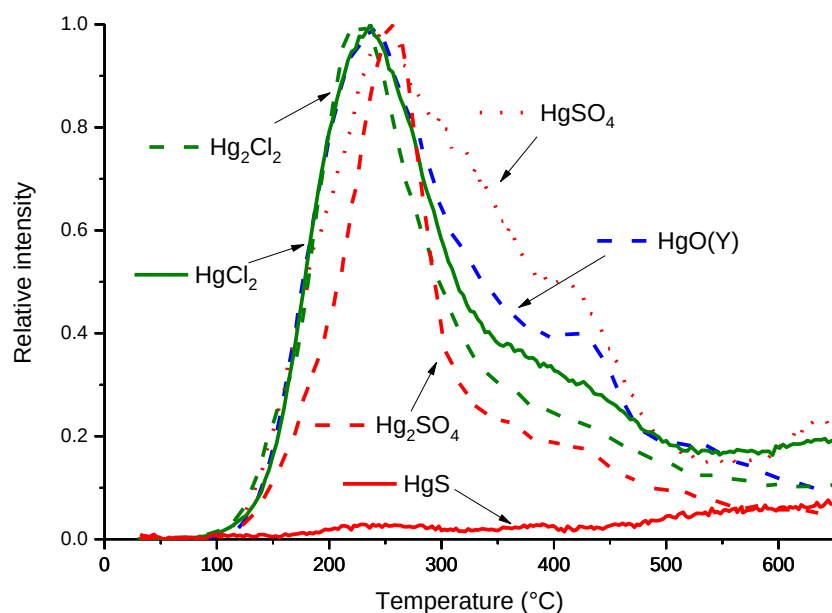


Figure 4.55: TPD spectra of mercury compounds in precipitates prepared by wet mixing various Hg-compounds in a saturated solution of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. *Note:* The absence of HgS peak is due to its low solubility.

4.2.3.5 Hg-compounds in a solution of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ with added FeOOH

The literature indicates that some oxides and hydroxides (e.g., Fe, Al, Mn) may govern the adsorption process (Inoue & Munemori, 1979; C. S. Kim et al., 2004a, 2004b; Lockwood & Chen, 1973; Stergaršek et al., 2013, 2010; Tiffreau et al., 1995). In actual WFGD samples, the mercury is mostly present in the fine fractions that are enriched with iron (Beatty et al., 2012; Kairies et al., 2006). To verify the presence (effect) of Fe-species on Hg TPD spectra in solid samples, FeOOH was added. As seen in Figure 4.56, the obtained TPD spectra have narrower peak half-widths, with their maximums at 237 ± 21 °C, similar to the WFGD samples from Šoštanj TPP (Figure 4.38). However, TPD curves in Figure 4.56 still do not adequately follow the TPD spectra of the actual gypsum samples. The difference

between the two sets of curves (Figures 4.55 and 4.56; wet preparation) is most visible regarding peak width and, to a lesser extent, peak positions. This indicates the influence of FeOOH on Hg TPD spectra.

The low solubility of HgS meant that Hg-mixture using the wet method could not be compared with other Hg-compounds.

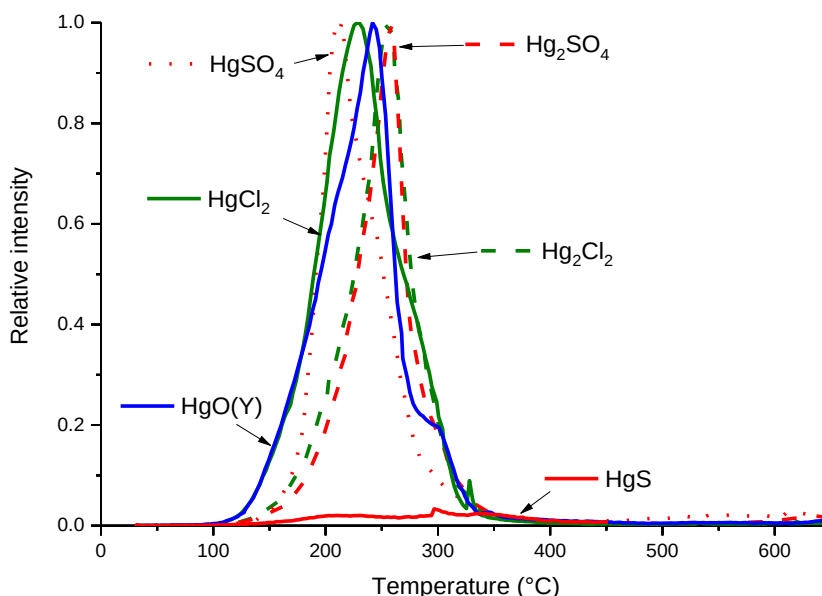


Figure 4.56: TPD spectra of mercury compounds in precipitate prepared by wet mixing various Hg-species in a solution of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and FeOOH. *Note:* The absence of HgS peak is due to its low solubility.

4.2.3.6 Hg-compounds mixed with dry FeOOH and in a solution of FeOOH

Figure 4.57a shows TPD spectra of selected Hg-compounds ($\text{HgO}(\text{Y})$, $\text{HgO}(\text{R})$, HgCl_2 and Hg_2Cl_2) after dry mixing with FeOOH. The Hg compounds cover the matrix surface in the form of small crystals, and decomposition resembles that of the pure compound, where its thermal stability determines the position of the peak (Figure 4.57a), similar to dry $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (Figure 4.54). Step decomposition of Hg_2Cl_2 into HgCl_2 is seen in Figure 4.57a (more in Chapter 4.2.3.2.). The decomposition profiles for both HgO mixed with FeOOH decompose at the same temperature compared to those mixed with $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. It follows that mercury compounds prepared using various dry substrates have different TPD spectra. The ability of different substrates to change the shape and the position of the TPD curves was confirmed in our previous study (Sedlar et al., 2015).

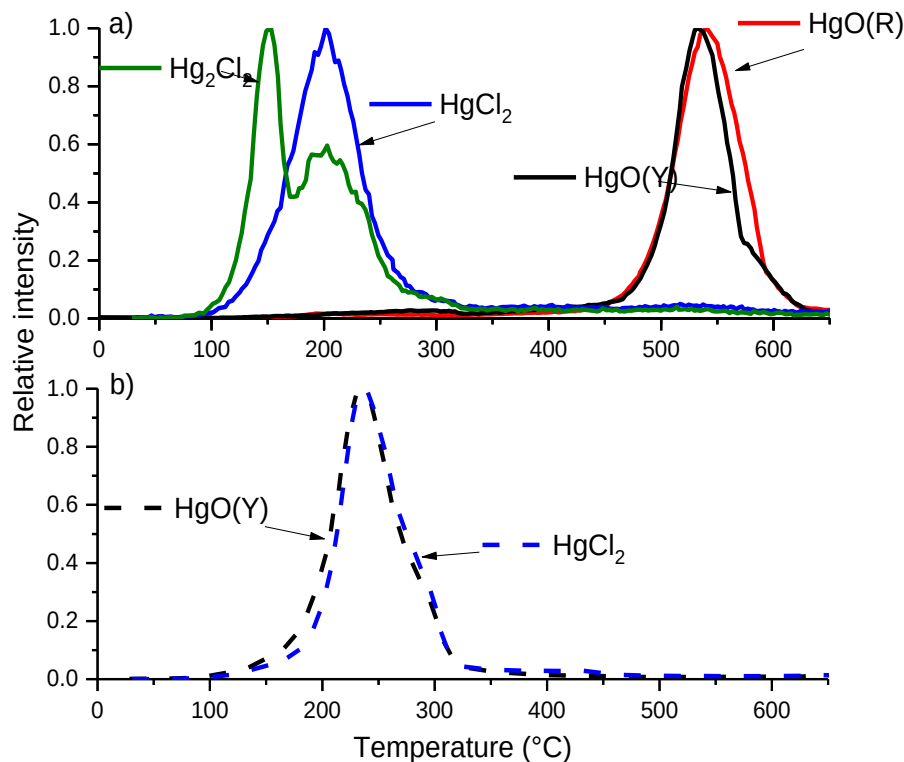


Figure 4.57: TPD spectra of Hg_2Cl_2 , HgCl_2 , HgO(Y) and HgO(R) mixed with dry FeOOH and b) TPD spectra of HgCl_2 and HgO(Y) in precipitates prepared by wet mixing of Hg-species in a solution of FeOOH .

In another experiment, HgCl_2 and HgO(Y) were mixed in a solution of FeOOH without the addition of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (Figure 4.57b). The TPD spectra of the precipitates prepared from chemically pure systems (HgO or HgCl_2 , FeOOH and distilled H_2O) show an almost identical desorption/decomposition profile suggesting the same Hg-species were formed after the dissolution of HgO or HgCl_2 . Literature data propose the presence of Hg in the fine fractions of gypsum with elevated concentrations of different elements such as iron (Al-Abed et al., 2008; Beatty et al., 2012; Kairies et al., 2006). Due to the similarities between the TPD spectra of actual WFGD samples from Šoštanj and the TPD spectra from the different experiments (Figures 4.38, 4.56 and 4.57b), the presence of Fe-species could influence the shape of the TPD spectra and the temperature (position of the peak) at which Hg-species desorbed/decompose. Literature data show that iron influences thermal stability where it acts as a catalyst and thus changes the temperature at which Hg released from the solid sample (Matsuyama et al., 1999).

Regarding the pH of the WFGD slurry, low chlorine content in gypsum obtained from block 6 and literature data describing adsorption of Hg to Fe-surfaces, the formation of Hg(OH)_2 and other Hg-O- surface complexes in the gypsum slurry are suggested. The decomposition of Hg(OH)_2 into HgO after drying could be the possible mechanisms for mercury removal in the solid gypsum. Due to the low Cl content, HgO is more favourable than Hg-Cl or other Hg species. WFGD system is a very complex system including a lot of diverse ligands (Cl^- , HSO_3^- , HSO_4^- , HCO_3^- , OH^- , etc.), and many different Hg complexes may form in the solution. More simulation experiments using different ligands together with Fe, Al, Mn and other compounds that could be involved in the process of Hg

accumulation in the gypsum are needed to identify the mechanisms which are responsible for Hg retention in the gypsum and to determine the mercury species formed on the particles.

4.2.3.7 Experiments with the addition of NaCl

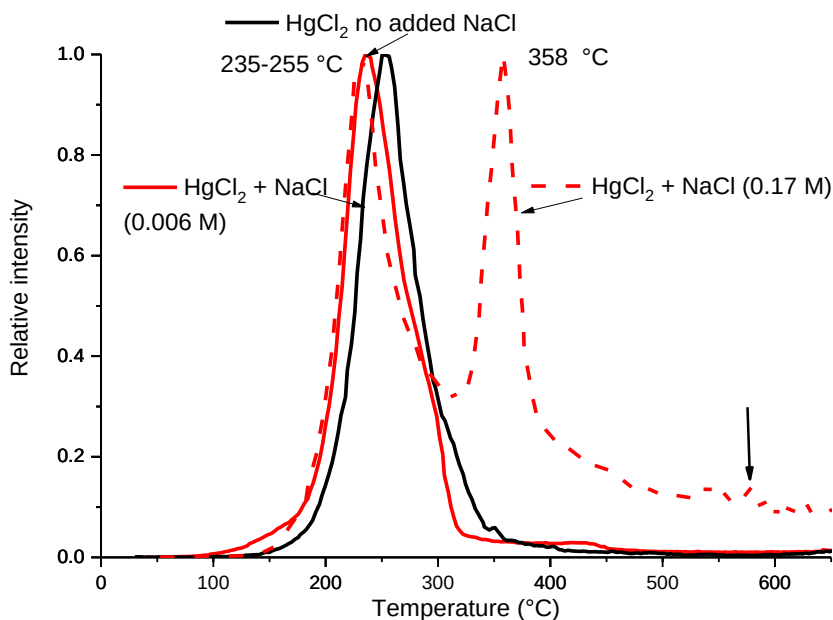


Figure 4.58: TPD spectra of precipitate of HgCl_2 in a saturated solution of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and FeOOH without the addition of NaCl and with two different concentrations of NaCl (0.006 and 0.17 M).

As already mentioned, in the WFGD gypsum slurry, different ions are present. The formation of Hg species is most likely attributed to the presence of SO_3^{2-} , OH^- and Cl^- (Heidel et al., 2016; Ochoa-González, Díaz-Somoano, & Rosa Martínez-Tarazona, 2013; Stergaršek et al., 2013; Sun, Cheng, et al., 2014). At a pH of 6 (pH in the WFGD system of Šoštanj TPP is 5.4-5.6), the Hg species present in solution depend mainly on the presence of Cl^- and OH^- ions. The literature shows the possibility of adsorption of Cl^- and Hg to FeOOH as a prevailing process, but at a higher concentration of Cl^- ions, Hg adsorption is inhibited (Bonnissel-Gissinger et al., 1999; C. S. Kim et al., 2004b; Tiffreau et al., 1995). In the presence of chlorine ions at a lower pH, HgCl_2 forms instead of $\text{Hg}(\text{OH})_2$; while at a higher pH, the formation of $\text{Hg}(\text{OH})_2$ is observed (Inoue & Munemori, 1979).

To evaluate the influence of chlorine on the TPD spectra of a solid precipitate prepared by dissolving HgCl_2 in a saturated solution of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}/\text{FeOOH}$, two different experiments were performed: one with low (0.006 mol L^{-1}) and one with high (0.17 mol L^{-1}) amounts of Cl^- . The TPD spectra reveal an additional peak at the higher concentration of Cl^- (Figure 4.58), while at the lower concentration, no change in the peak position or peak shape was observed, similar to the spectra with no addition of NaCl . Low concentration of Cl^- does not affect the TPD spectra whereas at higher NaCl levels more stable Hg compound form, which is shown by the existence of a peak at higher temperatures. However, the hydrolytic effect and specific experimental conditions mean that mass spectrometry cannot confirm the presence of HgCl_2 molecules from observing HgCl_2^+ ions.

4.2.3.8 Preliminary experiments with $\text{Al}(\text{OH})_3$

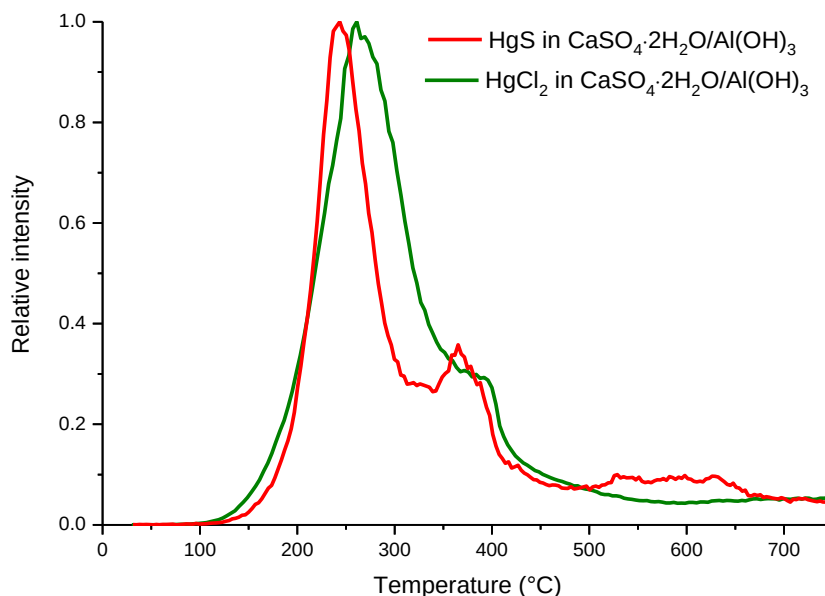


Figure 4.59: TPD spectra of HgS and HgCl_2 in precipitate prepared by wet mixing Hg-species in a saturated solution of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ with $\text{Al}(\text{OH})_3$ addition.

Intensive studies were done with FeOOH , whereas only a few experiments were performed using $\text{Al}(\text{OH})_3$. In addition to FeOOH , $\text{Al}(\text{OH})_3$ is another matrix that might adsorb Hg (C. S. Kim et al., 2004b). The multielemental analysis shows high accumulation of Al in the gypsum samples from Šoštanj TPP, in particular in fine fractions. For that purpose, we performed some experiments to see the influence on TPD spectra. Two different Hg-species were chosen (HgCl_2 and HgS). First, Hg compounds were diluted in pure $\text{Al}(\text{OH})_3$ solution and then in a saturated solution of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ with the addition of $\text{Al}(\text{OH})_3$.

In the experiments using a saturated solution of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ with the addition of $\text{Al}(\text{OH})_3$, two visible peaks are seen in the range between 100 and 500 °C (Figure 4.59). The first peak is strong for both Hg-compounds and released at around 250 °C, while the second peak appeared as a shoulder (with HgCl_2) or small peak (with HgS) in the range between 340 and 390 °C. It should be emphasised that HgS show very similar results as HgCl_2 which is in contradiction with FeOOH where no peak for HgS was obtained. These similarities indicate the impact of $\text{Al}(\text{OH})_3$ to the solubility of HgS in a saturated solution of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O} / \text{Al}(\text{OH})_3$.

The results of pure HgS or HgCl_2 added in the solution of $\text{Al}(\text{OH})_3$ are provided in Figure 4.60. Significantly different peaks were obtained. HgS shows one intensive peak at 390 °C with a small shoulder at 250 °C. The highest peak resembles the releasing temperature of the pure HgS peak without any matrices. On the other side, HgCl_2 represents two peaks at a lower temperature (215 °C) and the other at a relatively high temperature (595 °C).

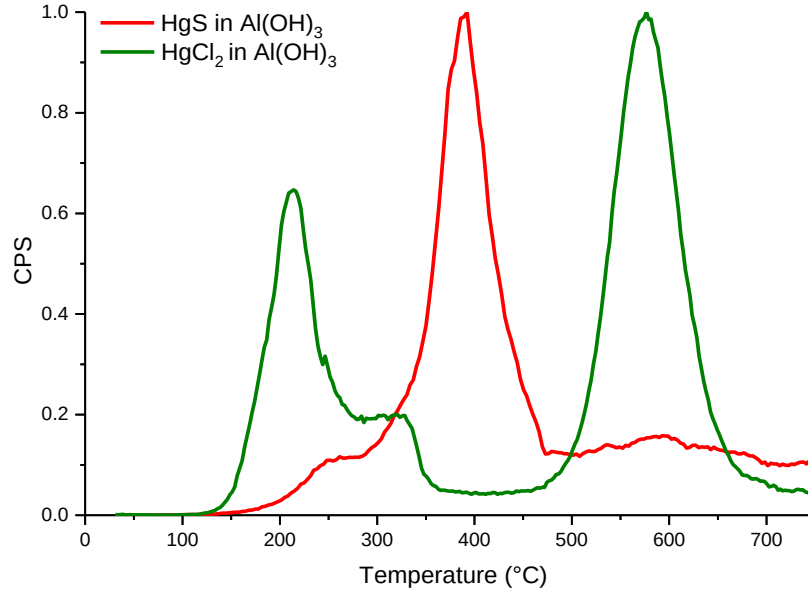


Figure 4.60: TPD spectra of HgS and HgCl₂ in precipitate prepared by wet mixing Hg-species in a solution of Al(OH)₃.

Results obtained by using Al(OH)₃ precipitates indicate different TPD spectra concerning the FeOOH. Moreover, using precipitates of pure mercury compounds added to a solution of CaSO₄ · 2H₂O/Al(OH)₃ show entirely different spectra as with pure Al(OH)₃ solution. However, only preliminary studies were done with Al(OH)₃ and further experiments are needed. Also, more Hg species need to be tested, and the processes that are present in the solution should be studied to understand the formation of the additional peak. Nevertheless, the results show that different substrates may completely change the TPD spectra of precipitates and the study of influences of different substrates to the changes of TPD spectra is very important. Unfortunately, we did not prepare dry mixtures with Al(OH)₃ to compare the TPD spectra with the spectra of other mixtures.

4.2.3.9 HgS in the gypsum sample

4.2.3.9.1 Different gypsum samples spiked with HgS

Mercury sulphide is commonly considered the most likely Hg species present in WFGD samples (X. Liu et al., 2013; Z. Zhu et al., 2016). Its formation is thought to occur at higher loads of sulphur due to the disproportionation of SO₃²⁻ into S²⁻ and SO₄²⁻ (Sui et al., 2015) as follows:



The solubility product of HgS is extremely low ($K_{\text{sp}} = 2 \cdot 10^{-53}$) (Hepler & Olofsson, 1975; Wagman et al., 1968), meaning that it should precipitate in the slurry. In the Šoštanj TPP samples, this is not the case because its decomposition temperature (Figure 4.54: HgS TPD spectrum obtained by dry preparation) is about 100 °C higher than the measured WFGD

gypsum samples (Figure 4.38). To prove this, gypsum sample from China and sample from Šoštanj TPP (ORIG-FF) were blended with pure solid HgS prepared by dry mixing (Figure 4.61). In the spectra, an additional peak appears as a consequence of HgS decomposition meaning that the original WFGD sample does not contain HgS. However, the shape of the peaks observed in Figure 4.38 all resemble HgS mercury standards. Therefore, HgS cannot be excluded from the set of possible species present in the gypsum, because matrix may change the position of TPD peak as confirmed in our previous study (Sedlar et al., 2015).

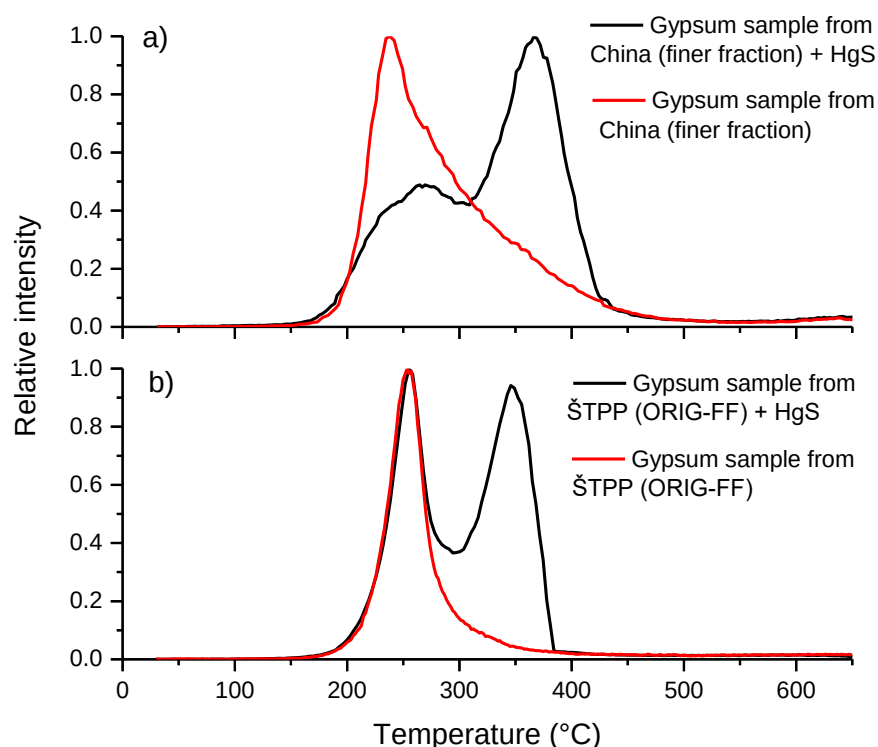


Figure 4.61: TPD spectra of DISP-FF and WFGD sample from China with and without HgS addition.

4.2.3.9.2 Hg-compounds in solution of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}/\text{FeOOH}$

Similar experiments than in previous subchapter were repeated using Hg compounds prepared in a saturated solution of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ with added FeOOH. Additional peaks appear (Figure 4.62) at similar temperatures than in the actual gypsum slurry (ORIG-FF). Although many authors identify HgS in their samples (J.-Y. Lee et al., 2009; Milobowski et al., 2001; Rallo et al., 2010; Sui et al., 2015; Z. Zhu et al., 2016), it was not possible to prove its presence in the gypsum samples in this study, since no characteristic TPD peak was observed between 300 and 400 °C.

Here are some reasons why HgS could not be detected by using HgS mercury standard in gypsum samples of Šoštanj TPP using mass spectrometric detection: i) HgS is not present in the gypsum samples, ii) the presence of HgS is too low to be detected by the TPD, and thus the peak for HgS is hidden in the background, iii) HgS could be present in the form of metacinnabar which is released at lower temperatures according to the publications of other researchers and has not been tested in the present work, and iv) HgS could be present as Hg-S bonded to the substrate (surface) contains Fe or other elements, where the strength of the S-Hg bonds are weaker than in the crystalline phase of HgS. It

follows that decomposition at lower temperatures than with crystalline HgS is possible and v) HgS is present in the gypsum, but it is released at lower temperatures than mixed with the dry mixtures due to the presence of unknown species such as Fe-compounds in the gypsum samples which have a catalytic role and cause the desorption/decomposition of HgS at lower temperatures.

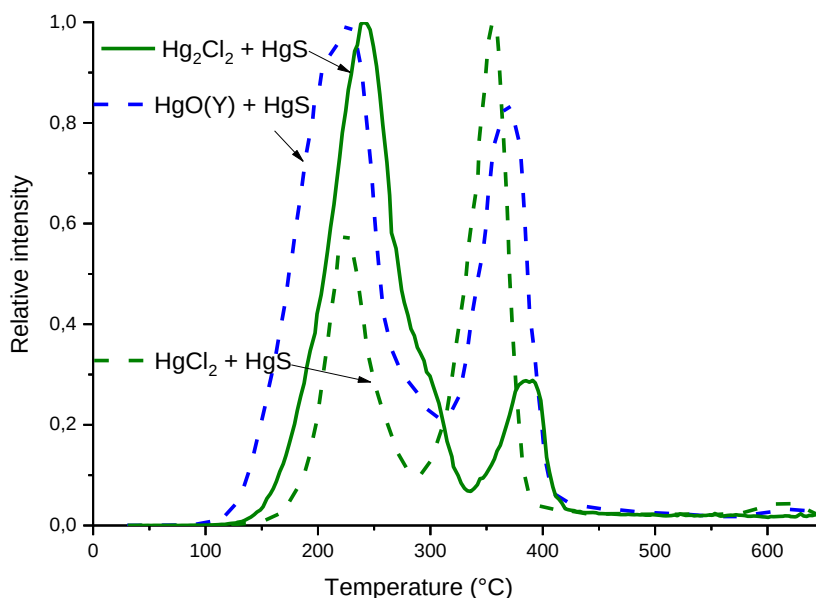


Figure 4.62: TPD spectra of various wet prepared standards blended with the dry prepared HgS.

4.2.3.9.3 Results of XAS experiments

The analysis of XANES spectra was performed with the IFEFFIT program package ATHENA (Ravel & Newville, 2005). The relative L_3 -shell contribution in the absorption spectra was obtained in the standard procedure (Ravel & Newville, 2005; Wong, Lytle, Messmer, & Maylotte, 1984) by removing the extrapolated best-fit linear function determined in the pre-edge region (-150 eV -30 eV), and by conventional normalization, extrapolating the post-edge spline background, determined in the range from 150 eV to 800 eV, to set the Hg L_3 -edge jump to 1. The best linear combination fit was obtained with the combination of standard reference compounds HgS and HgO (Kodre et al., 2017) (Figure 4.63), with HgS as predominant (>90%) type of coordination.

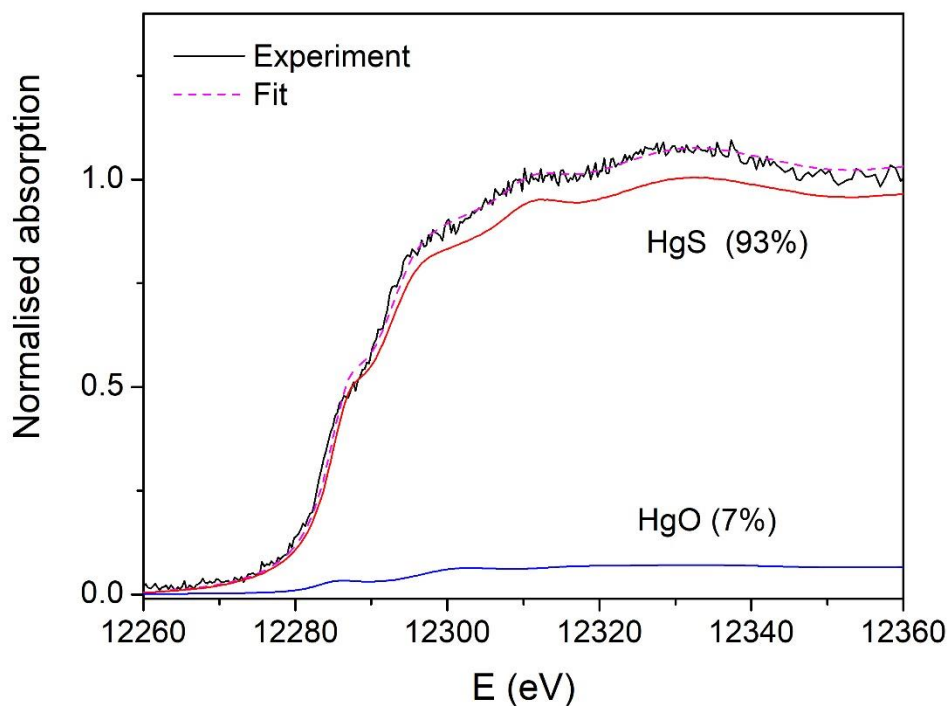


Figure 4.63: The results of XANES analysis.

The results of XANES confirm the presence of HgS in gypsum samples from block 6 (tested in the sample RECY). XAS is the only method that allows direct determination of Hg species present in our gypsum samples. Due to the stability of HgS, Hg form has not been changed after two years from the first analysis (Figure 4.43). However, Hg reduction into Hg(0) that adsorbed onto the surface of the matrix was observed in the samples of coarse fraction. Since $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is a prevailing matrix, crystal water may affect this process.

4.2.4 Gypsum samples from China

Bulk gypsum samples from ten different Chinese TPP were obtained. The main purpose was to compare different gypsum samples from China among themselves, and with the gypsum samples from Šoštanj. The concentrations of TMEs vary between Chinese gypsum samples, possibly due to the burning of different coal, APCDs installation and conditions in WFGD scrubber. All Chinese TPPs are equipped with ESP, SCR and WFGD, whereas Jiaaisi and Nanjing have also installed WESP. To see in which by-products during combustion process retains the highest amount of Hg, total Hg concentrations in coal, limestone, fly ash, slag and sludge in those TPP were also measured next to the gypsum samples. Unfortunately, we cannot provide Hg concentrations for all these samples because samples were not obtained from each APCDs. Total Hg concentrations and the properties of each TPP are provided in Appendix A in Table A.7.

Differences in gypsum composition and the concentration of Hg caused that TPD spectra of Hg differ in Chinese gypsum. It has been observed in Chapters 4.2.2 and 4.2.3 that identification of mercury compounds by using of QMS was possible in fine fractions of block 6, but the uncertainty is high, and other methods are needed to confirm the presence of a particular compound. It follows that because of lower concentrations in Chinese bulk samples we can only study the stability of mercury compounds in those samples.

4.2.4.1 General properties

Bulk gypsum samples (gypsum slurry samples) were not separated into fine and coarse fractions but represent a mixture of both fractions. Multielemental analyses for all ten samples were provided including 45 elements (Table A.8 in Appendix A). The amount of Hg and other TMEs in the samples represents an average concentration, which is lower compared to fine fractions from Šoštanj TPP. Chinese gypsum samples contain Hg concentration in the range 0.04-1.70 mg kg⁻¹ whereas fine gypsum fraction from Šoštanj typically contains around 10 mg kg⁻¹ of Hg. The total concentration of Hg was measured by two different procedures, k₀-INAA and direct mercury measurement (DMA-80) (Table 4.5).

Table 4.5: Concentrations of Hg in gypsum samples, the temperature at which peak attains its maximum and corresponding mass weight.

Gypsum sample	Concentration (mg kg ⁻¹) *DMA	Concentration (mg kg ⁻¹) **k ₀ -INAA	Peak maximum (°C)	Mass (mg)
Tianjin	0.038 ± 0.002	< LOD	250 (two peaks)	10.0
Jiaaisi	0.078 ± 0.0003	0.14 ± 0.02	250	10.6
Quijing	0.110 ± 0.006	0.12 ± 0.02	250	10.1
Turpan	0.117 ± 0.002	0.16 ± 0.03	370 (not defined)	7.8
Hongyanchi	0.211 ± 0.001	0.20 ± 0.03	230	9.8
Guizhou	0.479 ± 0.002	0.50 ± 0.03	250	8.5
Hubei	0.76 ± 0.01	0.74 ± 0.04	275	9.2
Xiasaishan	0.853 ± 0.003	0.88 ± 0.04	260	9.1
Shijiazhuang	1.44 ± 0.01	1.60 ± 0.06	220	9.8
Nanjing	1.66 ± 0.06	1.70 ± 0.07	230	8.6

†The data are obtained by two different methodologies, by DMA or by k₀-INAA method.

To compare elemental composition between the bulk gypsum samples from China and samples from Šoštanj TPP, the only possibility is to use the data of the bulk sample from block 4, containing about 1 mg kg^{-1} of Hg (the data is taken from the study of Stergaršek et al., 2008 (Stergaršek et al., 2008)).

The amount of mercury in different by-products: Additional data for some samples of coal, fly ash, slag and limestone have been provided. There are three data for the concentration of Hg in the coal samples (no information for coal type). Jiaaisi shows the highest concentration of Hg, followed by Guizhou and Nanjing. All coal samples contain a higher amount of Hg compared to the Velenje lignite. According to this, none of those samples probably represent lignite coal. Limestone used in Guizhou and Jiaaisi have a higher concentration than limestone used in Šoštanj TPP. There are few data for fly ash (Hubei, Jiaaisi, Shijiazhuang, Turpan, Nanjing, Tianjin TPP) but due to the incomplete data for mercury concentration present in other by-products, this is only applicable for Jiaaisi and Nanjing fly ash. Nanjing retains a five times higher concentration of Hg than fly ash of block 4, whereas fly ash from Jiaaisi accumulates almost 1 mg kg^{-1} of Hg which is similar than the concentration of Hg accumulates in bulk gypsum from Šoštanj TPP. Since limestone from Jiaaisi TPP contains a low proportion of Hg, and most of Hg probably retain in fly ash, the amount of Hg in the gypsum is low. It seems that conditions in coal combustion that enable accumulation of Hg into the fly ash caused the lower concentration of Hg in the gypsum. Similar to Jiaaisi is also Tianjin TPP which contains the lowest mercury concentration in the gypsum. There are also other options of low mercury accumulation in fly ash and gypsum: i) coal contains very low Hg concentration or ii) mercury is not retained in APCDs and goes alongside with flue gas in the atmosphere.

Comparison of bulk gypsum samples: Figure 4.64a represents some selected elements (Al, Br, Cl, Fe, Hg, I, Mg, Mn, Se) that could be related to mercury accumulation due to the adsorption, their catalytic role or due to the possible formation of Hg-species (e.g. halogens). The data for other TMEs are provided in Table A.8. In general, bulk gypsum samples from China show similar concentrations of elements to a bulk sample from Šoštanj TPP. TPPs from Shijiazhuang and Nanjing province show higher Hg concentrations than the sample from Šoštanj TPP. On the contrary, higher concentrations of Fe and Al were found in Šoštanj TPP related to Chinese samples. There are no connections observed between Hg and elements presented in Figure 4.64a, except with Se where Se shows increased concentration at elevated Hg concentration. However, this increasing is more noticeable at a lower concentration of Hg and Se.

The molar ratio of Ca and S indicates the purity of gypsum. In Figure 4.64b, the ratio for most samples is close to 1 as expected for bulk samples which contain approximately 10% of fine fraction. Gypsum from Quijing and Shijiazhuang shows the ratio higher than 1.3, possibly as a consequence of other impurities in the gypsum sample, unconsumed CaCO_3 or introduction of different additives. The ratio between Ca and S higher than 1 was observed in the fine fractions of gypsum from block 6. A higher ratio is expected in the samples with a lower particle size, where $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ represents a minor amount than in bulk or coarse samples. Less $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ means the formation or introduction of other species (e.g. additives) in the sample and the ratio between Ca and S changes.

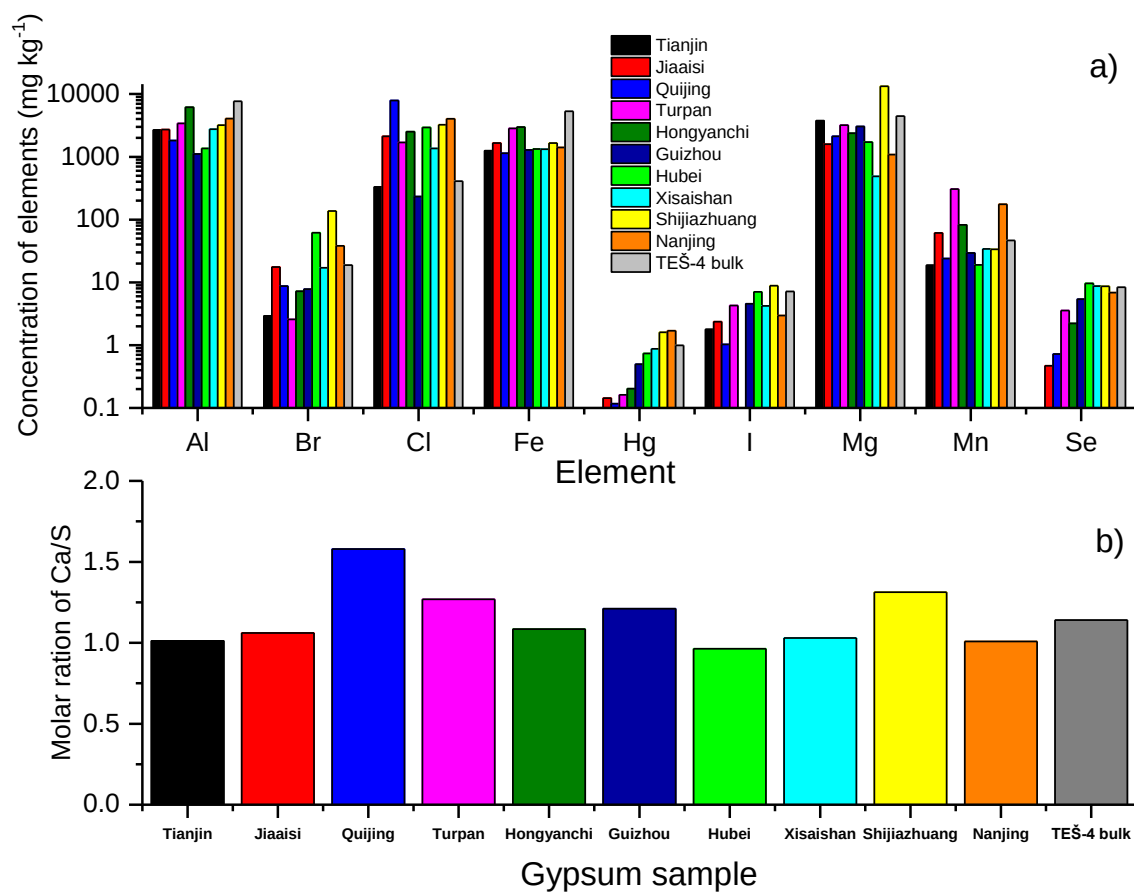


Figure 4.64: a) Concentrations of some TMEs in ten industrial gypsum samples from China and one sample of Šoštanj TPP, and b) molar ratio between Ca and S in gypsum samples.

Figure 4.65 represents particle size distributions for all ten Chinese samples. Similar distributions are found for all samples. As already mentioned, bulk gypsum samples are a mixture of a coarse and fine fraction with the domination of bigger particles. Therefore, particle size distribution is shifted toward smaller sizes concerning the coarse fraction of Šoštanj TPP. However, if we compare the distribution in Figure 4.65 with Figure 4.4 and Figure 4.10, all distribution curves in Figure 4.65 are positioned between fine and coarser particles, with the maxima between 31 and 44 μm . This distribution is expected due to the mixture of fine and coarse fractions, but we do not have the particle size distribution of bulk sample from Šoštanj to compare the results. Moreover, no information about the sampling and sample preparation of gypsum sample from China has been provided together with the samples (samples age, if samples are grinded or homogenized before transportation).

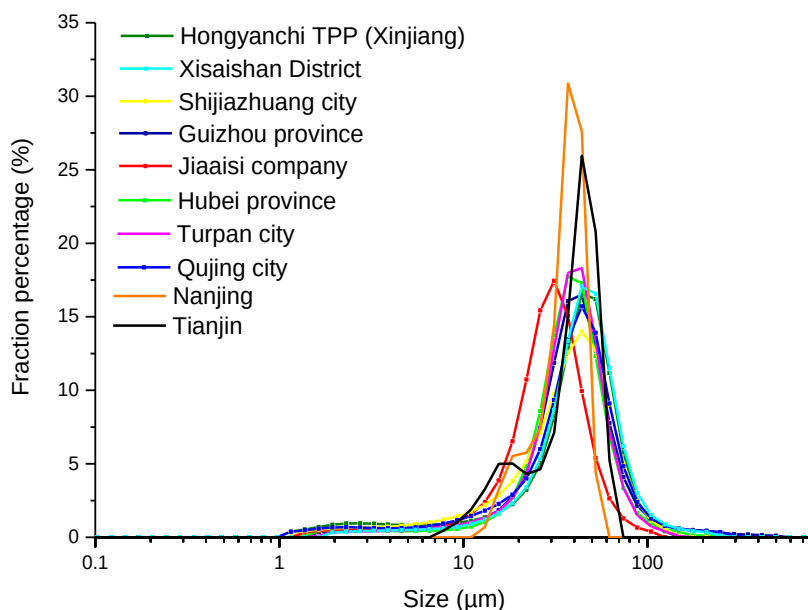


Figure 4.65: Particle size distribution for ten gypsum samples from a Chinese thermal power plant.

4.2.4.2 TPD spectra of bulk gypsum from different Chinese thermal power plants

In this chapter, we obtained TPD spectra to determine the stability of mercury compounds in Chinese gypsum samples. All TPD spectra were recorded by QMS. Samples are divided into three groups according to the concentrations of Hg present in those samples (Table 4.5). The TPD spectra are shown in Figures 4.66–4.68. All gypsum samples were washed and preheated before TPD analysis. However, a relatively high background in each TPD spectrum occurs.

Samples with a low amount of Hg ($< 0.16 \text{ mg kg}^{-1}$ **) show more peaks due to the influence of background, except for gypsum from Jiaaisi TPP (Figure 4.66). However, one major peak at 250°C is seen in the samples from Tianjin, Jiaaisi and Quijing TPP. Hg in Turpan gypsum reached the maximum peak at temperature higher than 370°C although Hg start to release from room temperature (the same as in other TPD spectra).

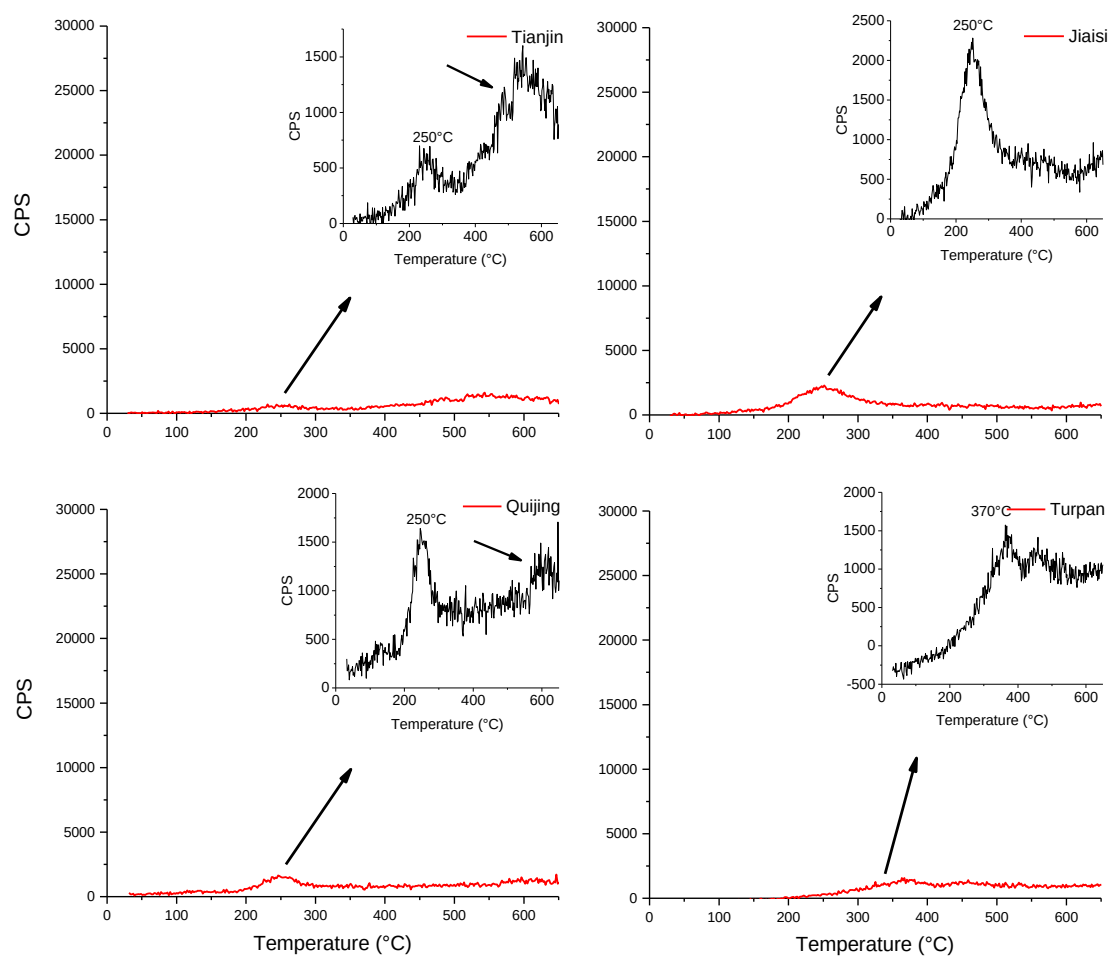


Figure 4.66: TPD spectra of Chinese gypsum samples contain the lowest Hg concentration.

According to our classification, gypsum samples containing middle Hg concentrations ($0.2 \text{ mg kg}^{-1} < \text{Hg} < 0.9 \text{ mg kg}^{-1}$ **, Hongyanchi, Guizhou, Hubei and Xisaishan) belong in the second group (Figure 4.67). All spectra show one peak in the temperature range 230-275 °C. Gypsum from Hongyanchi TPP indicates some smaller peaks at higher temperatures representing the presence of additional Hg compounds. However, this could also be the consequence of the background.

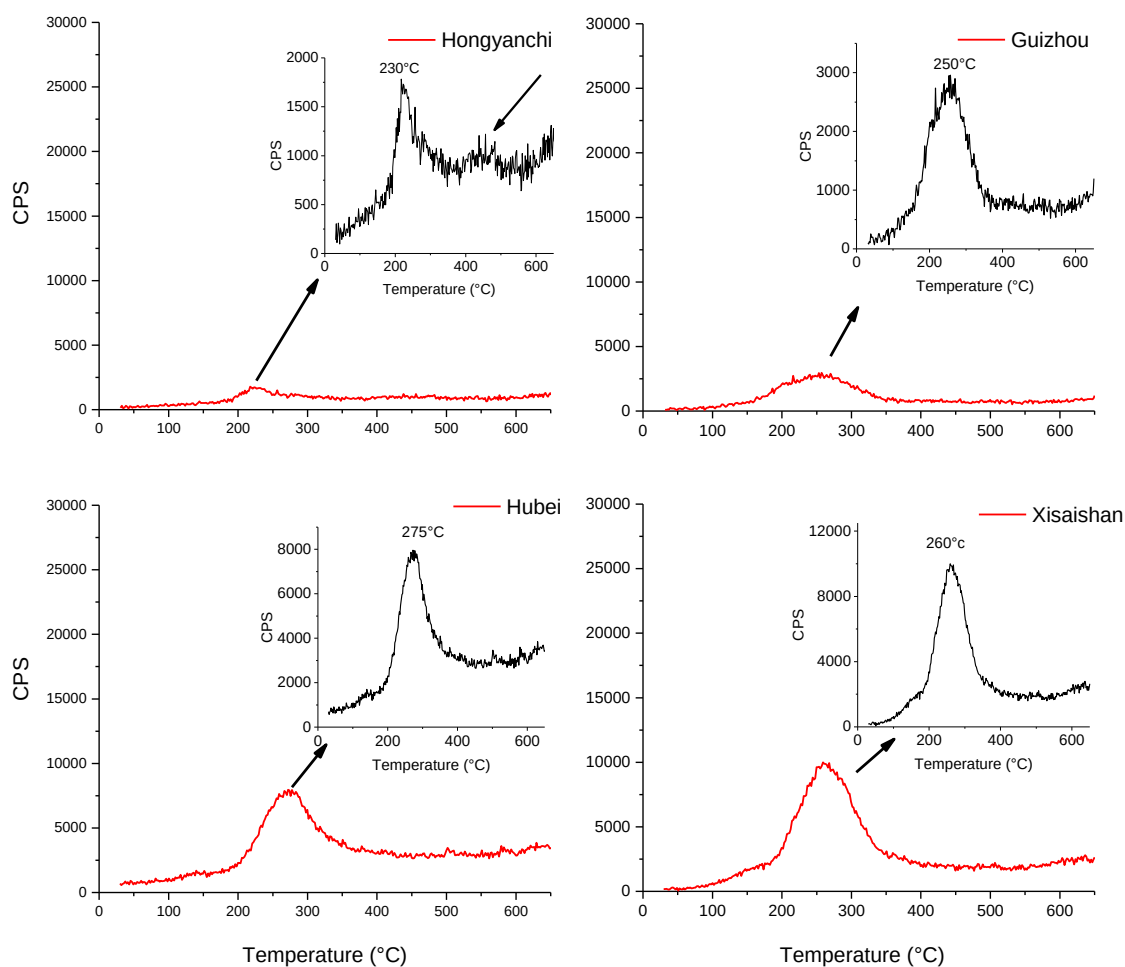


Figure 4.67: TPD spectra of Chinese gypsum samples contain medium Hg concentration.

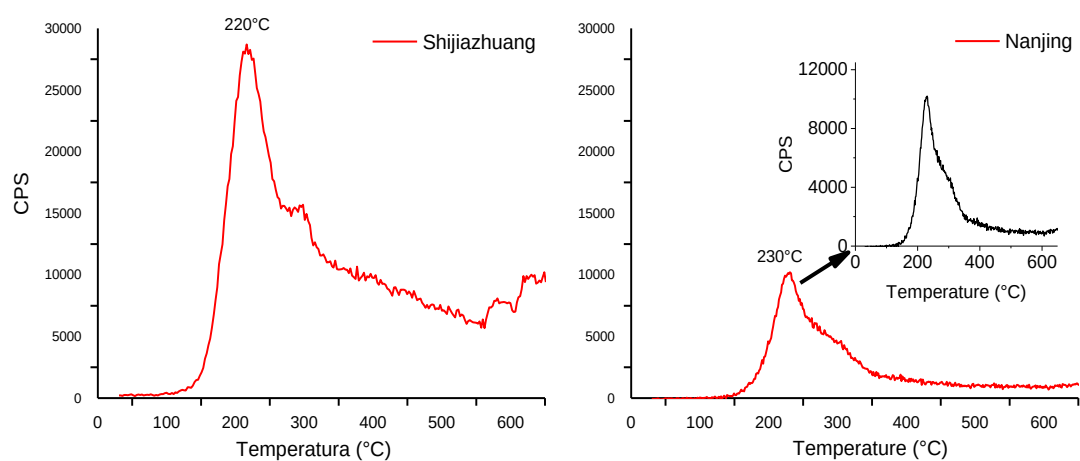


Figure 4.68: TPD spectra of Chinese gypsum samples contain higher Hg concentration.

Samples of Shijiazhuang and Nanjing contain much higher Hg concentration ($> 0.9 \text{ mg kg}^{-1}$ **) relative to other Chinese bulk gypsum (Figure 4.68). TPD spectra are positioned at 220 °C for Shijiazhuang and 230 °C for Nanjing sample. Both samples indicate one additional smaller peak (shoulder) around 300 °C.

Discussion: In general, all gypsum samples reached their maximum below 300°C, except Turpan gypsum. In the samples of Tianjin, Quijing, Turpan, Hongyanchi and Shijiazhuang the intensity of Hg signal in TPD spectra starts to increase above 550 °C. There are two possibilities for this: i) this resembles the influence of background, ii) and/or the rest of the Hg is released from the samples at higher temperatures due to structural changes in the samples or decomposition of the material in which Hg is entrapped. The release of Hg at temperatures higher than 650 °C was confirmed by scan mass spectrum recorded after TPD analysis, between m/z 195 and 205, where the presence of Hg is seen (figure not shown due to the similarities with Figure 4.18). It follows that Hg was still present in all Chinese samples after each TPD measurements was completed. However, the background effect is also present and is higher in some samples than in others.

Since gypsum slurry of Chinese samples has not been separated into a fine and coarse fraction, we cannot directly compare the thermograms of a separated fraction from Šoštanj with the samples from China. Problems regarding bulk samples are average concentration between fine and coarse fraction where some Chinese samples contain very low Hg concentration (compared to the coarse fractions of samples from Šoštanj TPP). Consequently, increase in the background in TPD spectra is observed. However, in samples from Šoštanj TPP, we found similar TPD spectra in samples from the same block no matter the particle size (coarse, bulk and finer fraction from block 4 and 6). TPD spectra differ only in intensities and the peak width that is a consequence of Hg concentration present in the sample. We predict that similar peaks as with bulk samples would occur in the separated fractions of Chinese gypsum samples.

In all Chinese samples, one strong peak around 250 °C appeared which is similar as in the case of gypsum from Šoštanj. We found Hg bound to sulphur in the finest gypsum sample of RECY (see Chapter 4.2.2). Many Chinese authors demonstrated HgS in their gypsum samples by using the TPD method with AAS detection where mercury standards were applied for identification. In our case, HgS standard released above 300 °C with similar peak shape as TPD spectra of actual gypsum samples from block 6. With respect to HgS standard we would not suggest the presence of HgS in our samples. However, additional study using XANES analysis confirmed the presence of HgS in our samples. Therefore, comparison with the standards is not always the case, and sample matrix has a big influence on Hg releasing from the sample. Similar precaution should be applied with Chinese gypsum where TPD spectra of bulk sample show smaller intensities than fine fractions and identification is even more difficult.

4.2.4.3 TPD spectra of finer fractions from Chinese samples

As it has already been mentioned, TPD spectra of gypsum samples from Šoštanj show similar thermograms in each particle size fraction. Therefore, we predict similar peaks with higher intensities and similar peak shapes in the case when Chinese samples would be separated into fine and coarse fractions. In addition to bulk samples, two gypsum slurries were prepared. All gypsum slurry samples should be separated into fine and coarse fraction because bulk samples represent the average concentration and not the concentration of Hg in different size fractions. Unfortunately, there were not enough samples to separate all bulk samples. Moreover, not all samples from Chinese TPPs have been provided.

Nanjing and Jiaaisi fine fractions were prepared from two slurry samples. Nanjing contains the highest Hg concentration (1.7 mg kg^{-1} **) compared with other bulk samples, whereas Jiaaisi represents one of the samples with a lower concentration (0.14 mg kg^{-1} **). In comparison to the fine fractions of block 5 and 6, the concentration of Hg measured by DMA-80 shows a relatively low amount of Hg in fine fraction of Jiaaisi, but Nanjing has a Hg concentration similar as in block 5 and 6 of Šoštanj TPP (Table 4.6). Relatively low Hg concentration in fine Jiaaisi gypsum is consistent with the low concentration of mercury in the bulk samples.

Table 4.6: Concentrations of Hg in gypsum samples, the temperature at which peak attains its maximum and corresponding mass weight for finer fractions from Chinese gypsum that were additionally separated.

Gypsum samples	Concentration (mg kg^{-1})	Peak maximum ($^{\circ}\text{C}$)	Mass (mg)
Nanjing finer fraction from the main block (slurry sample)	10.0 ± 0.2	240	8.9
Nanjing, finer fraction from slurry tank (slurry sample)	11.2 ± 0.3	230	4.6
Jiaaisi, fine fraction of the slurry vice tank (slurry sample)	1.66 ± 0.02	255	5.2

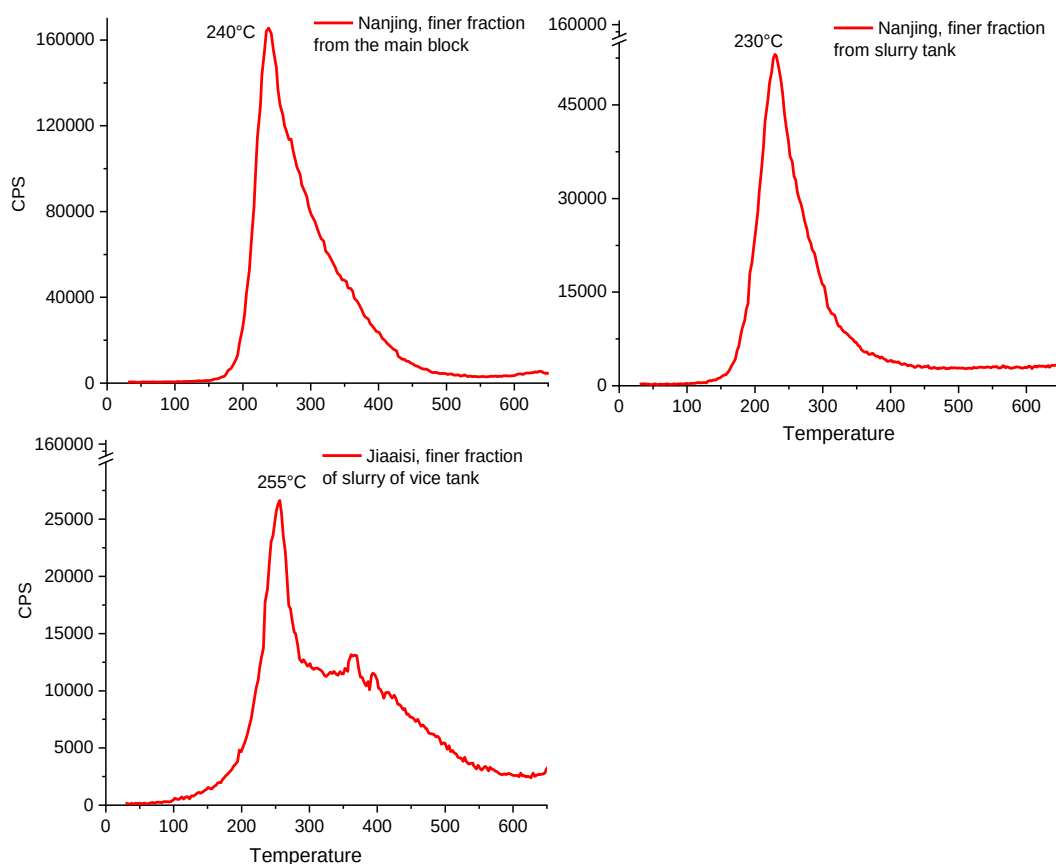


Figure 4.69: TPD spectra of a certain fine fraction from Chinese gypsum samples.

Nanjing fine fractions show a very similar TPD spectrum as samples from block 6 of Šoštanj TPP. The first peak in Jiaaisi sample is similar to the Nanjing samples. TPD spectra of fine gypsum from Jiaaisi also indicate one small peak at temperatures between 300 and 400 °C.

Discussion: In general, all TPD spectra of Chinese samples, except Turpan gypsum, show a peak between 200 and 300 °C, similar to the in Šoštanj TPP. Although the coal, APCDs and conditions during combustion differ among the TPPs, the Hg releasing pattern suggests the presence of similar Hg-compounds in most of the TPPs.

Chinese bulk gypsum samples serve as a good indication of the stability of Hg species in WFGD gypsum using different coal with the different APCDs installation than Šoštanj. Introduction of additives and the presence of different catalysts/metals in the WFGD scrubbers may significantly change the Hg chemistry there. However, their use in these TPP is unknown. Since the Hg peaks found in samples from China do not differ a lot from the Šoštanj samples, it is proposed that similar processes govern the formation and accumulation of Hg in all cases. The intensity of the peak and the peak shape is mainly dependent on sample preparation and the amount of Hg. In the samples with the concentrations much lower than 1 mg kg⁻¹, the presence of other peaks is mostly due to the low concentrations and the influence of background and does not represent the additional Hg peak. However, the presence of additional Hg-species in the samples cannot be excluded in all cases. Separation into fine and coarse fractions is therefore desirable, since the concentration in the fine fraction is much higher compared to bulk samples, and the intensity of TPD spectrum enables easier identification of Hg species present.

Chapter 5

Summary and Conclusions

The main conclusions:

1. Although fine fraction represents a small mass portion of the gypsum, it contains a large proportion of TMEs.
 2. The mass spectrometer has a better limit of detection than CV AAS. It also enables observation of decomposition fragments of volatile species. Identification of mercury compounds based on the decomposition fragment is possible only in the samples containing elevated Hg concentrations.
 3. Sampling and sample preparation influences the Hg TPD spectra. In addition, the sample may change over time and TPD spectra could differ with the thermograms of fresh samples.
 4. The distinction between weakly adsorbed Hg(0) and Hg bound in a matrix is possible.
 5. TPD spectra from different blocks of Šoštanj TPP differ, whereas there are no significant differences among TPD spectra of different Chinese gypsum samples.
 6. Identification of HgCl₂ depends on a) the concentration in the sample, and b) various factors affecting the decomposition of HgCl₂ in the mass spectrometer and thus inability to detect HgCl₂⁺ ion.
 7. Dry prepared mercury standards that are typically used for determination of mercury species present in the actual samples are not suitable due to the sample matrix and interferences during the heating process.
 8. The presence of selected elements (e.g. Fe, Al) has an influence on TPD spectra with changing the shape and the position of the peak. This makes identification of mercury compounds more difficult.
 9. Since QMS can measure low mercury concentration present in the samples (LOQ > 5 ng g⁻¹), TPD-QMS method is very useful for determination of stability of mercury compounds in the solid samples containing small Hg concentration. Unfortunately, identification of Hg-species in those samples is not possible.
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Ad 1) This doctoral dissertation represents the distribution of TMEs in fine and coarse particles of gypsum samples in a lignite-burning power plant Šoštanj, Slovenia. The presence of TMEs in gypsum is primarily related to (1) small size fraction of fly ash not retained by the particle control devices, (2) volatile elements (e.g. Hg, Se and halogens) that are highly accumulated in the WFGD with respect to coal (3) introduction of limestone as an additional source of TMEs (e.g. Mg, Ca, Sr) associated mostly with coarse fraction, (4) and the conditions present in a WFGD scrubber (e.g. oxidation-reduction, temperature, pH, etc).

In general, the concentrations of TMEs in the coarse and fine fractions of gypsum varied, demonstrating the importance of particle size. Small particles retain much higher concentrations of most elements, especially Hg, Se and halogens (dependent on APCDs present in TPP), which are highly enriched relative to their occurrence in coal. Finer fraction represents a small mass portion of the gypsum as a whole (about 10%) but contains a large proportion of TMEs. Removal of fine gypsum fraction in the process of recirculation of gypsum slurry, therefore, represents one of the possible cost-effective remediation technologies. Thus, the appropriate approach based on the removal of the smallest size fraction of gypsum could eliminate most TMEs. The study also shows that the methodologies for sampling and separation of gypsum particle sizes need to be standardized to assure comparability of the results. Moreover, concentrations of TMEs in coal (lignite), limestone, fly ash, and various size fractions of gypsum could provide a good indication of the removal efficiency of APCDs.

Ad 2) The most important part of this dissertation was focused on the identification of Hg-species present in gypsum samples. The use of a mass spectrometer, as a detector for studying desorption/decomposition processes of Hg compounds from WFGD samples, proved to be a good choice. For example, the observation of decomposition fragments of volatile species evolved during decomposition, and the high sensitivity of the mass spectrometer meant it was possible to measure samples with Hg contents $> 5 \text{ ng g}^{-1}$. Therefore, TPD method with the mass spectrometric detection is very useful for recording TPD spectra of samples with low Hg concentrations. The background level of ions with a mass number around m/z 200 governs the limits of detection and not electronic sensitivity. The drawback of using a mass spectrometer is the high background levels as a result of other substances evaporating from the sample along with mercury. By using pure Hg-compounds decomposition fragment and thus decomposition reactions, which occur during elevated temperatures could be investigated. This is more difficult to implement in actual samples due to the presence of interfering substances that are typically present in much higher concentrations than Hg.

Ad 3 and 4) It has to be taken into account that sampling and sample preparation affect TPD spectra. It was observed that modifications in the separation of bulk gypsum, drying and washing of the gypsum samples might show different Hg TPD spectra. Sample perturbation changes the matrix which then influences on mercury transformation. Washing procedure does not have a strong influence in the samples where HgS or other stable Hg-compounds are present. On the other hand, soluble Hg compounds and weakly adsorbed Hg may be removed with this procedure. Moreover, pre-heating has been applied to remove the surplus of humidity, which disturbs ionization, but the obtained spectra differ compared to TPD spectra without heating. Significantly different TPD spectra were observed in the aged samples (after two years of the first measurement) but not with fresh gypsum samples. It follows that samples are changing over time where mercury transformations depend on the sample composition and mercury species present in the sample. We anticipate fewer transformations (e.g. reduction in $\text{Hg}(0)$) in the samples where more stable Hg compounds are present, and mercury is present at higher concentrations. In the aged samples, constant evaporation of $\text{Hg}(0)$ was observed at room temperatures. Also, at least two peaks were obtained in unwashed and not heated samples. Therefore, with QMS we can differ between $\text{Hg}(0)$ that is weakly adsorbed and (strong) matrix-bound Hg. This is very useful for studying Hg stability and transformations in the different environmental solid sample.

Ad 5) In this doctoral dissertation, the results (TPD spectra) for gypsum samples from block 4, 5 and 6 of Šoštanj TPP are provided. Moreover, TPD analysis in Chinese gypsum has also been performed. Chinese samples serve more for comparison with samples from Šoštanj in the view of Hg stability at elevated temperatures since samples were not

separated into finer and coarse fraction as samples from Šoštanj. In this work, we were mainly focused on the identification of Hg species present in the samples from block 6. However, TPD spectra of samples from block 4 and 5 were measured to compare the data. In gypsum samples from block 6, one sharp symmetrical peak was observed in all samples. Peak shape resembles the presence of HgS where the releasing temperature of Hg from gypsum samples at around 260 °C is much lower than the decomposition temperature of the pure HgS mixed with the pure substrate (either SiO₂ or CaSO₄ · 2H₂O). Although HgS is thought to be a volatile compound in some literature data, this was not observed with the QMS. The presence of H₂S and SO₂ peaks that fit with Hg TPD spectra suggest the presence of HgS in the samples of block 6. However, due to the presence of other volatile compounds that have not been identified, the presence of some other Hg species cannot be excluded. The only method which could identify the nearest neighbour of Hg in the sample is XAS which is very promising in characterizing Hg binding to different surfaces. The only problem with analysing gypsum samples with XAS method is relatively low Hg concentration since at least 100 mg kg⁻¹ is a recommended value to get the reliable data. However, after a long analysing time due to low Hg content in the gypsum RECY of block 6, the results obtained with XANES analysis proposed the majority of Hg in the form of Hg-S and only a small part indicates the presence of HgO. Unfortunately, these experiments could not provide information about the second neighbour. This information would be very useful for understanding the much lower temperature of desorption for HgS compared to the mercury standard. It follows that HgS in the form of crystalline decomposes differently than if bonded to the surface of the sample matrix and therefore species on this surface are important. TPD spectra in block 4 and block 6 are very similar, only the amount of Hg is much higher in the samples from block 6. Since we do not have multielemental analysis from samples of block 4, it is hard to compare these samples with gypsum from block 6. However, due to the TPD spectra, which are very similar to those from block 6, Hg-S is proposed as an Hg-species present in the samples from block 4. Similar, Chinese gypsum samples show TPD spectra with one major peak at similar temperatures than in block 4 and 6 of Šoštanj TPP. However, samples from China are mixtures of coarse and fine fractions (bulk sample), and the concentration of Hg are lower. Therefore, thermograms are sometimes under the influence of the background.

Ad 6) Since Hg-Cl species were proposed in the samples of block 5, identification of Hg-Cl species with QMS was one of the aims in the present doctoral dissertation. However, this is not possible with the concentrations that are normally present in the gypsum samples. Regarding HgCl₂, hydrolysis prevented the direct identification of HgCl₂⁺ ions in the mass spectrum that would otherwise have confirmed the presence of HgCl₂ in the WFGD samples. Furthermore, the possibility of hydrolysis was confirmed theoretically. The presence of Hg-Cl species in the samples of block 6 has not been proposed. Considerably lower chlorine concentrations were obtained by k₀-INAA in all gypsum samples from block 6 of Šoštanj TPP (Table A.4) compared with the gypsum from block 5 (Table A.3). As seen from the TPD spectra (Figure 4.38), releasing spectra for block 6 differ among thermograms obtained in block 5 (Figures 4.34 and 4.35). Block 5 shows two or three peaks whereas in block 6 only one peak was found. Variations in elemental concentrations, especially the concentrations of halogens, Hg and Se, are probably dependent on the presence of APCDs such as SCR, as well as conditions during the combustion process and in WFGD scrubber. It follows that the distribution of elements in the by-products is a result of many factors and is not only the consequence of the coal composition since Šoštanj TPP use the same coal in all three blocks (4, 5 and 6). The experiments in the present work also show the effect of elevated concentration of chlorine ions on a change of the thermograms (Figure 4.58). No changes were observed with the addition of a small amount of Cl⁻ ions. TPD spectra in Figures 4.34 and 4.35 indicate at

least two peaks, similar than with experiments containing higher Cl⁻ concentration. Therefore, Hg-Cl species might be present in the gypsum from block 5. Since we were not able to detect HgCl₂ in industrial WFGD gypsum, we can only predict the presence of Hg-Cl species in the sample by observing the stability of Hg-Cl compounds in different matrices and by simulation of the conditions present, e.g. in WFGD scrubber.

Ad 7) Due to the inability to detect HgCl₂ and other volatile species that are directly connected with Hg decomposition/desorption, identification of mercury compounds in the gypsum samples still based on a comparison of TPD spectra with released Hg from mercury standards. When comparing samples from block 6 of Šoštanj TPP, none of the peaks obtained from actual gypsum samples overlaps with the "standards" prepared by dry mixing. Similar is also in the case with other gypsum samples from block 4 and 5. Although TPD spectra of mercury standard released at the same or similar temperature this does not mean that the same Hg-compound is present in the actual sample. Moreover, peaks can overlap and sometimes it is very hard to differentiate between them. To our knowledge, releasing of Hg from the gypsum samples is usually observed between 200 and 300 °C. Although the sample peak fits with the standards, we simply cannot confirm the presence of exact Hg species with certainty. Samples matrix has an important influence on the desorption/decomposition of Hg-species present in any solid sample. In the previous study of Sedlar et al. we noticed that even with the simple mixing of pure Hg-species with a different substrate, the decomposition/desorption of Hg from those "standards" shows different Hg releasing. This means that none of the substrates is inert and interactions between Hg-species and powder substrates exist. The situation becomes more complicated with higher temperatures and reactions that are present at elevated temperatures (when heating) is unknown.

Ad 8) In addition to dry mercury standards, wet-prepared mercury compounds were applied in this study to observe the effect of Fe and Al on TPD spectra. Experimental work was mainly devoted to the study of desorption/decomposition of different Hg-species mixed in a solution of CaSO₄ · 2H₂O, FeOOH and Al(OH)₃. The TPD curves of solid precipitates prepared with CaSO₄ · 2H₂O and FeOOH showed only a single peak similar in the position of the peak maximum and different in peak shape and to the Šoštanj TPP samples of block 6. This suggests the formation of similar (or the same) Hg species in the precipitates after drying of the water solution. Similarities in the peak positions and the peak shapes between the TPD curves of block 6 (Figure 4.38) and those obtained by different experiments with FeOOH (Figures 4.56 and 4.57b) proposed that FeOOH or other Fe species may affect the adsorption/binding of Hg (Hg-species) to these surfaces. It seems that metals such as Fe and its compounds have an influence on TPD spectra, which makes identification of Hg-species even more difficult.

Ad 9) TPD-QMS is a very useful method for determination of stability of mercury compounds in the solid samples, even in the samples containing a low concentration of Hg. However, identification of Hg compounds in actual samples by using mercury standards prepared with pure substrates should be used with the greatest care. This doctoral dissertation indicates that simply a comparison of the TPD spectra is misleading. More comprehensive studies are needed to characterize the Hg compounds formed at the surface of different actual gypsum samples as well as in other solid samples. Further experimental work is needed to confirm the presence of Hg-S, Hg-Cl and other Hg compounds by using mass spectrometry. Using other techniques, such as mass spectrometry with soft ionization, laser ablation to determine the preferable location of Hg in the sample and the presence of other elements in the near vicinity of Hg, as well as using classical extraction methods to study the soluble part of Hg that leached from the sample and represents the most important part in the view of Hg exposure to the environment, are needed for interpretation and better understanding of TPD spectra obtained from different solid samples. Additional

studies with XAS are also recommended to explain the proposed mechanism of Hg-binding to the substrate (only for samples containing high Hg concentration).

Appendix A

A.1 Tables

Table A.1: Elemental content and uncertainty with a coverage factor $k=1$ (mg kg^{-1}) in coal (LIG08), fly ash, bottom ash, limestone, bulk gypsum and process water in block 4 obtained by k_0 -instrumental neutron activation analyses. The multielemental analysis was done for 45 elements where only Hg in coal, fly ash, bottom ash and limestone were measured by CVAAS since the data obtained by k_0 -INAA were below LOD. Results were taken from a study of Stergaršek et al. (Stergaršek et al., 2008).

The concentration of elements and their uncertainties (mg kg^{-1})												
	Lignite (LIG08)		Fly ash		Bottom ash		Limestone		Bulk gypsum		Process water	
Ag	^a 0.11	-	^a 0.32	-	^a 0.21	-	^a 0.02	-	^a 0.1	-	0.102	0.016
Al	^a 7290	-	111000	6000	^a 42100	-	^a 2430	-	7650	280	^a 0.001	-
As	7.27	0.26	35.5	1.3	5.41	0.23	1.32	0.05	7.52	0.27	^a 0.009	-
Au	^a 0.001	-	^a 0.003	-	^a 0.002	-	^a 0.0003	-	^a 0.001	-	^a 0.00001	-
Ba	77.5	2.9	415	17	201	7	19.9	0.9	48.8	2.1	^a 0.009	-
Br	4.75	0.17	1.14	0.09	0.47	0.04	0.29	0.01	18.8	0.7	0.089	0.003
Ca	14200	500	88700	3200	82300	2900	365000	13000	200000	7000	35.4	2.0
Cd	^a 0.87	-	^a 1.69	-	^a 0.91	-	^a 0.33	-	^a 0.85	-	^a 0.005	-
Ce	14.2	0.5	68.5	2.4	28.0	1.0	2.03	0.08	4.61	0.17	0.0002	-
Cl	12.0	-	^a 12.2	-	^a 63.1	-	^a 6.20	-	409	16	24.2	0.9

Co	3.28	0.12	16.6	0.6	6.40	0.22	0.37	0.01	1.04	0.04	^a 0.0001	-
Cr	20.3	0.7	99.5	3.5	41.1	1.5	6.94	0.27	24.3	0.90	^a 0.001	-
Cs	2.31	0.08	12.4	0.4	4.28	0.15	0.34	0.01	1.38	0.05	^a 0.0002	-
Dy	1.08	0.06	6.20	0.24	2.50	0.19	0.35	0.01	0.56	0.02	^a 0.0002	-
Eu	0.29	0.01	1.56	0.06	0.68	0.03	0.06	0.01	0.11	0.01	-	
Fe	14500	500	72700	2600	37300	1300	1060	40	5320	190	^a 0.09	-
Ga	5.32	0.24	28.7	1.3	10.6	0.7	0.45	0.03	2.91	0.12	^a 0.005	-
Hf	0.55	0.02	2.96	0.11	1.18	0.04	0.14	0.01	0.24	0.01	^a 0.0001	-
Hg	^b 0.088	0.009	^b 0.051	0.004	^b 0.025	0.002	^b 0.0054	0.0005	0.95	0.09	^a 0.0001	-
I	^a 3.12	-	^a 5.96	-	^a 12.8	-	^a 0.95	-	7.17	0.45	^a 0.002	-
In	^a 0.02	-	^a 0.07	-	^a 0.08	-	^a 0.005	-	^a 0.01	-	^a 0.0001	-
K	3240	120	16500	600	5970	220	383	15	1920	70	2.62	0.16
La	7.30	0.26	34.4	1.2	14.0	0.5	1.49	0.06	3.18	0.12	^a 0.0002	-
Mg	^a 1960	-	17600	1000	^a 3570	-	^a 1380	-	4450	180	13.4	0.6
Mn	488	17	1960	70	2080	70	37.6	1.4	46.5	1.6	0.0023	0.0002
Mo	8.09	0.33	43.5	1.7	14.8	0.7	^a 0.19	-	2.61	0.23	0.007	0.001
Na	1320	50	7170	250	3070	110	90.9	3.2	431	15	6.86	0.24
Nd	6.17	0.36	32.1	1.5	14.0	0.7	2.30	0.17	3.72	0.35	^a 0.001	-
Rb	24.1	0.9	123	4	41.9	1.5	2.84	0.18	13.6	0.5	^a 0.002	-
S	^a 18900	-	^a 12800	-	^a 38200	-	^a 6030	-	143000	14600	^a 7.5	-
Sb	0.77	0.03	4.16	0.17	1.09	0.04	0.21	0.01	0.75	0.03	0.0002	0.00002
Sc	3.70	0.13	19.7	0.7	8.45	0.30	0.42	0.02	1.57	0.06	^a 0.00001	-
Se	0.61	0.03	0.72	0.03	^a 0.29	-	^a 0.04	-	8.37	0.30	^a 0.0003	-
Sm	1.37	0.05	7.23	0.29	3.06	0.12	0.33	0.01	0.60	0.02	^a 0.0001	-

Sr	98.1	4.3	479	19	280	11	366	13	168	7	0.146	0.015
Ta	0.21	0.01	1.11	0.04	0.43	0.02	0.020	0.002	0.08	0.003	^a 0.0002	-
Tb	0.17	0.01	0.94	0.03	0.40	0.01	0.052	0.002	0.087	0.003	^a 0.0001	-
Th	2.68	0.10	13.1	0.5	5.50	0.19	0.32	0.01	0.99	0.04	^a 0.0001	-
Ti	^a 1090	-	5090	480	^a 4290	-	^a 250	-	282	31	^a 0.2	-
U	5.91	0.21	33.1	1.2	18.4	0.6	4.55	0.16	5.11	0.18	0.0012	0.0001
V	45.3	5.8	185	11	91.0	16.4	13.5	1.4	29.0	1.2	^a 0.002	-
W	0.65	0.05	3.06	0.20	1.20	0.14	0.04	0.01	0.29	0.02	^a 0.002	-
Yb	0.53	0.02	2.94	0.11	1.29	0.05	0.18	0.001	0.33	0.01	^a 0.0001	-
Zn	32.0	1.2	176	6	34.0	1.3	4.74	0.21	30.9	1.1	^a 0.018	0.001
Zr	20.2	2.8	^a 40.8	-	54.9	5.8	^a 5.06	-	^a 9.5	-	0.06	-

^a<LOD; results are given as LOD/2; ^b results obtained by CVAAS (Stergaršek et al., 2008)

Table A.2: Elemental concentration and uncertainty with a coverage factor $k=1$ (mg kg^{-1}) in coal (LIG12) and slurry waters from block 5. The multielemental analysis was completed for 45 elements.

The concentration of elements and their uncertainties						
	Lignite (LIG12)		FGD-W ₁		FGD-W ₂	
Ag	^a 0.12	-	^a 0.003	-	^a 0.003	-
Al	22200	800	^a 3.00	-	^a 2.50	-
As	8.19	0.30	^a 0.03	-	^a 0.04	-
Au	^a 0.0008	-	^a 0.0002	-	^a 0.0001	-
Ba	122	5	^a 0.20	-	^a 0.15	-
Br	6.19	0.23	55.8	2.0	60.3	2.1
Ca	19400	700	519	25	544	25
Cd	^a 0.50	-	^a 0.07	-	^a 0.14	-
Ce	14.5	0.5	^a 0.01	-	^a 0.01	-
Cl	69.9	7.4	962	35	958	34
Co	3.07	0.11	0.082	0.003	0.066	0.003
Cr	20.8	0.7	^a 0.01	-	^a 0.005	-
Cs	3.26	0.11	0.0008	0.0002	0.0011	0.0002
Dy	^a 0.35	-	^a 0.02	-	^a 0.02	-
Eu	0.31	0.01	^a 0.0002	-	^a 0.0002	-
Fe	15600	500	^a 0.55	-	^a 0.40	-
Ga	^a 0.80	-	^a 0.50	-	^a 0.50	-
Hf	0.66	0.02	^a 0.0005	-	^a 0.0001	-
Hg	0.119	0.02	^a 0.02	-	^a 0.02	-
I	^a 5.00	-	24.6	0.9	24.3	0.9

In	/	/	^a 0.001	-	0.002	-
K	2890	110	53.4	8.5	57.1	9.1
La	7.34	0.27	^a 0.002	-	^a 0.002	-
Mg	4160	240	2600	90	2590	90
Mn	600	20	15.3	0.5	14.8	0.5
Mo	11.3	0.5	0.40	0.02	0.41	0.02
Na	1370	50	140	5	149	5
Nd	6.92	0.32	^a 0.02	-	^a 0.02	-
Rb	25.5	0.9	0.12	0.01	0.16	0.01
S	^a 2450	-	3300	478	2980	479
Sb	2.07	0.07	0.0060	0.0003	0.0064	0.0003
Sc	4.74	0.13	^a 0.00004	-	^a 0.00001	-
Se	0.79	0.03	0.23	0.01	0.23	0.01
Sm	1.40	0.05	^a 0.004	-	^a 0.004	-
Sr	103	4	2.20	0.13	2.71	0.13
Ta	0.21	0.01	^a 0.0005	-	^a 0.0005	-
Tb	0.19	0.01	^a 0.0005	-	^a 0.0003	-
Th	2.88	0.10	^a 0.0005	-	^a 0.0005	-
Ti	815	73	^a 14.0	-	^a 13.0	-
U	8.94	0.32	0.13	0.01	0.103	0.004
V	34.2	1.40	0.18	0.02	0.23	0.02
W	0.80	0.08	^a 0.05	-	^a 0.07	-
Yb	0.57	0.02	^a 0.001	-	^a 0.001	-
Zn	49.0	1.70	0.22	0.01	0.08	0.01

Zr	^a 14.5	-	^a 0.35	-	^a 0.25	-
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^a<LOD; results are given as LOD/2.

Table A.3: Elemental concentration and uncertainty with a coverage factor $k=1$ (mg kg^{-1}) for six gypsum samples of block 5 (TEŠ5-FF, TEŠ5-CF, TEŠ5-FF1, TEŠ5-CF1, TEŠ5-FF2 and TEŠ5-CF2) obtained by k_0 -instrumental neutron activation analyses. The multielemental analysis was done for 45 elements.

Concentration of elements and their uncertainties												
	TEŠ5-CF		TEŠ5-FF		TEŠ5-CF1		TEŠ5-FF1		TEŠ5-CF2		TEŠ5-FF2	
Ag	^a 0.07	-	^a 0.21	-	^a 0.04	-	^a 0.27	-	^a 0.04	-	^a 0.33	-
Al	1000	40	52100	1800	544	20	42200	1500	650	23	67500	2400
As	0.93	0.04	39.4	1.4	0.74	0.03	42.5	1.5	0.60	0.02	52.6	1.9
Au	^a 0.0003	-	^a 0.001	-	^a 0.0005	-	0.0056	0.0006	^a 0.0003	-	0.0073	0.0007
Ba	11.0	0.9	262	11	^a 2.28	-	177	10	^a 1.86	-	294	16
Br	8.01	0.28	35.1	1.2	14.6	0.5	249	9	13.2	0.5	408	14
Ca	223000	8000	144000	5000	232000	8200	118000	4000	232000	8000	43100	1630
Cd	^a 0.20	-	9.58	0.51	^a 0.60	-	8.27	1.44	^a 0.39	-	11.7	1.5
Ce	0.95	0.05	40.6	1.5	0.77	0.04	27.1	1.0	0.88	0.05	40.1	1.5
Cl	147	6	568	22	266	10	4150	150	254	10	7760	280
Co	0.16	0.01	8.39	0.30	0.13	0.01	7.07	0.25	0.13	0.01	10.7	0.4
Cr	2.58	0.15	178	6	2.14	0.10	149	5	2.24	0.19	227	8
Cs	0.18	0.01	10.4	0.4	0.108	0.004	8.51	0.30	0.13	0.01	13.5	0.5
Dy	0.15	0.01	5.82	0.21	0.125	0.006	2.35	0.10	0.13	0.01	3.32	0.17
Eu	^a 0.005	-	1.20	0.05	^a 0.03	-	0.63	0.03	^a 0.03	-	0.91	0.06
Fe	726	26	33700	1200	482	17	34100	1200	452	16	46800	1700
Ga	^a 0.33	-	25.1	1.1	^a 0.17	-	^a 3.26	-	^a 0.15	-	28.6	4.2

Hf	0.043	0.003	1.50	0.06	0.036	0.003	1.44	0.05	0.050	0.002	2.33	0.08
Hg	0.22	0.01	10.6	0.4	0.12	0.02	8.62	0.31	0.15	0.01	11.9	0.4
I	3.14	0.13	22.5	0.9	1.40	0.09	42.5	2.0	1.22	0.09	112	4
In	^a 0.002	-	0.09	0.01	^a 0.005	-	^a 0.03	-	^a 0.005	-	0.13	0.02
K	300	20	14500	500	179	9	10500	400	176	9	17600	600
La	0.75	0.03	29.1	1.1	0.61	0.02	15.2	0.6	0.66	0.02	21.8	0.9
Mg	1920	90	36500	1400	1900	85	36300	1300	1370	70	50900	1900
Mn	7.68	0.27	207	7	7.12	0.25	237	8	6.21	0.22	322	11
Mo	^a 0.26	-	3.87	1.17	^a 0.50	-	26.5	1.6	^a 0.36	-	43.2	2.4
Na	58.9	2.1	1570	60	96.5	3.4	3500	100	109	4	4900	200
Nd	^a 0.27	-	25.2	1.1	1.18	0.15	10.6	0.8	^a 0.36	-	15.7	1.4
Rb	1.73	0.12	97.9	3.6	1.46	0.14	77.8	3.7	1.37	0.09	126	5
S	-	-	-	-	188000	11000	110000	13000	178000	11000	86600	11900
Sb	0.120	0.005	4.68	0.17	0.097	0.004	5.68	0.22	0.108	0.005	8.69	0.31
Sc	0.25	0.01	11.1	0.4	0.146	0.005	9.33	0.33	0.20	0.01	14.6	0.5
Se	2.35	0.09	87.0	3.1	1.31	0.05	54.7	1.9	1.08	0.05	72.7	2.6
Sm	0.15	0.01	5.90	0.22	0.131	0.006	2.76	0.18	0.14	0.01	4.55	0.38
Sr	180	7	271	16	235	9	224	19	204	7	196	14
Ta	^a 0.01	-	0.50	0.02	^a 0.01	-	0.48	0.02	^a 0.005	-	0.74	0.03
Tb	0.021	0.002	0.88	0.03	0.022	0.001	0.41	0.01	0.020	0.001	0.57	0.02
Th	0.16	0.01	6.43	0.23	0.124	0.005	6.49	0.23	0.11	0.01	9.36	0.33
Ti	^a 53.1	-	1910	130	^a 50.3	-	1630	110	^a 48.5	-	2630	150
U	1.03	0.04	46.9	1.7	0.81	0.03	39.2	1.4	0.58	0.02	65.9	2.4
V	4.65	0.20	227	8	3.16	0.15	199	7	3.27	0.16	352	13

W	^a 0.06	-	1.65	0.22	^a 0.05	-	^a 0.80	-	^a 0.05	-	^a 1.04	-
Yb	0.074	0.004	3.19	0.12	0.073	0.004	1.71	0.07	0.073	0.003	2.46	0.10
Zn	3.69	0.26	227	8	2.88	0.20	183	6	2.65	0.12	241	9
Zr	^a 5.60	-	^a 34.9	-	^a 5.01	-	^a 31.0	-	^a 4.41	-	120	11

^a<LOD; results are given as LOD/2.

Table A.4: Elemental concentration and uncertainty with a coverage factor $k=1$ (mg kg^{-1}) in gypsum samples (ORIG-FF, ORIG-CF, DISP-FF, DISP-CF, RECY) obtained by k_0 -instrumental neutron activation analyses. The multielemental analysis was done for 43 elements.

The concentration of elements and their uncertainties										
	DISP-CF (mg kg^{-1})		DIPS-FF (mg kg^{-1})		RECY (mg kg^{-1})		ORIG-CF (mg kg^{-1})		ORIG-FF (mg kg^{-1})	
Al	522	19	36100	1300	52900	1900	622	22	21000	700
As	0.45	0.02	24.4	0.9	44.7	1.6	0.55	0.02	15.0	0.5
Ba	^a	3.2	188	9	361	14	^a	3.84	118	5
Br	0.87	0.03	21.5	0.8	2.98	0.11	16.6	0.6	14.7	0.5
Ca	232000	8000	144000	5000	98000	3500	228000	8000	176000	6000
Cd	^a	0.12	5.89	0.25	3.52	0.24	^a	0.24	2.17	0.16
Ce	0.95	0.04	24.2	0.9	43.6	1.6	0.93	0.04	15.6	0.6
Cl	38.2	1.8	202	12	41.7	4.5	247	10	214	8
Co	0.133	0.005	8.28	0.29	7.59	0.27	0.13	0.01	3.30	0.12
Cr	1.82	0.09	98.7	3.5	153	5	2.23	0.10	59.9	2.1
Cs	0.113	0.004	8.38	0.29	12.6	0.4	0.15	0.01	5.11	0.18
Dy	0.17	0.01	2.72	0.11	4.15	0.15	0.16	0.01	1.68	0.06
Eu	0.034	0.002	0.60	0.03	0.97	0.04	0.03	0.00	0.35	0.02
Fe	393	14	22200	800	35200	1200	474	17	13600	500
Ga	^a	0.14	8.37	0.47	16.4	0.7	^a	0.31	6.07	0.26
Hf	0.026	0.002	1.17	0.04	1.97	0.07	0.03	0.00	0.71	0.03
Hg	0.22	0.01	12.5	0.5	20.6	0.7	0.31	0.02	8.94	0.32
I	0.44	0.04	15.5	0.8	18.6	0.8	1.17	0.11	10.4	0.4
In	^a	0.001	^a	0.02	0.06	0.01	^a	0.01	0.023	0.002
K	155	6	10100	400	15800	600	246	10	6200	200

La	0.65	0.02	15.0	0.7	25.1	1.1	0.69	0.03	9.33	0.38
Mg	1040	50	39400	1400	53300	1900	1520	60	23700	900
Mn	3.61	0.13	203	7	129	5	7.09	0.25	73.7	2.6
Mo	1.38	0.10	44.0	2.0	78.2	3.3	1.57	0.08	29.3	1.2
Na	24.6	0.9	978	34	1180	40	129	5	594	21
Nd	^a	0.61	12.1	0.7	21.9	1.0	0.68	0.09	8.08	0.36
Rb	1.56	0.12	74.3	2.7	111	4	1.91	0.12	44.6	1.6
S	180000	11000	64700	10600	^a	5077	183000	9000	131000	12000
Sb	0.091	0.004	4.71	0.17	8.28	0.29	0.14	0.01	2.84	0.10
Sc	0.16	0.01	8.20	0.29	12.5	0.4	0.19	0.01	5.01	0.18
Se	1.21	0.05	52.0	1.9	83.8	2.9	1.57	0.06	34.4	1.2
Sm	0.13	0.01	3.15	0.12	5.06	0.19	0.14	0.01	1.68	0.11
Sr	211	8	195	10	191	8	208	8	177	8
Ta	^a	0.006	0.49	0.02	0.64	0.02	^a	0.013	0.22	0.01
Tb	0.021	0.001	0.38	0.01	0.62	0.02	0.02	0.00	0.24	0.01
Th	0.10	0.01	4.86	0.17	8.04	0.28	0.11	0.00	2.96	0.10
Ti	^a	92	1800	80	2700	100	^a	78	1040	50
U	0.97	0.04	57.2	2.0	82.1	2.9	0.99	0.04	24.8	0.9
V	3.42	0.15	212	8	317	11	4.05	0.17	126	5
W	^a	0.03	0.98	0.07	1.59	0.10	^a	0.03	0.71	0.04
Yb	0.08	0.00	1.71	0.06	2.79	0.10	0.086	0.003	1.06	0.04
Zn	2.02	0.11	209	7	148	5	2.11	0.11	62.4	2.2
Zr	^a	8.5	89.0	7.0	168	9	^a	10.1	43.9	3.4

^a<LOD; results are given as LOD/2.

Table A.5: The data for positive and negative correlations between Hg and 34 other elements are provided. Only the elements of which the concentrations are measured in all five gypsum fractions and the data are above the limit of detection are used for calculation.

Element	Pearson correlation (r value)	Statistical significance (p value)
Al	0.996	**0.0004
As	0.994	**0.0005
Br	-0.050	0.9365
Ca	-0.998	0.0001
Ce	0.996	**0.0003
Cl	-0.272	0.6584
Co	0.915	*0.0294
Cr	0.998	**0.0001
Cs	0.997	**0.0002
Dy	0.997	**0.0001
Eu	0.996	**0.0003
Fe	0.998	**0.0001
Hf	0.997	**0.0002
I	0.978	**0.004
K	0.998	**0.0001
La	0.997	**0.0002
Mg	0.992	**0.0009
Mn	0.791	0.1114
Mo	0.997	**0.0002
Na	0.978	**0.0038
Nd	0.995	**0.0047
Rb	0.997	**0.0002
S	-0.962	0.0378
Sb	0.995	**0.0004
Sc	0.998	**0.0001
Se	0.999	**0
Sm	0.993	**0.0008
Sr	-0.622	0.2623
Tb	0.998	**0.0001
Th	0.998	**0.0001
U	0.984	**0.0025
V	0.997	**0.0002
Yb	0.998	**0.0001
Zn	0.826	0.085

** Correlation is significant at the 0.01 level. * Correlation is significant at the 0.05 level.

Table A.6 Releasing temperatures of various mercury compounds mixed with dry $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, in a saturated solution of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and a saturated solution of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ with added FeOOH .

Mercury compounds	Dry $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (°C)	Saturated solution of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (°C)	Saturated solution of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O} + \text{FeOOH}$ (°C)
HgCl_2	154	236	228
Hg_2Cl_2	150	230	257
$\text{HgO}(\text{red, R})$	270-345; 580	-	-
$\text{HgO}(\text{yellow, Y})$	307; 485	240	242
HgSO_4	676	250	216
Hg_2SO_4	315; 564	256	258
HgS	368	-	-

Table A.7: Table represents the concentrations of coal, limestone, fly ash, slag, sludge and mixture of sludge + slag for various Chinese samples and the main working properties of each TPP. All samples were measured with DMA-80.

					Concentration (mg kg ⁻¹)					
TPP	Capacity (MW)	APCD	Type of FGD	Absorber	Coal	Limestone	Fly ash	Slag	Sludge	Sludge + coal
Hubei	300	SCR+ESP+WFGD	Forced oxidation	Limestone	/	0.628	0.323	/	/	/
Guizhou	600	SCR+ESP+WFGD	Forced oxidation	Limestone	0.231	0.196	/	/	/	/
Jiaaisi	300	SCR+ESP+WFGD+WESP	Forced oxidation	Limestone	0.481	0.048	0.916	0.003	0.290	0.216
Hongyanchi	200	SCR+ESP+WFGD	Forced oxidation	Limestone	/	0.018	/	/	/	/
Shijiazhuang	300	SCR+ESP+WFGD	Forced oxidation	Limestone	/	/	0.107	/	/	/
Turpan	135	SCR+ESP+WFGD	Forced oxidation	Limestone	/	/	0.053	/	/	/
Nanjing	660	SCR+ESP+WFGD+WESP	Forced oxidation	Limestone	0.170	/	0.207	/	/	/
Quijing	300	SCR+ESP+WFGD	Forced oxidation	Limestone	/	0.216	/	/	/	/
Tianjin	300	SCR+ESP+WFGD	Forced oxidation	Limestone	/	0.015	0.395	/	/	/
Xisaishan	330	SCR+ESP+WFGD	Forced oxidation	Limestone	/	/	/	/	/	/
Šoštanj TPP (bulk, block 4)	275	ESP+WFGD	Forced oxidation	Limestone	0.09	0.005	0.05	0.03	/	/

Table A.8: Elemental concentration and uncertainty with a coverage factor $k=1$ (mg kg^{-1}) ten gypsum samples from Chinese obtained by k_0 -instrumental neutron activation analyses. The multielemental analysis was done for 45 elements.

The concentration of elements and their uncertainties										
	Tianjin (mg kg^{-1})		Jiasisi (mg kg^{-1})		Quijing (mg kg^{-1})		Turpan (mg kg^{-1})		Hongyanchi (mg kg^{-1})	
Ag	^a 0.07	-	^a 0.07	-	^a 0.06	-	^a 0.09	-	^a 0.11	-
Al	2670	90	2730	100	1820	60	3410	120	6160	220
As	0.74	0.03	3.37	0.12	0.74	0.03	4.03	0.14	4.01	0.14
Au	^a 0.0005	-	^a 0.0005	-	^a 0.0003	-	^a 0.0004	-	^a 0.001	-
Ba	22.7	1.0	13.4	0.8	22.7	1.0	45.0	1.7	52.3	2.0
Br	2.92	0.11	17.6	0.6	8.71	0.31	2.57	0.09	7.22	0.25
Ca	225000	7900	229000	8100	256000	9000	219000	8000	225000	8000
Cd	^a 0.55	-	^a 0.13	-	^a 0.24	-	^a 0.49	-	^a 0.27	-
Ce	3.41	0.12	3.35	0.12	1.43	0.06	2.34	0.09	4.66	0.17
Cl	331	12	2120	80	7900	280	1690	60	2520	90
Co	0.49	0.02	0.56	0.02	0.40	0.02	1.38	0.05	1.47	0.06
Cr	2.47	0.11	19.8	0.7	24.5	0.9	13.8	0.5	6.11	0.23
Cs	0.227	0.008	0.156	0.007	0.17	0.01	0.12	0.01	0.43	0.02
Dy	0.25	0.01	0.33	0.02	^a 0.12	-	0.46	0.04-	0.54	0.03-
Eu	0.052	0.006	0.09	0.01	0.05	0.01	0.10	0.01	0.14	0.01
Fe	1250	50	1650	60	1140	40	2830	100	2970	100
Ga	0.95	0.07	0.63	0.06	^a 0.32	-	1.09	0.09	2.85	0.13
Hf	0.216	0.009	0.24	0.01	0.102	0.004	0.158	0.007	0.38	0.01
Hg	^a 0.027	-	0.14	0.02	0.12	0.02	0.16	0.03	0.20	0.03
I	1.78	0.12	2.36	0.19	^a 1.03	-	4.27	0.60	^a 0.7	-

In	^a 0.001	-	a0.07	-	^a 0.02	-	^a 0.02	-	^a 0.07	-
K	765	30	213	10	436	19	682	28	951	36
La	1.79	0.06	1.89	0.07	0.95	0.04	1.73	0.06	2.29	0.08
Mg	3760	150	1590	70	2120	90	3206	128	2380	110
Mn	18.7	0.7	61.4	2.2	23.9	0.8	307	11	82.3	2.9
Mo	^a 0.24	-	a0.3	-	a0.38	-	1.09	0.09	1.02	0.08
Na	327	12	136	5	630	22	868	30	880	31
Nd	^a 0.44	-	a0.4	-	^a 0.36	-	1.59	0.15	^a 0.43	-
Rb	2.63	0.14	1.43	0.19	2.39	0.16	2.37	0.18	4.75	0.22
S	178000	10000	173000	10500	130000	8000	138000	10000	166000	12000
Sb	0.054	0.003	2.64	0.09	0.13	0.01	0.23	0.01	0.26	0.01
Sc	0.53	0.02	0.54	0.02	0.34	0.01	0.98	0.03	1.58	0.06
Se	^a 0.13	-	0.47	0.04	0.72	0.04	3.57	0.13	2.22	0.09
Sm	0.28	0.01	0.31	0.01	0.19	0.01	0.41	0.01	0.53	0.02
Sr	153	6	112	4	1500	50	156	6	153	6
Ta	0.041	0.003	0.03	0.003	^a 0.007	-	0.033	0.003	0.041	0.002
Tb	0.034	0.001	0.046	0.002	0.032	0.002	0.097	0.004	0.078	0.003
Th	0.64	0.02	0.66	0.02	0.22	0.01	0.38	0.01	0.73	0.03
Ti	161	14	^a 55	-	^a 29	-	223	20	263	19
U	0.32	0.02	0.66	0.02	1.17	0.04	0.65	0.02	0.52	0.02
V	3.83	0.17	6.57	0.27	3.74	0.19	11.4	0.5	13.9	0.5
W	^a 0.05	-	^a 0.06	-	^a 0.05	-	a0.1	-	a0.09	-
Yb	0.128	0.005	0.18	0.01	0.14	0.01			0.35	0.01
Zn	7.31	0.32	19.6	0.7	6.30	0.32			16.7	0.7

Zr	^a 6.35	-	^a 6.9	-	^a 6	-			^a 11.7	-
	Guizhou (mg kg⁻¹)		Hubei (mg kg⁻¹)		Xisaishan (mg kg⁻¹)		Shijiazhuang (mg kg⁻¹)		Nanjing (mg kg⁻¹)	
Ag	^a 0.04	-	^a 0.06	-	^a 0.07	-	^a 0.08	-	^a 0.08	-
Al	1110	40	1360	50	2750	100	3200	110	4050	140
As	0.79	0.03	1.58	0.06	3.58	0.13	0.62	0.04	3.75	0.13
Au	^a 0.0001	-	^a 0.0002	-	^a 0.0004	-	^a 0.0006	-	0.0021	0.0001
Ba	5.67	0.50	28.2	1.3	43.2	1.6	16.2	1.1	22.6	1.1
Br	7.79	0.27	61.7	2.2	17.1	0.6	137	5	38.1	1.3
Ca	232000	8000	232000	8000	226000	8000	231000	8000	223000	8000
Cd	^a 0.28	-	^a 0.27	-	3.12	0.11	^a 0.66	-	^a 0.42	-
Ce	1.92	0.07	2.22	0.09	1360	50	3.72	0.14	4.74	0.17
Cl	233	9	2940	110	0.62	0.02	3240	110	4040	140
Co	0.55	0.02	0.34	0.02	11.5	0.4	0.65	0.02	0.72	0.03
Cr	43.1	1.5	39.9	1.5	0.24	0.01	3.68	0.15	8.23	0.30
Cs	0.126	0.008	0.14	0.01	0.24	0.01-	0.33	0.01	0.52	0.02
Dy	0.16	0.01-	0.23	0.01-	0.28	0.01	^a 0.07	-	0.39	0.03
Eu	0.04	0.01	0.053	0.003	0.05	0.01	0.06	0.01	0.07	0.01
Fe	1290	50	1330	50	1320	50	1650	60	1400	50
Ga	0.50	0.04	0.84	0.09	1.40	0.08	^a 0.71	-	2.16	0.11
Hf	0.115	0.005	0.091	0.004	0.21	0.01	0.22	0.01	0.35	0.01
Hg	0.50	0.03	0.74	0.04	0.88	0.04	1.60	0.06	1.70	0.07
I	4.56	0.22	7.08	0.29	4.21	0.02	8.84	0.42	2.97	0.38
In	^a 0.004	-	^a 0.003	-	^a 0.002	-	^a 0.015	-	^a 0.016	-
K	433	18	301	13	458	19	1470	60	672	26

La	1.00	0.04	1.27	0.05	1.67	0.06	1.95	0.07	2.64	0.09
Mg	3050	120	1710	70	487	37	13300	500	1080	70
Mn	29.4	1.0	19.0	0.7	34.1	1.2	33.7	1.2	176	6
Mo	^a 0.2	-	0.89	0.07	1.49	0.10	^a 0.36	-	^a 0.40	-
Na	133	5	90.7	3.2	87.7	3.1	1070	40	182	6
Nd	^a 0.36	-	^a 0.46	-	1.34	0.17	^a 0.43	-	2.41	0.23
Rb	1.56	0.12	1.70	0.14	2.31	0.12	4.44	0.31	4.11	0.18
S	153000	9000	193000	11000	176000	11000	141000	9000	177000	12000
Sb	0.032	0.001	0.62	0.03	0.31	0.01	0.051	0.004	0.42	0.02
Sc	0.32	0.01	0.32	0.01	0.55	0.02	0.59	0.02	0.73	0.03
Se	5.40	0.19	9.64	0.34	8.72	0.31	8.65	0.32	6.86	0.24
Sm	0.19	0.01	0.22	0.01	0.28	0.01	0.32	0.01	0.39	0.01
Sr	389	14	196	7	217	8	105	4	149	6
Ta	0.035	0.002	^a 0.08	-	0.044	0.002	0.049	0.003	0.059	0.003
Tb	0.024	0.001	0.032	0.002	0.037	0.001	0.034	0.002	0.055	0.002
Th	0.21	0.01	0.39	0.01	0.64	0.02	0.77	0.03	1.01	0.04
Ti	205	17	^a 29	-	^a 54	-	171	22	223	20
U	0.25	0.1	0.51	0.02	0.96	0.04	0.45	0.02	0.81	0.03
V	3.81	0.16	6.93	0.27	6.70	0.27	4.26	0.19	7.12	0.30
W	^a 0.04	-	0.18	0.02	0.20	0.01	^a 0.21	-	0.27	0.04
Yb	0.075	0.003	0.12	0.01	0.13	0.01	0.14	0.01	0.21	0.01
Zn	4.80	0.20	7.69	0.32	22.5	0.9	4.33	0.25	15.1	0.7
Zr	^a 2.7	-	^a 2.7	-	^a 5.9	-	^a 8.2	-	^a 8.2	-

^a<LOD; results are given as LOD/2.

References

- Abad-Valle, P., Lopez-Anton, M. A., Diaz-Somoano, M., & Martinez-Tarazona, M. R. (2011). The role of unburned carbon concentrates from fly ashes in the oxidation and retention of mercury. *Chemical Engineering Journal*, 174(1), 86–92. <https://doi.org/https://doi.org/10.1016/j.cej.2011.08.053>
- Ackermann, F. (1980). A procedure for correcting the grain size effect in heavy metal analyses of estuarine and coastal sediments. *Environmental Technology Letters*, 1(11), 518–527. <https://doi.org/10.1080/09593338009384008>
- Acuña-Caro, C., Brechtel, K., Scheffknecht, G., & Braß, M. (2009). The effect of chlorine and oxygen concentrations on the removal of mercury at an FGD-batch reactor. *Fuel*, 88(12), 2489–2494. <https://doi.org/http://dx.doi.org/10.1016/j.fuel.2008.11.028>
- Akiho, H., Nunokawa, M., & Shiras, H. (2003). The behaviour of gaseous mercury in a wet scrubber. In *Proceedings of the IV International Air Quality Conference*. , Mariott Crystal Gateway Arlington, VA, USA.
- Al-Abed, S. R., Jegadeesan, G., Scheckel, K. G., & Tolaymat, T. (2008). Speciation, Characterization, and Mobility of As, Se, and Hg in Flue Gas Desulphurization Residues. *Environmental Science & Technology*, 42(5), 1693–1698. <https://doi.org/10.1021/es702479n>
- Alp, E. E., Mini, S. M., & Ramanathan, M. (1990). X-ray absorption spectroscopy: EXAFS and XANES - A versatile tool to study the atomic and electronic structure of materials. Retrieved from https://inis.iaea.org/search/search.aspx?orig_q=RN:22075463
- Álvarez-Ayuso, E., & Querol, X. (2007). Stabilization of FGD gypsum for its disposal in landfills using amorphous aluminium oxide as a fluoride retention additive. *Chemosphere*, 69(2), 295–302. <https://doi.org/http://dx.doi.org/10.1016/j.chemosphere.2007.03.062>
- Álvarez-Ayuso, E., Querol, X., & Tomás, A. (2006). Environmental impact of a coal combustion-desulphurisation plant: Abatement capacity of desulphurisation process and environmental characterisation of combustion by-products. *Chemosphere*, 65(11), 2009–2017. <https://doi.org/http://dx.doi.org/10.1016/j.chemosphere.2006.06.070>
- American Coal Ash Association. (2009). *Coal Combustion Product Production and Use Survey Report 10/5/2009*.
- Amirbahman, A., Reid, A. L., Haines, T. A., Kahl, J. S., & Arnold, C. (2002). Association of Methylmercury with Dissolved Humic Acids. *Environmental Science & Technology*,

- 36(4), 690–695. <https://doi.org/10.1021/es011044q>
- Amos, H. M., Jacob, D. J., Kocman, D., Horowitz, H. M., Zhang, Y., Dutkiewicz, S., ... Sunderland, E. M. (2014). Global Biogeochemical Implications of Mercury Discharges from Rivers and Sediment Burial. *Environmental Science & Technology*, 48(16), 9514–9522. <https://doi.org/10.1021/es502134t>
- Ariya, P. A., Amyot, M., Dastoor, A., Deeds, D., Feinberg, A., Kos, G., ... Toyota, K. (2015). Mercury Physicochemical and Biogeochemical Transformation in the Atmosphere and at Atmospheric Interfaces: A Review and Future Directions. *Chemical Reviews*, 115(10), 3760–3802. <https://doi.org/10.1021/cr500667e>
- Ariya, P. A., Khalizov, A., & Gidas, A. (2002). Reactions of Gaseous Mercury with Atomic and Molecular Halogens: Kinetics, Product Studies, and Atmospheric Implications. *The Journal of Physical Chemistry A*, 106(32), 7310–7320. <https://doi.org/10.1021/jp020719o>
- Azzaria, L. M., & Aftabi, A. (1991). Stepwise thermal analysis technique for estimating mercury phases in soils and sediments. *Water Air & Soil Pollution*, 56(1), 203–217. <https://doi.org/10.1007/BF00342272>
- Babko, S. V. ., Monttgomery, J. L. ., Battleson, D. M. ., Whitworth, C. G. ., Sears, J. ., Summer, J. ., & Gingery, D. (2001). Mercury speciation analysis by gas chromatography/electron impact/mass spectrometry. In *Waste Management Conference*. Tucson, AZ, USA.
- Bacon, J. R., & Davidson, C. M. (2008). Is there a future for sequential chemical extraction? *The Royal Society of Chemistry*, 133, 25–46. <https://doi.org/10.1039/b711896a>
- Baláz, P., & Godočíková, E. (2001). Thermal Reduction of Mechanically Activated Cinnabar (HgS) and Stibnite (Sb₂S₃). *Journal of Thermal Analysis and Calorimetry*, 65(1), 51–57. <https://doi.org/10.1023/A:1011564232088>
- Balek, V., & Subrt, J. (1995). Thermal behaviour of iron(III) oxide hydroxides. *Pure and Applied Chemistry*. <https://doi.org/10.1351/pac199567111839>
- Bank, M. S. (Ed.). (2012). *Mercury in environment. Pattern and process*. University of California Press.
- Barcelos, G. R. M., Grotto, D., de Marco, K. C., Valentini, J., Lengert, A. van H., Oliveira, A. Á. S. de, ... Barbosa, F. (2013). Polymorphisms in glutathione-related genes modify mercury concentrations and antioxidant status in subjects environmentally exposed to methylmercury. *Science of The Total Environment*, 463–464(Supplement C), 319–325. <https://doi.org/https://doi.org/10.1016/j.scitotenv.2013.06.029>
- Beatty, W. L., Schroeder, K., & Beatty, C. L. K. (2012). Mineralogical Associations of Mercury in FGD Products. *Energy & Fuels*, 26(6), 3399–3406. <https://doi.org/10.1021/ef300033u>
- Benson, S. A., Laumb, J. D., Crocker, C. R., & Pavlish, J. H. (2005). SCR catalyst performance in flue gases derived from subbituminous and lignite coals. *Fuel Processing Technology*, 86(5), 577–613.

- <https://doi.org/http://dx.doi.org/10.1016/j.fuproc.2004.07.004>
- Bhangare, R. C., Ajmal, P. Y., Sahu, S. K., Pandit, G. G., & Puranik, V. D. (2011). Distribution of trace elements in coal and combustion residues from five thermal power plants in India. *International Journal of Coal Geology*, 86(4), 349–356. <https://doi.org/10.1016/j.coal.2011.03.008>
- Bhardwaj, R., Chen, X., & Vidic, R. D. (2009). Impact of Fly Ash Composition on Mercury Speciation in Simulated Flue Gas. *Journal of the Air & Waste Management Association*, 59(11), 1331–1338. <https://doi.org/10.3155/1047-3289.59.11.1331>
- Biester, H. (1994). *Möglichkeiten der Anwendung eines temperaturgesteuerten Pyrolyseverfahrens zur Bestimmung der Bindungsform des Quecksilbers in Böden und Sedimenten*.
- Biester, H., Gosar, M., & Müller, G. (1999). Mercury speciation in tailings of the Idrija mercury mine. *Journal of Geochemical Exploration*, 65(3), 195–204. [https://doi.org/http://dx.doi.org/10.1016/S0375-6742\(99\)00027-8](https://doi.org/http://dx.doi.org/10.1016/S0375-6742(99)00027-8)
- Biester, H., Müller, G., & Schöler, H. F. (2002). Binding and mobility of mercury in soils contaminated by emissions from chlor-alkali plants. *Science of The Total Environment*, 284(1), 191–203. [https://doi.org/http://dx.doi.org/10.1016/S0048-9697\(01\)00885-3](https://doi.org/http://dx.doi.org/10.1016/S0048-9697(01)00885-3)
- Biester, H., & Scholz, C. (1997). Determination of Mercury Binding Forms in Contaminated Soils: Mercury Pyrolysis versus Sequential Extractions. *Environmental Science & Technology*, 31(1), 233–239. <https://doi.org/10.1021/es960369h>
- Bloom, N. S., & Preus, E. (2003). Anoxic sediment incubation to assess the methylation potential of mercury contaminated solids. In *Proceedings of the 2nd International Symposium on Contaminated Sediments* (pp. 331–336).
- Blythe, G. M. (2003). *Pilot Testing of Mercury Oxidation Catalysts for Upstream of Wet FGD Systems*. Austin, Texas. Retrieved from <https://www.osti.gov/scitech/servlets/purl/815465>
- Blythe, G. M., Currie, J., DeBerry, D. W., & Miller, C. (2008). *Bench scale kinetics study of mercury reactions in FGD liquors; Cooperative Agreement No. DE-FC26-04NT42314*.
- Blythe, G. M., DeBerry, D., Marsh, B., Paradis, J., & Range, J. (2004). Bench-scale evaluation of the fate of mercury in wet FGD systems. In *Proceedings of the EPRI-EPA-DOE-AWMA mega symposium and mercury conference*. Washington, DC.
- Bombach, G., Bombach, K., & Klemm, W. (1994). Speciation of mercury in soils and sediments by thermal evaporation and cold vapor atomic absorption. *Fresenius' Journal of Analytical Chemistry*, 350(1), 18–20. <https://doi.org/10.1007/BF00326246>
- Bonnissel-Gissinger, P., Alnot, M., Lickes, J.-P., Ehrhardt, J.-J., & Behra, P. (1999). Modeling the Adsorption of Mercury(II) on (Hydr)oxides II: α -FeOOH (Goethite) and Amorphous Silica. *Journal of Colloid and Interface Science*, 215(2), 313–322. <https://doi.org/http://dx.doi.org/10.1006/jcis.1999.6263>
- Borrachero, M., Payá, J., Bonilla, M., & Monzó, J. (2008). The use of thermogravimetric

- analysis technique for the characterization of construction materials. *Journal of Thermal Analysis and Calorimetry*, 91(2), 503–509. <https://doi.org/10.1007/s10973-006-7739-3>
- Boszke, L., Głosińska, G., & Siepak, J. (2002). Some Aspects of Speciation of Mercury in a Water Environment. *Polish Journal of Environmental Studies*, 11(1), 285–298.
- Branfireun, B. a., Hilbert, D., & Roulet, N. T. (1998). Sinks and sources of methylmercury in a boreal catchment. *Biogeochemistry*, 41(3), 277–291. <https://doi.org/10.1023/A:1005964603828>
- BREFs. (2006). *Reference document on best available techniques for large combustion plants*.
- Briggs, C., & Gustin, M. S. (2013). Building upon the Conceptual Model for Soil Mercury Flux: Evidence of a Link Between Moisture Evaporation and Hg Evasion. *Water, Air, & Soil Pollution*, 224(10), 1744. <https://doi.org/10.1007/s11270-013-1744-5>
- Brimblecombe, P. (2005). The global sulfur cycle, *Treatise on Geochemistry*. In W. H. Schlesinger (Ed.), *Biogeochemistry* (Volume 8, pp. 645–682). Elsevier.
- Brown, G. E., & Parks, G. A. (1989). Synchrotron-based X ray absorption studies of cation environments in Earth materials. *Reviews of Geophysics*, 27(4), 519–533. <https://doi.org/10.1029/RG027i004p00519>
- Buleev, Y. M., Grudinkina, N. P., & Pevzner, H. G. (1968). Studies in Physico-Chemical Measurements. In *Proceedings of the Metrological Institutes of the USSR* (p. 96, pp. 176, 180).
- Bullock, O. R., & Brehme, K. A. (2002). Atmospheric mercury simulation using the CMAQ model: formulation description and analysis of wet deposition results. *Atmospheric Environment*, 36(13), 2135–2146. [https://doi.org/http://dx.doi.org/10.1016/S1352-2310\(02\)00220-0](https://doi.org/http://dx.doi.org/10.1016/S1352-2310(02)00220-0)
- Bunt, J. R., & Waanders, F. B. (2010). Trace element behaviour in the Sasol-Lurgi fixed-bed dry-bottom gasifier. Part 3 – The non-volatile elements: Ba, Co, Cr, Mn, and V. *Fuel*, 89(3), 537–548. <https://doi.org/10.1016/j.fuel.2009.04.018>
- Cain, A., Disch, S., Twaroski, C., Reindl, J., & Case, C. R. (2007). Substance Flow Analysis of Mercury Intentionally Used in Products in the United States. *Journal of Industrial Ecology*, 11(3), 61–75. <https://doi.org/10.1162/jiec.2007.1214>
- Carroll, R. W. H., Warwick, J. J., James, A. I., & Miller, J. R. (2004). Modeling erosion and overbank deposition during extreme flood conditions on the Carson River, Nevada. *Journal of Hydrology*, 297(1), 1–21. <https://doi.org/https://doi.org/10.1016/j.jhydrol.2004.04.012>
- Chakraborty, P., Raghunadh Babu, P. V., Vudamala, K., Ramteke, D., & Chennuri, K. (2014). Mercury speciation in coastal sediments from the central east coast of India by modified BCR method. *Marine Pollution Bulletin*, 81(1), 282–288. <https://doi.org/http://dx.doi.org/10.1016/j.marpolbul.2013.12.054>
- Chang, J. C. S., & Ghorishi, S. B. (2003). Simulation and Evaluation of Elemental Mercury Concentration Increase in Flue Gas Across a Wet Scrubber. *Environmental Science*

- Energy Technology*, 37(24), 5763–5766. <https://doi.org/10.1021/es034352s>
- Chang, J. C. S., & Zhao, Y. (2008). Pilot Plant Testing of Elemental Mercury Reemission from a Wet Scrubber. *Energy & Fuels*, 22(1), 338–342. <https://doi.org/10.1021/ef700355q>
- Chen, J., Yuan, D., Li, Q., Zheng, J., Zhu, Y., Hua, X., ... Zhou, J. (2008). Effect of flue-gas cleaning devices on mercury emission from coal-fired boiler. In *Proceedings of the CSEE* (pp. 72–76).
- Chen, L., Duan, Y., Zhuo, Y., Yang, L., Zhang, L., Yang, X., ... Xu, X. (2007). Mercury transformation across particulate control devices in six power plants of China: The co-effect of chlorine and ash composition. *Fuel*, 86(4), 603–610. <https://doi.org/http://dx.doi.org/10.1016/j.fuel.2006.07.030>
- Cheng, C.-M., Hack, P., Chu, P., Chang, Y.-N., Lin, T.-Y., Ko, C.-S., ... Pan, W.-P. (2009). Partitioning of Mercury, Arsenic, Selenium, Boron, and Chloride in a Full-Scale Coal Combustion Process Equipped with Selective Catalytic Reduction, Electrostatic Precipitation, and Flue Gas Desulfurization Systems. *Energy & Fuels*, 23(10), 4805–4816. <https://doi.org/10.1021/ef900293u>
- Choi, B. H. (1991). Effects of Methylmercury on the Developing Brain. In T. Suzuki, N. Imura, & T. W. Clarkson (Eds.), *Advances in Mercury Toxicology* (pp. 315–337). Boston, MA: Springer US. https://doi.org/10.1007/978-1-4757-9071-9_20
- Clark, R. B., Ritchey, K. D., & Baligar, V. C. (2001). Benefits and constraints for use of FGD products on agricultural land. *Fuel*, 80(6), 821–828. [https://doi.org/http://dx.doi.org/10.1016/S0016-2361\(00\)00162-9](https://doi.org/http://dx.doi.org/10.1016/S0016-2361(00)00162-9)
- Clarke, L. B., & Sloss, L. L. (1992). *Trace Elements From Coal Combustion and Gasification. IEACR/49, IEA Coal Research*. London.
- Córdoba, P. (2015). Status of Flue Gas Desulphurisation (FGD) systems from coal-fired power plants: Overview of the physic-chemical control processes of wet limestone FGDs. *Fuel*, 144, 274–286. <https://doi.org/http://dx.doi.org/10.1016/j.fuel.2014.12.065>
- Córdoba, P. (2017). Partitioning and speciation of selenium in wet limestone flue gas desulphurisation systems: A review. *Fuel*, 202, 184–195. <https://doi.org/http://dx.doi.org/10.1016/j.fuel.2017.04.015>
- Córdoba, P., Castro, I., Maroto-Valer, M., & Querol, X. (2015). The potential leaching and mobilization of trace elements from FGD-gypsum of a coal-fired power plant under water re-circulation conditions. *Journal of Environmental Sciences*, 32, 72–80. <https://doi.org/10.1016/j.jes.2014.11.009>
- Córdoba, P., Font, O., Izquierdo, M., Querol, X., Tobías, A., López-Antón, M. A., ... Giménez, A. (2011). Enrichment of inorganic trace pollutants in re-circulated water streams from a wet limestone flue gas desulphurisation system in two coal power plants. *Fuel Processing Technology*, 92(9), 1764–1775. <https://doi.org/http://dx.doi.org/10.1016/j.fuproc.2011.04.025>
- Córdoba, P., Maroto-Valer, M., Ayora, C., Perry, R., Rallo, M., Font, O., ... Querol, X.

- (2012). Unusual Speciation and Retention of Hg at a Coal-Fired Power Plant. *Environmental Science & Technology*, 46(14), 7890–7897. <https://doi.org/10.1021/es301106x>
- Córdoba, P., Ochoa-Gonzalez, R., Font, O., Izquierdo, M., Querol, X., Leiva, C., ... Tomás, A. (2012). Partitioning of trace inorganic elements in a coal-fired power plant equipped with a wet Flue Gas Desulphurisation system. *Fuel*, 92, 145–157. <https://doi.org/10.1016/j.fuel.2011.07.025>
- Coufalík, P., Pavel, K., Marek, D., & Josef, K. (2012). Sequential extraction and thermal desorption of mercury from contaminated soil and tailings from Mongolia. *Open Chemistry*. <https://doi.org/10.2478/s11532-012-0074-6>
- Council Decision 2003/33/EC. (2002). *Council Decision 2003/33/EC of 19 December 2002 establishing criteria and procedures for the acceptance of waste at landfills pursuant to Article 16 of and Annex II to Directive 1999/31/EC*.
- Cremer, D., Kraka, E., & Filatov, M. (2008). Bonding in Mercury Molecules Described by the Normalized Elimination of the Small Component and Coupled Cluster Theory. *ChemPhysChem*, 9(17), 2510–2521. <https://doi.org/10.1002/cphc.200800510>
- Cusack, L. K., Smit, E., Kile, M. L., & Harding, A. K. (2017). Regional and temporal trends in blood mercury concentrations and fish consumption in women of child bearing Age in the united states using NHANES data from 1999–2010. *Environmental Health*, 16, 10. <https://doi.org/10.1186/s12940-017-0218-4>
- Dajnak, D., Clark, K. D., Lockwood, F. C., & Reed, G. (2003). The prediction of mercury retention in ash from pulverised combustion of coal and sewage sludge. *Fuel*, 82(15), 1901–1909. [https://doi.org/http://dx.doi.org/10.1016/S0016-2361\(03\)00166-2](https://doi.org/http://dx.doi.org/10.1016/S0016-2361(03)00166-2)
- Davidson, R., & Clarke, L. B. (1996). *Trace elements in coal*. London.
- Deeds, D. A., Ghoshdastidar, A., Raofie, F., Guérette, É.-A., Tessier, A., & Ariya, P. A. (2015). Development of a Particle-Trap Preconcentration-Soft Ionization Mass Spectrometric Technique for the Quantification of Mercury Halides in Air. *Analytical Chemistry*, 87(10), 5109–5116. <https://doi.org/10.1021/ac504545w>
- Delnomdedieu, M., Boudou, A., Georgescauld, D., & Dufourc, E. J. (1992). Specific interactions of mercury chloride with membranes and other ligands as revealed by mercury-NMR. *Chemico-Biological Interactions*, 81(3), 243–269. [https://doi.org/http://dx.doi.org/10.1016/0009-2797\(92\)90081-U](https://doi.org/http://dx.doi.org/10.1016/0009-2797(92)90081-U)
- Diao, X., Yuan, C.-G., Wu, J., Gui, B., Zhang, K., & Zhang, C. (2018). Mercury release and fraction transformation during desulfurization gypsum aging process (UV irradiation). *Fuel*, 217, 522–528. <https://doi.org/https://doi.org/10.1016/j.fuel.2017.12.120>
- Drasch, G., Horvat, M., & Stoeppler, M. (2004). Mercury. In *Elements and Their Compounds in the Environment* (pp. 931–1005). Wiley-VCH Verlag GmbH. <https://doi.org/10.1002/9783527619634.ch38>
- Drexel, R. T., Haitzer, M., Ryan, J. N., Aiken, G. R., & Nagy, K. L. (2002). Mercury(II) Sorption to Two Florida Everglades Peats: Evidence for Strong and Weak Binding

- and Competition by Dissolved Organic Matter Released from the Peat. *Environmental Science & Technology*, 36(19), 4058–4064. <https://doi.org/10.1021/es0114005>
- Driscoll, C. T., Mason, R. P., Chan, H. M., Jacob, D. J., & Pirrone, N. (2013). Mercury as a Global Pollutant: Sources, Pathways, and Effects. *Environmental Science & Technology*, 47(10), 4967–4983. <https://doi.org/10.1021/es305071v>
- Díaz-Somoano, M., Unterberger, S., & Hein, K. R. G. (2007). Mercury emission control in coal-fired plants: The role of wet scrubbers. *Fuel Processing Technology*, 88(3), 259–263. <https://doi.org/http://dx.doi.org/10.1016/j.fuproc.2006.10.003>
- Ebinghaus, R., Jennings, S. G., Schroeder, W. H., Berg, T., Donaghy, T., Guentzel, J., ... Xiao, Z. (1999). International field intercomparison measurements of atmospheric mercury species at Mace Head, Ireland. *Atmospheric Environment*, 33(18), 3063–3073. [https://doi.org/http://dx.doi.org/10.1016/S1352-2310\(98\)00119-8](https://doi.org/http://dx.doi.org/10.1016/S1352-2310(98)00119-8)
- Enghag, P. (2004). Mercury. In *Encyclopedia of the Elements* (pp. 791–804). Wiley-VCH Verlag GmbH & Co. KGaA. <https://doi.org/10.1002/9783527612338.ch35>
- Engström, K. S., Strömberg, U., Lundh, T., Johansson, I., Vessby, B., Hallmans, G., ... Broberg, K. (2008). Genetic Variation in Glutathione-Related Genes and Body Burden of Methylmercury. *Environmental Health Perspectives*, 116(6), 734–739. <https://doi.org/10.1289/ehp.10804>
- Esenlik, S., Karayigit, A. I., Bulut, Y., Querol, X., Alastuey, A., & Font, O. (2006). Element behaviour during combustion in coal-fired Orhaneli power plant, Bursa-Turkey. *Geologica Acta*, 4(4), 439–449. <https://doi.org/10.1344/105.000000345>
- Evans, M. A., & Elmore, R. D. (2006). Fluid control of localized mineral domains in limestone pressure solution structures. *Journal of Structural Geology*, 28(2), 284–301. <https://doi.org/http://dx.doi.org/10.1016/j.jsg.2005.10.004>
- EVISA, E. V. I. for S. A. (2017). Mercury “speciation analysis” by using thermal desorption analysis. Retrieved August 23, 2017, from <http://www.speciation.net/News/Mercury-speciation-analysis-by-using-thermal-desorption-analysis-;~/2017/04/17/8335.html>
- Fatu, D. (2001). Kinetics of Gypsum Dehydration. *Journal of Thermal Analysis and Calorimetry*, 65(1), 213–220. <https://doi.org/10.1023/A:1011597106589>
- Feng, X., Lu, J. Y., Grégoire, D. C., Hao, Y., Banic, C. M., & Schroeder, W. H. (2004). Analysis of inorganic mercury species associated with airborne particulate matter/aerosols: method development. *Analytical and Bioanalytical Chemistry*, 380(4), 683–689. <https://doi.org/10.1007/s00216-004-2803-y>
- Fernández-Martínez, R., & Rucandio, M. I. (2003). Study of extraction conditions for the quantitative determination of Hg bound to sulfide in soils from Almaden (Spain). *Analytical and Bioanalytical Chemistry*, 375, 1089–1096.
- Finkelman, R. B. (1994). Modes of occurrence of potentially hazardous elements in coal: levels of confidence. *Fuel Processing Technology*, 39(1), 21–34. [https://doi.org/http://dx.doi.org/10.1016/0378-3820\(94\)90169-4](https://doi.org/http://dx.doi.org/10.1016/0378-3820(94)90169-4)
- Finkelman, R. B. (1995). Modes of Occurrence of Environmentally-Sensitive Trace Elements in Coal. In Dalway J. Swaine & F. Goodarzi (Eds.), *Environmental Aspects*

- of Trace Elements in Coal* (p. pp 24-50). Springer Netherlands. https://doi.org/10.1007/978-94-015-8496-8_3
- Fitzgerald, W. F. (1995). Is Mercury Increasing in the Atmosphere? The Need for an Atmospheric Mercury Network (Amnet). In D. B. Porcella, J. W. Huckabee, & B. Wheatley (Eds.), *Mercury as a Global Pollutant: Proceedings of the Third International Conference held in Whistler, British Columbia, July 10--14, 1994* (pp. 245–254). Dordrecht: Springer Netherlands. https://doi.org/10.1007/978-94-011-0153-0_28
- Fitzgerald, W. F., Lamborg, C. H., Heinrich, D. H., & Karl, K. T. (2007). *Geochemistry of mercury in the environment: Treatise on geochemistry*. Oxford: Pergamon.
- Frandsen, F., Dam-Johansen, K., & Rasmussen, P. (1994). Trace elements from combustion and gasification of coal—An equilibrium approach. *Progress in Energy and Combustion Science*, 20(2), 115–138. [https://doi.org/http://dx.doi.org/10.1016/0360-1285\(94\)90007-8](https://doi.org/http://dx.doi.org/10.1016/0360-1285(94)90007-8)
- Freyer, D., & Voigt, W. (2003). Crystallization and Phase Stability of CaSO₄ and CaSO₄ - Based Salts. *Monatshefte Fur Chemie*, 134(5), 693–719. <https://doi.org/10.1007/s00706-003-0590-3>
- Frkal, P. (n.d.). Modelling and experimental measurements of limestone dissolution under enhanced wet limestone FGD process conditions. (M. Gerbec, Ed.), *Acta chimica slovenica*.
- Frkal, P. (2013). *Odtranjevanje živega srebra iz dimnih plinov pri mokrem postopku razžvepljevanja*.
- Galbreath, K. C., Toman, D. L., Zygarlicke, C. J., & Pavlish, J. H. (2000). Trace Element Partitioning and Transformations During Combustion of Bituminous and Subbituminous U. S. Coals In a 7-kW Combustion System. *Energy & Fuels*, 14(6), 1265–1279. <https://doi.org/10.1021/ef000105n>
- Galbreath, K. C., & Zygarlicke, C. J. (2000). Mercury transformations in coal combustion flue gas. *Fuel Processing Technology*, 65, 289–310. [https://doi.org/10.1016/S0378-3820\(99\)00102-2](https://doi.org/10.1016/S0378-3820(99)00102-2)
- Galbreath, K. C., Zygarlicke, C. J., Tibbetts, J. E., Schulz, R. L., & Dunham, G. E. (2005). Effects of NO_x, α -Fe₂O₃, γ -Fe₂O₃, and HCl on mercury transformations in a 7-kW coal combustion system. *Fuel Processing Technology*, 86(4), 429–448. <https://doi.org/http://dx.doi.org/10.1016/j.fuproc.2004.03.003>
- Galwey, A. K., & Brown, M. E. (1999). Chapter 8 Thermal dehydration of hydroxides. In Andrew K Galwey and Michael E Brown B T - Studies in Physical and Theoretical (Ed.), *Thermal Decomposition of Ionic Solids* (Vol. Volume 86, pp. 269–290). Elsevier. [https://doi.org/https://doi.org/10.1016/S0167-6881\(99\)80010-X](https://doi.org/https://doi.org/10.1016/S0167-6881(99)80010-X)
- Gao, L., Wang, Y., Huang, Q., & Guo, S. (2017). Modes of occurrence and thermal stability of mercury in different samples from Guandi coal preparation plant. *Fuel*, 200(Supplement C), 22–30. <https://doi.org/https://doi.org/10.1016/j.fuel.2017.03.045>

- Gerbec, M., Stergaršek, A., & Kocjančič, R. (1995). Simulation model of wet flue gas desulphurization plant. *Computers & Chemical Engineering*, 19, 283–286. [https://doi.org/10.1016/0098-1354\(95\)87050-4](https://doi.org/10.1016/0098-1354(95)87050-4)
- Germani, M. S., & Zoller, W. H. (1988). Vapor-phase concentrations of arsenic, selenium, bromine, iodine, and mercury in the stack of a coal-fired power plant. *Environmental Science & Technology*, 22(9), 1079–1085. <https://doi.org/10.1021/es00174a013>
- Ghorishi, B., & Gullett, B. K. (1999). Sorption of mercury species by activated carbons and calcium-based sorbents: effect of temperature, mercury concentration and acid gases. *Waste Management and Research* 1998; 16 (6), 582–593. *Waste Management and Research*, 17(4), 324. <https://doi.org/10.1034/j.1399-3070.1999.00049.x>
- Gibb, W. H., Clarke, F., & Mehta, A. K. (2000). The fate of coal mercury during combustion. *Fuel Processing Technology*, 65, 365–377. [https://doi.org/http://dx.doi.org/10.1016/S0378-3820\(99\)00104-6](https://doi.org/http://dx.doi.org/10.1016/S0378-3820(99)00104-6)
- Gilmour, C. C., Henry, E. ., & Mitchell, R. (1992). Sulfate stimulation of mercury methylation in freshwater sediments. *Environmental Science & Technology*, 26(11), 2281–2287. <https://doi.org/10.1021/es00035a029>
- Gochfeld, M. (2003). Cases of mercury exposure, bioavailability, and absorption. *Ecotoxicology and Environmental Safety*, 56(1), 174–179. [https://doi.org/http://dx.doi.org/10.1016/S0147-6513\(03\)00060-5](https://doi.org/http://dx.doi.org/10.1016/S0147-6513(03)00060-5)
- Gonzalez-Raymat, H., Liu, G., Liriano, C., Li, Y., Yin, Y., Shi, J., ... Cai, Y. (2017). Elemental mercury: Its unique properties affect its behavior and fate in the environment. *Environmental Pollution*, 229, 69–86. <https://doi.org/https://doi.org/10.1016/j.envpol.2017.04.101>
- Gordon, G. E., & Zoller, W. H. (1973). Normalization and interpretation of atmospheric trace element concentration patterns. In *Proceedings of the 1st Annual NSF Trace Contaminants Conference* (pp. 314–325).
- Grousset, F. E., Quétel, C. R., Thomas, B., Donard, O. F. X., Lambert, C. E., Guillard, F., & Monaco, A. (1995). Anthropogenic vs. lithogenic origins of trace elements (As, Cd, Pb, Rb, Sb, Sc, Sn, Zn) in water column particles: northwestern Mediterranean Sea. *Marine Chemistry*, 48(3), 291–310. [https://doi.org/http://dx.doi.org/10.1016/0304-4203\(94\)00056-J](https://doi.org/http://dx.doi.org/10.1016/0304-4203(94)00056-J)
- Gundacker, C., Gencik, M., & Hengstschläger, M. (2010). The relevance of the individual genetic background for the toxicokinetics of two significant neurodevelopmental toxicants: Mercury and lead. *Mutation Research/Reviews in Mutation Research*, 705(2), 130–140. <https://doi.org/https://doi.org/10.1016/j.mrrev.2010.06.003>
- Gunneriusson, L., & Sjöberg, S. (1993). Surface Complexation in the H⁺-Goethite (α-FeOOH)-Hg (II)-Chloride System. *Journal of Colloid and Interface Science*, 156(1), 121–128. <https://doi.org/https://doi.org/10.1006/jcis.1993.1090>
- Guo, X., Zheng, C.-G., & Xu, M. (2004). Characterization of Arsenic Emissions from a Coal-Fired Power Plant. *Energy & Fuels*, 18(6), 1822–1826. <https://doi.org/10.1021/ef049921b>

- Gustin, M. S., Evers, D. C., Bank, M. S., Hammerschmidt, C. R., Pierce, A., Basu, N., ... Selin, N. (2016). Importance of Integration and Implementation of Emerging and Future Mercury Research into the Minamata Convention. *Environmental Science & Technology*, 50(6), 2767–2770. <https://doi.org/10.1021/acs.est.6b00573>
- Gustin, M. S., & Jaffe, D. (2010). Reducing the Uncertainty in Measurement and Understanding of Mercury in the Atmosphere. *Environmental Science & Technology*, 44(7), 2222–2227. <https://doi.org/10.1021/es902736k>
- Gustin, M. S., & Ladwig, K. (2010). Laboratory Investigation of Hg Release from Flue Gas Desulfurization Products. *Environmental Science & Technology*, 44(10), 4012–4018. <https://doi.org/10.1021/es903673q>
- Gustin, M. S., Lindberg, S. E., & Weisberg, P. J. (2008). An update on the natural sources and sinks of atmospheric mercury. *Applied Geochemistry*, 23(3), 482–493. <https://doi.org/http://dx.doi.org/10.1016/j.apgeochem.2007.12.010>
- Haitzer, M., Aiken, G. R., & Ryan, J. N. (2002). Binding of Mercury(II) to Dissolved Organic Matter: The Role of the Mercury-to-DOM Concentration Ratio. *Environmental Science & Technology*, 36(16), 3564–3570. <https://doi.org/10.1021/es025699i>
- Hall, B. (1995). The gas phase oxidation of elemental mercury by ozone. *Water, Air, and Soil Pollution*, 80(1), 301–315. <https://doi.org/10.1007/BF01189680>
- Hall, B., Schager, P., & Lindqvist, O. (1991). Chemical reactions of mercury in combustion flue gases. *Water Air & Soil Pollution*, 56(1), 3–14. <https://doi.org/10.1007/BF00342256>
- Han, Y., Kingston, H. M., Boylan, H. M., Rahman, G. M. M., Shah, S., Richter, R. C., ... Bhandari, S. (2003). Speciation of mercury in soil and sediment by selective solvent and acid extraction. *Analytical and Bioanalytical Chemistry*, 375, 428–436.
- Hao, Y., Wu, S., Pan, Y., Li, Q., Zhou, J., Xu, Y., & Qian, G. (2016). Characterization and leaching toxicities of mercury in flue gas desulfurization gypsum from coal-fired power plants in China. *Fuel*. <https://doi.org/10.1016/j.fuel.2016.02.091>
- Hassett, D. J., & Eylands, K. E. (1999). Mercury capture on coal combustion fly ash. *Fuel*, 78(2), 243–248. [https://doi.org/http://dx.doi.org/10.1016/S0016-2361\(98\)00150-1](https://doi.org/http://dx.doi.org/10.1016/S0016-2361(98)00150-1)
- Hazen, R. M., J. Golden, R. T., Downs, G., Hystad, E. S., Grew, D. A., & Sverjensky, D. A. (2012). Mercury (Hg) mineral evolution: A mineralogical record of supercontinent assembly, changing ocean geochemistry, and the emerging terrestrial biosphere. *American Mineralogist*, 97, 1013–1042.
- Heebink, L. V., & Hassett, D. J. (2005). Mercury release from FGD. *Fuel*, 84(11), 1372–1377. <https://doi.org/http://dx.doi.org/10.1016/j.fuel.2004.06.040>
- Heidel, B., Rogge, T., & Scheffknecht, G. (2016). Controlled desorption of mercury in wet FGD waste water treatment. *Applied Energy*, 162, 1211–1217. <https://doi.org/http://dx.doi.org/10.1016/j.apenergy.2015.05.016>
- Helble, J. J., & Sarofim, A. F. (1993). Trace element behaviour during coal combustion. *Preprints of Papers - American Chemical Society, Division of Fuel Chemistry*, 38(1),

257–264.

- Hepler, L. G., & Olofsson, G. (1975). Mercury: Thermodynamic Properties, Chemical Equilibria, and Standard Potentials. *Chemical Reviews*, 75(5), 585–602.
- Hintelmann, H., Welbourn, P. . M., & Evans, R. D. (1995). Binding of methylmercury compounds by humic and fulvic acids. *Water, Air, and Soil Pollution*, 80(1), 1031–1034. <https://doi.org/10.1007/BF01189760>
- Hojdová, M., Navrátil, T., Rohovec, J., Pen'žek, V., & Grygar, T. (2009). Mercury Distribution and Speciation in Soils Affected by Historic Mercury Mining. *Water, Air, and Soil Pollution*, 200(1), 89–99. <https://doi.org/10.1007/s11270-008-9895-5>
- Holmes, C. D., Jacob, D. J., Mason, R. P., & Jaffe, D. A. (2009). Sources and deposition of reactive gaseous mercury in the marine atmosphere. *Atmospheric Environment*, 43(14), 2278–2285. <https://doi.org/http://dx.doi.org/10.1016/j.atmosenv.2009.01.051>
- Horowitz, H. M., Jacob, D. J., Amos, H. M., Streets, D. G., & Sunderland, E. M. (2014). Historical Mercury Releases from Commercial Products: Global Environmental Implications. *Environmental Science & Technology*, 48(17), 10242–10250. <https://doi.org/10.1021/es501337j>
- Horvat, M. (2005). *Determination of Mercury and its Compounds in Water, Sediment, Soil and Biological Samples. Dynamics of Mercury Pollution on Regional and Global Scales: Atmospheric Processes and Human Exposures Around the World.* https://doi.org/10.1007/0-387-24494-8_8
- Horvat, M., Covelli, S., Faganeli, J., Logar, M., Mandić, V., Rajar, R., ... Žagar, D. (1999). Mercury in contaminated coastal environments; a case study: the Gulf of Trieste. *Science of The Total Environment*, 237–238(Supplement C), 43–56. [https://doi.org/https://doi.org/10.1016/S0048-9697\(99\)00123-0](https://doi.org/https://doi.org/10.1016/S0048-9697(99)00123-0)
- Horvat, M., Kotnik, J., Logar, M., Fajon, V., Zvonarić, T., & Pirrone, N. (2003). Speciation of mercury in surface and deep-sea waters in the Mediterranean Sea. *Atmospheric Environment*, 37(1), 93–108.
- Hower, J. C., Robl, T. L., Anderson, C., Thomas, G. A., Sakulpitakphon, T., Mardon, S. M., & Clark, W. L. (2005). Characteristics of coal combustion products (CCP's) from Kentucky power plants, with emphasis on mercury content. *Fuel*, 84(11), 1338–1350. <https://doi.org/https://doi.org/10.1016/j.fuel.2004.09.029>
- Hsu-Kim, H., Kucharzyk, K. H., Zhang, T., & Deshusses, M. A. (2013). Mechanisms Regulating Mercury Bioavailability for Methylating Microorganisms in the Aquatic Environment: A Critical Review. *Environmental Science & Technology*, 47(6), 2441–2456. <https://doi.org/10.1021/es304370g>
- Huang, J., Miller, M. B., Weiss-Penzias, P., & Gustin, M. S. (2013). Comparison of Gaseous Oxidized Hg Measured by KCl-Coated Denuders, and Nylon and Cation Exchange Membranes. *Environmental Science & Technology*, 47(13), 7307–7316. <https://doi.org/10.1021/es4012349>
- Huggins, F. E., & Huffman, G. P. (1996). Modes of occurrence of trace elements in coal

- from XAFS spectroscopy. *International Journal of Coal Geology*, 32(1), 31–53. [https://doi.org/http://dx.doi.org/10.1016/S0166-5162\(96\)00029-8](https://doi.org/http://dx.doi.org/10.1016/S0166-5162(96)00029-8)
- Huggins, F. E., Senior, C. L., Chu, P., Ladwig, K., & Huffman, G. P. (2007). Selenium and Arsenic Speciation in Fly Ash from Full-Scale Coal-Burning Utility Plants. *Environmental Science & Technology*, 41(9), 3284–3289. <https://doi.org/10.1021/es062069y>
- Inoue, Y., & Munemori, M. (1979). Coprecipitation of mercury(II) with iron(III) hydroxide. *Environmental Science & Technology*, 13(4), 443–445. <https://doi.org/10.1021/es60152a001>
- International Mineralogical Association. (2014). IMA Database of Mineral Properties. Retrieved from <http://rruff.info/ima/>
- Iorish, V. S., Belov, G. V., & Gurvich, L. V. (2005). IVTANTHERMO database. Glushko Thermocenter of Russian Academy of Sciences.
- Issaro, N., Abi-Ghanem, C., & Bermond, A. (2009). Fractionation studies of mercury in soils and sediments: A review of the chemical reagents used for mercury extraction. *Analytica Chimica Acta*, 631(1), 1–12. <https://doi.org/http://dx.doi.org/10.1016/j.aca.2008.10.020>
- Ito, S., Yokoyama, T., & Asakura, K. (2006). Emissions of mercury and other trace elements from coal-fired power plants in Japan. *Science of The Total Environment*, 368(1), 397–402. <https://doi.org/10.1016/j.scitotenv.2005.09.044>
- Jaćimović, R., Smodiš, B., Bučar, T., & Stegnar, P. (2003). k0-NAA quality assessment by analysis of different certified reference materials using the KAYZERO/SOLCOI software. *Journal of Radioanalytical and Nuclear Chemistry*, 257(3), 659–663. <https://doi.org/10.1023/A:1026116916580>
- Jasinski, S. M. (1995). The materials flow of mercury in the United States. *Resources, Conservation and Recycling*, 15(3), 145–179. [https://doi.org/http://dx.doi.org/10.1016/0921-3449\(95\)00032-1](https://doi.org/http://dx.doi.org/10.1016/0921-3449(95)00032-1)
- Jones, C. P., Lyman, S. N., Jaffe, D. A., Allen, T., & O’Neil, T. L. (2016). Detection and quantification of gas-phase oxidized mercury compounds by GC/MS. *Atmospheric Measurement Techniques*, 9(5), 2195–2205. <https://doi.org/10.5194/amt-9-2195-2016>
- Juda-Rezler, K., & Kowalczyk, D. (2013). Size distribution and trace elements contents of coal fly ash from pulverized boilers. *Polish Journal of Environmental Studies*, 22(1), 25–40.
- Kairies, C. L., Schroeder, K. T., & Cardone, C. R. (2006). Mercury in gypsum produced from flue gas desulfurization. *Fuel*, 85(17–18), 2530–2536. <https://doi.org/http://dx.doi.org/10.1016/j.fuel.2006.04.027>
- Karlsson, T., & Skyllberg, U. (2003). Bonding of ppb Levels of Methyl Mercury to Reduced Sulfur Groups in Soil Organic Matter. *Environmental Science & Technology*, 37(21), 4912–4918. <https://doi.org/10.1021/es034302n>
- Kaupp, M., & von Schnering, H. G. (1993). Gaseous Mercury(IV) Fluoride, HgF₄: An Ab Initio Study. *Angewandte Chemie International Edition in English*, 32(6), 861–863.

<https://doi.org/10.1002/anie.199308611>

- Keeler, J., & Wothers, P. (2013). *Chemical Structure and Reactivity: an Integrated Approach*. OUP Oxford, New York.
- Khalizov, A. F., Viswanathan, B., Larregaray, P., & Ariya, P. A. (2003). A Theoretical Study on the Reactions of Hg with Halogens: Atmospheric Implications. *The Journal of Physical Chemistry A*, 107(33), 6360–6365. <https://doi.org/10.1021/jp0350722>
- Khan, M. A. K., & Wang, F. (2009). Mercury-selenium compounds and their toxicological significance: toward a molecular understanding of the mercury-selenium antagonism. *Environmental Toxicology and Chemistry / SETAC*, 28(8), 1567–1577. <https://doi.org/10.1897/08-375.1>
- Kim, C. S., Brown, G. E., & Rytuba, J. J. (2000). Characterization and speciation of mercury-bearing mine wastes using X-ray absorption spectroscopy. *Science of The Total Environment*, 261(1), 157–168. [https://doi.org/http://dx.doi.org/10.1016/S0048-9697\(00\)00640-9](https://doi.org/http://dx.doi.org/10.1016/S0048-9697(00)00640-9)
- Kim, C. S., Rytuba, J. J., & Brown, G. E. (2004a). EXAFS study of mercury(II) sorption to Fe- and Al-(hydr)oxides: I. Effects of pH. *Journal of Colloid and Interface Science*, 271(1), 1–15. [https://doi.org/http://dx.doi.org/10.1016/S0021-9797\(03\)00330-8](https://doi.org/http://dx.doi.org/10.1016/S0021-9797(03)00330-8)
- Kim, C. S., Rytuba, J. J., & Brown, G. E. (2004b). EXAFS study of mercury(II) sorption to Fe- and Al-(hydr)oxides: II. Effects of chloride and sulfate. *Journal of Colloid and Interface Science*, 270(1), 9–20. <https://doi.org/http://dx.doi.org/10.1016/j.jcis.2003.07.029>
- Kim, E.-A., Seyfferth, A. L., Fendorf, S., & Luthy, R. G. (2011). Immobilization of Hg(II) in water with polysulfide-rubber (PSR) polymer-coated activated carbon. *Water Research*, 45(2), 453–460. <https://doi.org/http://dx.doi.org/10.1016/j.watres.2010.08.045>
- Kim, J.-H., Pudasainee, D., Yoon, Y.-S., Son, S.-U., & Seo, Y.-C. (2010). Studies on Speciation Changes and Mass Distribution of Mercury in a Bituminous Coal-Fired Power Plant by Combining Field Data and Chemical Equilibrium Calculation. *Industrial & Engineering Chemistry Research*, 49(11), 5197–5203. <https://doi.org/10.1021/ie901361q>
- King, R. B. (2006). *Encyclopedia of inorganic chemistry*. Chichester, West Sussex, England; Hoboken, NJ: Wiley.
- Kiser, R. W., Dillard, J. G., & Dugger, D. L. (1968). Mass Spectrometry of Inorganic Halides. In *Mass Spectrometry in Inorganic Chemistry* (Vol. 72, pp. 12–153). AMERICAN CHEMICAL SOCIETY. <https://doi.org/doi:10.1021/ba-1968-0072.ch012>
- Klein, D. H., Andren, A. W., Carter, J. A., Emery, J. F., Feldman, C., Fulkerson, W., ... Talmi, Y. (1975). Pathways of thirty-seven trace elements through coal-fired power plant. *Environmental Science & Technology*, 9(10), 973–979. <https://doi.org/10.1021/es60108a007>
- Kocman, D., Horvat, M., & Kotnik, J. (2004). Mercury fractionation in contaminated soils

- from the Idrija mercury mine region. *Journal of Environmental Monitoring*, 6(8), 696–703. <https://doi.org/10.1039/B403625E>
- Kocman, D., Wilson, J. S., Amos, M. H., Telmer, H. K., Steenhuisen, F., Sunderland, M. E., ... Horvat, M. (2017). Toward an Assessment of the Global Inventory of Present-Day Mercury Releases to Freshwater Environments. *International Journal of Environmental Research and Public Health*. <https://doi.org/10.3390/ijerph14020138>
- Kodre, A., Arčon, I., Debeljak, M., Potisek, M., Likar, M., & Vogel-Mikuš, K. (2017). Arbuscular mycorrhizal fungi alter Hg root uptake and ligand environment as studied by X-ray absorption fine structure. *Environmental and Experimental Botany*, 133, 12–23. <https://doi.org/10.1016/j.envexpbot.2016.09.006>
- Kokkonen, E., Löytynoja, T., Hautala, L., Jänkälä, K., & Huttula, M. (2015). Fragmentation of mercury compounds under ultraviolet light irradiation. *The Journal of Chemical Physics*, 143(7), 7.
- Koksoy, M., Bradshaw, P. M. D., & Tooms, J. S. (1967). Notes on the determination of mercury in geological samples. *Trans. Inst. Min. Metall.*, B76, 121–124.
- Kotnik, J., Horvat, M., Tessier, E., Ogrinc, N., Monperrus, M., Amouroux, D., ... Pirrone, N. (2007). Mercury speciation in surface and deep waters of the Mediterranean Sea. *Marine Chemistry*, 107(1), 13–30. <https://doi.org/http://dx.doi.org/10.1016/j.marchem.2007.02.012>
- Kozin, L. F., & Hansen, S. C. (2013). *Mercury Handbook*. The Royal Society of Chemistry. <https://doi.org/10.1039/9781849735155>
- Kraka, E., & Cremer, D. (2008). Bonding in Mercury-Alkali Molecules: Orbital-driven van der Waals Complexes. *International Journal of Molecular Sciences*. <https://doi.org/10.3390/ijms9060926>
- Krishnan, S. V., Gullett, B. K., & Jozewicz, W. (1997). Mercury control in municipal waste combustors and coal-fired utilities. *Environmental Progress*, 16(1), 47–53. <https://doi.org/10.1002/ep.3300160120>
- Krüger, R.-R., & Abriel, W. (1991). Growth and structure refinement of $\text{CaSeO}_4 \cdot 2\text{H}_2\text{O}$. *Acta Crystallographica Section C*, 47(9), 1958–1959. <https://doi.org/10.1107/S0108270191002676>
- Kubaschewski, O., Alcock, C. B., & Evans, A. L. (1967). *No Title*. Oxford: Pergamon. Retrieved from <http://cds.cern.ch/record/445069?ln=en>
- Laudal, D. L. (2002). *Selective Catalytic Reduction Mercury Field Sampling Project; EPRI Report No. 1005400*.
- Laudal, D. L., Pavlish, J. H., Galbreath, K. C., Thompson, J. S., Weber, G. F., & Sondreal, E. (2000). *Pilot-scale evaluation of the impact of selective catalytic reduction for NO_x on mercury speciation*. Grand Forks. Retrieved from <https://www.osti.gov/scitech/servlets/purl/824958/>
- Laumb, J. D., Benson, S. A., & Olson, E. A. (2004). X-ray photoelectron spectroscopy analysis of mercury sorbent surface chemistry. *Fuel Processing Technology*, 85(6), 577–585. <https://doi.org/http://dx.doi.org/10.1016/j.fuproc.2003.11.008>

- Leckey, J. H., & Nulf, L. E. (1994). *Thermal decomposition of mercuric sulfide*. United States. <https://doi.org/10.2172/41313>
- Lee, C. W., Srivastava, R. K., Ghorishi, S. B., Hastings, T. W., & Stevens, F. M. (2003). Study of speciation of mercury under simulated SCR NO_x emission control conditions. In *U.S. Environmental Protection Agency-Department of Energy-EPRI Combined Power Plant Air Pollutant Control Symposium* (p. 13). Retrieved from https://www.researchgate.net/publication/242756862_Study_of_Speciation_of_Mercury_under_Simulated_SCR_NOx_Emission_Control_Conditions
- Lee, J.-Y., Cho, K., Cheng, L., Keener, T. C., Jegadeesan, G., & Al-Abed, S. R. (2009). Investigation of a Mercury Speciation Technique for Flue Gas Desulfurization Materials. *Journal of the Air & Waste Management Association*, 59(8), 972–979. <https://doi.org/10.3155/1047-3289.59.8.972>
- Lee, S. H., Rhim, Y. J., Cho, S. P., & Baek, J. I. (2006). Carbon-based novel sorbent for removing gas-phase mercury. *Fuel*, 85(2), 219–226. <https://doi.org/http://dx.doi.org/10.1016/j.fuel.2005.02.030>
- Lee, S. J., Seo, Y.-C., Jang, H.-N., Park, K.-S., Baek, J.-I., An, H.-S., & Song, K.-C. (2006). Speciation and mass distribution of mercury in a bituminous coal-fired power plant. *Atmospheric Environment*, 40(12), 2215–2224. <https://doi.org/http://dx.doi.org/10.1016/j.atmosenv.2005.12.013>
- Leopold, K., Foulkes, M., & Worsfold, P. (2010). Methods for the determination and speciation of mercury in natural waters—A review. *Analytica Chimica Acta*, 663(2), 127–138. <https://doi.org/http://dx.doi.org/10.1016/j.aca.2010.01.048>
- Li, J., Zhuang, X., Querol, X., Font, O., Moreno, N., & Zhou, J. (2012). Environmental geochemistry of the feed coals and their combustion by-products from two coal-fired power plants in Xinjiang Province, Northwest China. *Fuel*, 95, 446–456. <https://doi.org/10.1016/j.fuel.2011.10.025>
- Li, S., Cheng, C.-M., Chen, B., Cao, Y., Vervynckt, J., Adebambo, A., & Pan, W.-P. (2007). Investigation of the Relationship between Particulate-Bound Mercury and Properties of Fly Ash in a Full-Scale 100 MWe Pulverized Coal Combustion Boiler. *Energy & Fuels*, 21(6), 3292–3299. <https://doi.org/10.1021/ef0701384>
- Li, Z., Clemens, a. H., Moore, T. a., Gong, D., Weaver, S. D., & Eby, N. (2005). Partitioning behaviour of trace elements in a stoker-fired combustion unit: An example using bituminous coals from the Greymouth coalfield (Cretaceous), New Zealand. *International Journal of Coal Geology*, 63(1–2), 98–116. <https://doi.org/http://dx.doi.org/10.1016/j.coal.2005.02.007>
- Lide, D. R. (2009). CRC Handbook of Chemistry and Physics, 2009–2010, 90th ed. *Journal of the American Chemical Society*, 131(35), 12862. <https://doi.org/10.1021/ja906434c>
- Lin, C.-J., & Pehkonen, S. O. (1999). Aqueous phase reactions of mercury with free radicals and chlorine: Implications for atmospheric mercury chemistry. *Chemosphere*, 38(6), 1253–1263. [https://doi.org/http://dx.doi.org/10.1016/S0045-6535\(98\)00526-8](https://doi.org/http://dx.doi.org/10.1016/S0045-6535(98)00526-8)
- Lindquist, O., Johansson, K., Aastrup, M., Anderson, A., Bringmark, L., Housenius, G., ...

- Timm, B. (1991). *Mercury in the Swedish Environment — Recent Research on Causes, Consequences and Corrective Methods. Water Air & Soil Pollution* (Vol. 55). Sweden.
- Liu, X., Wang, S., Zhang, L., Wu, Y., Duan, L., & Hao, J. (2013). Speciation of mercury in FGD gypsum and mercury emission during the wallboard production in China. *Fuel*, 111, 621–627. <https://doi.org/http://dx.doi.org/10.1016/j.fuel.2013.03.052>
- Liu, Y. K., Zhuo, Y. Q., Zhu, Z. W., & Chen, C. H. (2013). Leaching Characteristics of Trace Elements in Desulphurization Gypsum from a Coal-Fired Power plant. In Q. Haiying & B. Zhao (Eds.), *Cleaner Combustion and Sustainable World* (pp. 377–385). Springer Berlin Heidelberg. https://doi.org/10.1007/978-3-642-30445-3_53
- Liu, Y., Wang, Y., Wang, Q., Pan, J., Zhang, Y., Zhou, J., & Zhang, J. (2015). A study on removal of elemental mercury in flue gas using fenton solution. *Journal of Hazardous Materials*, 292, 164–172. <https://doi.org/http://dx.doi.org/10.1016/j.jhazmat.2015.03.027>
- Llop, S., Engström, K., Ballester, F., Franforte, E., Alhamdow, A., Pisa, F., ... Broberg, K. (2014). Polymorphisms in ABC Transporter Genes and Concentrations of Mercury in Newborns – Evidence from Two Mediterranean Birth Cohorts. *PLOS ONE*, 9(5), e97172. Retrieved from <https://doi.org/10.1371/journal.pone.0097172>
- Lockwood, R. A., & Chen, K. Y. (1973). Adsorption of Hg(II) by hydrous manganese oxides. *Environmental Science and Technology*, 7(11), 1028–1034. Retrieved from <http://pubs.acs.org/doi/pdf/10.1021/es60083a006>
- López-Antón, M. A., Abad-Valle, P., Díaz-Somoano, M., Suárez-Ruiz, I., & Martínez-Tarazona, M. R. (2009). The influence of carbon particle type in fly ashes on mercury adsorption. *Fuel*, 88(7), 1194–1200. <https://doi.org/https://doi.org/10.1016/j.fuel.2007.07.029>
- López-Antón, M. A., Díaz-Somoano, M., Ochoa-González, R., & Martínez-Tarazona, M. R. (2011). Distribution of trace elements from a coal burned in two different spanish power stations. *Industrial and Engineering Chemistry Research*, 50(21), 12208–12216. <https://doi.org/10.1021/ie2018542>
- Lopez-Anton, M. A., Yuan, Y., Perry, R., & Maroto-Valer, M. M. (2010). Analysis of mercury species present during coal combustion by thermal desorption. *Fuel*, 89(3), 629–634. <https://doi.org/http://dx.doi.org/10.1016/j.fuel.2009.08.034>
- Lu, D., Anthony, E. J., Tan, Y., Dureau, R., Ko, V., & Douglas, M. A. (2007). Mercury removal from coal combustion by Fenton reactions – Part A: Bench-scale tests. *Fuel*, 86(17), 2789–2797. <https://doi.org/http://dx.doi.org/10.1016/j.fuel.2007.03.025>
- Lu, Y., Rostam-Abadi, M., Chang, R., Richardson, C., & Paradis, J. (2007). Characteristics of Fly Ashes from Full-Scale Coal-Fired Power Plants and Their Relationship to Mercury Adsorption. *Energy & Fuels*, 21(4), 2112–2120. <https://doi.org/10.1021/ef070145s>
- Luo, G., Yao, H., Xu, M., Gupta, R., & Xu, Z. (2011). Identifying modes of occurrence of mercury in coal by temperature programmed pyrolysis. *Proceedings of the*

- Combustion Institute*, 33(2), 2763–2769.
<https://doi.org/http://dx.doi.org/10.1016/j.proci.2010.06.108>
- Mac Naughton, M. G., & James, R. O. (1974). Adsorption of aqueous mercury (II) complexes at the oxide/water interface. *Journal of Colloid and Interface Science*, 47(2), 431–440. [https://doi.org/https://doi.org/10.1016/0021-9797\(74\)90275-6](https://doi.org/https://doi.org/10.1016/0021-9797(74)90275-6)
- Mahaffey, K. R., Clickner, R. P., & Bodurow, C. C. (2004). Blood organic mercury and dietary mercury intake: National Health and Nutrition Examination Survey, 1999 and 2000. *Environmental Health Perspectives*, 112(5), 562–570. Retrieved from <http://www.ncbi.nlm.nih.gov/pmc/articles/PMC1241922/>
- Manceau, A., & Nagy, K. L. (2008). Relationships between Hg(II)-S bond distance and Hg(II) coordination in thiolates. *Dalton Transactions (Cambridge, England: 2003)*, (11), 1421–1425. <https://doi.org/10.1039/b718372k>
- Mashyanov, N. R., Pogarev, S. E., Panova, E. G., Panichev, N., & Ryzhov, V. (2017). Determination of mercury thermospecies in coal. *Fuel*, 203(Supplement C), 973–980. <https://doi.org/https://doi.org/10.1016/j.fuel.2017.03.085>
- Mason, R. P. (2005). Air-sea Exchange and Marine Boundary Layer Atmospheric Transformation of Hg and their Importance in the Global Mercury Cycle. In N. Pirrone & K. R. Mahaffey (Eds.), *Dynamics of Mercury Pollution on Regional and Global Scales: Atmospheric Processes and Human Exposures Around the World* (pp. 213–239). Boston, MA: Springer US. https://doi.org/10.1007/0-387-24494-8_10
- Mason, R. P., & Sheu, G. R. (2002). Role of the ocean in the global mercury cycle. *Global Biogeochemical Cycles*, 16(4), 14–40. <https://doi.org/10.1029/2001GB001440>
- Matsumoto, K., Sasaki, Y., & Takeuchi, T. (1972). Direct determination of mercury halides by electron impact mass spectrometry. *Analytical Chemistry*, 44(13), 2246–2247. <https://doi.org/10.1021/ac60321a031>
- Matsuyama, A., Iwasaki, H., Higaki, K., Yabuta, H., Sano, T., & Akagi, H. (1999). Basic Study on the Remediation Technology of Mercury Compound-Contaminated Soil by Low-Temperature Thermal Treatment. In R. Ebinghaus, R. R. Turner, L. D. de Lacerda, O. Vasiliev, & W. Salomons (Eds.), *Mercury Contaminated Sites: Characterization, Risk Assessment and Remediation* (pp. 421–440). Berlin, Heidelberg: Springer Berlin Heidelberg. https://doi.org/10.1007/978-3-662-03754-6_24
- Meij, R. (1992). Analysis of Coal and its By-products. *World Scientific Publishing Co .*, 299–318.
- Meij, R. (1994a). Trace element behavior in coal-fired power plants. *Fuel Processing Technology*, 39(1–3), 199–217. [https://doi.org/10.1016/0378-3820\(94\)90180-5](https://doi.org/10.1016/0378-3820(94)90180-5)
- Meij, R. (1994b). Trace element behaviour in coal fired power plants. *Fuel Processing Technology*, 39, 199–217.
- Meij, R., & te Winkel, H. (2006). Mercury emissions from coal-fired power stations: The current state of the art in the Netherlands. *The Science of the Total Environment*, 368(1), 393–396. <https://doi.org/10.1016/j.scitotenv.2005.09.083>

- Meij, R., & te Winkel, H. (2007). The emissions of heavy metals and persistent organic pollutants from modern coal-fired power stations. *Atmospheric Environment*, 41(40), 9262–9272. <https://doi.org/http://dx.doi.org/10.1016/j.atmosenv.2007.04.042>
- Milobowski, M. G., Amrhein, G. T., Kudlac, G. A., & Yurchhison, D. M. (2001). Wet FGD Enhanced Mercury Control for Coal-Fired Utility Boilers. In *Proceedings of the US EPA/DOE/EPRI Combined Power Plant Air. Pollutant Control Symposium: The Mega Symposium*. Chicago, 20-23. August. Retrieved from <http://www.babcock.com/library/Documents/br-1716.pdf>
- Monterroso, R., Argyle, M., & Fan, M. (2011). Mercury removal (Chapter 9). In *Coal gasification and its application* (William An, p. 411). Elsevier. <https://doi.org/10.1016/B978-0-8155-2049-8.10009-9>
- Moore, C., & Carpi, A. (2005). Mechanisms of the emission of mercury from soil: Role of UV radiation. *Journal of Geophysical Research: Atmospheres*, 110(D24), n/a-n/a. <https://doi.org/10.1029/2004JD005567>
- Mukherjee, A. B., Zevenhoven, R., Bhattacharya, P., Sajwan, K. S., & Kikuchi, R. (2008). Mercury flow via coal and coal utilization by-products: A global perspective. *Resources, Conservation and Recycling*, 52(4), 571–591. <https://doi.org/http://dx.doi.org/10.1016/j.resconrec.2007.09.002>
- Nagy, K. L., Manceau, A., Gasper, J. D., Ryan, J. N., & Aiken, G. R. (2011). Metallothionein-like multinuclear clusters of mercury(II) and sulfur in peat. *Environmental Science and Technology*, 45(17), 7298–7306. <https://doi.org/10.1021/es201025v>
- Nalbandian, H. (2012). *Trace element emissions from coal*. IEA Clean Coal Centre Reports.
- Neville, M., Quann, R. J., Haynes, B. S., & Sarofim, A. F. (1981). Vaporization and condensation of mineral matter during pulverized coal combustion. *Symposium (International) on Combustion*, 18(1), 1267–1274. [https://doi.org/10.1016/S0082-0784\(81\)80130-0](https://doi.org/10.1016/S0082-0784(81)80130-0)
- Niksa, S., Helble, J. J., & Fujiwara, N. (2001). Kinetic Modeling of Homogeneous Mercury Oxidation: The Importance of NO and H₂O in Predicting Oxidation in Coal-Derived Systems. *Environmental Science & Technology*, 35(18), 3701–3706. <https://doi.org/10.1021/es010728v>
- NIST Chemistry WebBook. (2014). Mass spectrum of HgCl₂ (electron ionization). Retrieved November 9, 2016, from <http://webbook.nist.gov/cgi/cbook.cgi?Spec=C7487947&Index=0&Type=Mass&Large=on&SVG=on>
- Niu, X., Guo, S., Gao, L., Cao, Y., & Wei, X.-X. (2017). Mercury Release during Thermal Treatment of Two Coal Gangues and Two Coal Slimes under N₂ and in Air. *Energy & Fuels*, 31(8), 8648–8654. <https://doi.org/10.1021/acs.energyfuels.7b00883>
- Nix, R. M. (2013). An Introduction to Surface Chemistry. Retrieved August 23, 2017, from <http://www.chem.qmul.ac.uk/surfaces/scc/>

- Noda, N., & Makino, H. (2010). Influence of operating temperature on performance of electrostatic precipitator for pulverized coal combustion boiler. *Advanced Powder Technology*, 21(4), 495–499. <https://doi.org/https://doi.org/10.1016/j.appt.2010.04.012>
- Norrby, L. J. (1991). Why is mercury liquid? Or, why do relativistic effects not get into chemistry textbooks? *Journal of Chemical Education*, 68(2), 110. <https://doi.org/10.1021/ed068p110>
- Nriagu, J. O. (1986). The Role of the Oceans as a Waste Disposal Option .
- Ochoa-González, R., Díaz-Somoano, M., & Martínez-Tarazona, M. R. (2013). Influence of Limestone Characteristics on Mercury Re-emission in WFGD Systems. *Environmental Science & Technology*, 47(6), 2974–2981. <https://doi.org/10.1021/es304090e>
- Ochoa-González, R., Díaz-Somoano, M., & Rosa Martínez-Tarazona, M. (2013). Control of Hg⁰ re-emission from gypsum slurries by means of additives in typical wet scrubber conditions. *Fuel*, 105, 112–118. <https://doi.org/http://dx.doi.org/10.1016/j.fuel.2012.05.044>
- Ochoa González, R., Díaz-Somoano, M., López Antón, M. A., & Martínez-Tarazona, M. R. (2012). Effect of adding aluminum salts to wet FGD systems upon the stabilization of mercury. *Fuel*, 96, 568–571. <https://doi.org/http://dx.doi.org/10.1016/j.fuel.2012.01.054>
- Official technical information. (2016). Official technical information. Retrieved August 19, 2016, from <http://www.te-sostanj.si/en/>
- Otero-Rey, J. R., López-Vilariño, J. M., Moreda-Piñeiro, J., Alonso-Rodríguez, E., Muniategui-Lorenzo, S., López-Mahía, P., & Prada-Rodríguez, D. (2003). As, Hg, and Se Flue Gas Sampling in a Coal-Fired Power Plant and Their Fate during Coal Combustion. *Environmental Science and Technology*, 37(22), 5262–5267. <https://doi.org/10.1021/es020949g>
- Ozaki, M., Uddin, M. A., Sasaoka, E., & Wu, S. (2008). Temperature programmed decomposition desorption of the mercury species over spent iron-based sorbents for mercury removal from coal derived fuel gas. *Fuel*, 87(17–18), 3610–3615. <https://doi.org/http://dx.doi.org/10.1016/j.fuel.2008.06.011>
- Pacyna, E. G., Pacyna, J. M., Steenhuisen, F., & Wilson, S. (2006). Global anthropogenic mercury emission inventory for 2000. *Atmospheric Environment*, 40(22), 4048–4063. <https://doi.org/http://dx.doi.org/10.1016/j.atmosenv.2006.03.041>
- Pacyna, E. G., Pacyna, J. M., Sundseth, K., Munthe, J., Kindbom, K., Wilson, S., ... Maxson, P. (2010). Global emission of mercury to the atmosphere from anthropogenic sources in 2005 and projections to 2020. *Atmospheric Environment*, 44(20), 2487–2499. <https://doi.org/http://dx.doi.org/10.1016/j.atmosenv.2009.06.009>
- Pacyna, J. M. (1982). *The spatial distribution of trace element emissions from conventional thermal power plants in Europe. Norwegian Institute for Air Research, NILU technical report* (Vol. 5).
- Pacyna, J. M., Pacyna, E. G., Steenhuisen, F., & Wilson, S. (2003). Mapping 1995 global

- anthropogenic emissions of mercury. *Atmospheric Environment*, 37, 109–117. [https://doi.org/http://dx.doi.org/10.1016/S1352-2310\(03\)00239-5](https://doi.org/http://dx.doi.org/10.1016/S1352-2310(03)00239-5)
- Pacyna, J. M., Travnikov, O., De Simone, F., Hedgecock, I. M., Sundseth, K., Pacyna, E. G., ... Kindbom, K. (2016). Current and future levels of mercury atmospheric pollution on a global scale. *Atmospheric Chemistry and Physics*, 16(19), 12495–12511. <https://doi.org/10.5194/acp-16-12495-2016>
- Park, K. S., Seo, Y.-C., Lee, S. J., & Lee, J. H. (2008). Emission and speciation of mercury from various combustion sources. *Powder Technology*, 180(1), 151–156. <https://doi.org/http://dx.doi.org/10.1016/j.powtec.2007.03.006>
- Pavlish, J. H., Sondreal, E. A., Mann, M. D., Olson, E. S., Galbreath, K. C., Laudal, D. L., & Benson, S. A. (2003). Status review of mercury control options for coal-fired power plants. *Fuel Processing Technology*, 82(2–3), 89–165. [https://doi.org/10.1016/S0378-3820\(03\)00059-6](https://doi.org/10.1016/S0378-3820(03)00059-6)
- Pires, M., Fiedler, H., & Teixeira, E. C. (1997). Geochemical distribution of trace elements in coal: modelling and environmental aspects. *Fuel*, 76(14–15), 1425–1437. [https://doi.org/10.1016/S0016-2361\(97\)00127-0](https://doi.org/10.1016/S0016-2361(97)00127-0)
- Pirrone, N., Cinnirella, S., Feng, X., Finkelman, R. B., Friedli, H. R., Leaner, J., ... Telmer, K. (2010). Global mercury emissions to the atmosphere from anthropogenic and natural sources. *Atmospheric Chemistry and Physics*, 10(13), 5951–5964. <https://doi.org/10.5194/acp-10-5951-2010>
- Pirrone, N., Costa, P., Pacyna, J. M., & Ferrara, R. (2001). Mercury emissions to the atmosphere from natural and anthropogenic sources in the Mediterranean region. *Atmospheric Environment*, 35(17), 2997–3006. [https://doi.org/http://dx.doi.org/10.1016/S1352-2310\(01\)00103-0](https://doi.org/http://dx.doi.org/10.1016/S1352-2310(01)00103-0)
- Pirrone, N., Keeler, G. J., & Nriagu, J. O. (1996). Regional differences in worldwide emissions of mercury to the atmosphere. *Atmospheric Environment*, 30(17), 2981–2987. [https://doi.org/http://dx.doi.org/10.1016/1352-2310\(95\)00498-X](https://doi.org/http://dx.doi.org/10.1016/1352-2310(95)00498-X)
- Pirrone, N., & Mason, R. P. (2009). *Mercury Fate and Transport in the Global Atmosphere: Emissions, Measurements and Models*. Springer US. <https://doi.org/10.1007/978-0-387-93958-2>
- Piskunov, A. V, Aivaz'yan, I. A., Cherkasov, V. K., & Abakumov, G. A. (2006). New paramagnetic N-heterocyclic stannylenes: An EPR study. *Journal of Organometallic Chemistry*, 691(8), 1531–1534. <https://doi.org/http://dx.doi.org/10.1016/j.jorganchem.2005.11.064>
- Presto, A. A., & Granite, E. J. (2006). Survey of Catalysts for Oxidation of Mercury in Flue Gas. *Environmental Science & Technology*, 40(18), 5601–5609. <https://doi.org/10.1021/es060504i>
- Pudasainee, D., Kim, J.-H., Yoon, Y.-S., & Seo, Y.-C. (2012). Oxidation, reemission and mass distribution of mercury in bituminous coal-fired power plants with SCR, CS-ESP and wet FGD. *Fuel*, 93(Supplement C), 312–318. <https://doi.org/https://doi.org/10.1016/j.fuel.2011.10.012>

- Querol, X., Fernández-Turiel, J., & López-Soler, A. (1995). Trace elements in coal and their behaviour during combustion in a large power station. *Fuel*, 74(3), 331–343. [https://doi.org/10.1016/0016-2361\(95\)93464-O](https://doi.org/10.1016/0016-2361(95)93464-O)
- Querol, X., Juan, R., Lopez-Soler, A., Fernandez-Turiel, J. L., & Ruiz, C. R. (1996). Mobility of trace elements from coal and combustion wastes. *Fuel*, 75(7), 821–838. [https://doi.org/10.1016/0016-2361\(96\)00027-0](https://doi.org/10.1016/0016-2361(96)00027-0)
- Rakić, V., & Damjanović, L. (2013). Temperature-Programmed Desorption (TPD) Methods. In A. Auroux (Ed.), *Calorimetry and Thermal Methods in Catalysis* (pp. 131–174). Berlin, Heidelberg: Springer Berlin Heidelberg. https://doi.org/10.1007/978-3-642-11954-5_4
- Rallo, M., Lopez-Anton, M. A., Perry, R., & Maroto-Valer, M. M. (2010). Mercury speciation in gypsums produced from flue gas desulfurization by temperature programmed decomposition. *Fuel*, 89(8), 2157–2159. <https://doi.org/http://dx.doi.org/10.1016/j.fuel.2010.03.037>
- Raposo, C., Windmüller, C. C., & Durão Júnior, W. A. (2003). Mercury speciation in fluorescent lamps by thermal release analysis. *Waste Management*, 23(10), 879–886. [https://doi.org/http://dx.doi.org/10.1016/S0956-053X\(03\)00089-8](https://doi.org/http://dx.doi.org/10.1016/S0956-053X(03)00089-8)
- Ratafia-Brown, J. A. (1994). Overview of trace element partitioning in flames and furnaces of utility coal-fired boilers. *Fuel Processing Technology*, 39(1–3), 139–157. [https://doi.org/10.1016/0378-3820\(94\)90177-5](https://doi.org/10.1016/0378-3820(94)90177-5)
- Ravel, B., & Newville, M. (2005). ATHENA, ARTEMIS, HEPHAESTUS: Data analysis for X-ray absorption spectroscopy using IFEFFIT. In *Journal of Synchrotron Radiation* (Vol. 12, pp. 537–541). <https://doi.org/10.1107/S0909049505012719>
- Reis, A. T., Coelho, J. P., Rodrigues, S. M., Rocha, R., Davidson, C. M., Duarte, A. C., & Pereira, E. (2012). Development and validation of a simple thermo-desorption technique for mercury speciation in soils and sediments. *Talanta*, 99, 363–368. <https://doi.org/http://dx.doi.org/10.1016/j.talanta.2012.05.065>
- Reis, A. T., Coelho, J. P., Rucandio, I., Davidson, C. M., Duarte, A. C., & Pereira, E. (2015). Thermo-desorption: A valid tool for mercury speciation in soils and sediments? *Geoderma*, 237, 98–104. <https://doi.org/http://dx.doi.org/10.1016/j.geoderma.2014.08.019>
- Reis, A. T., Rodrigues, S. M., Davidson, C. M., Pereira, E., & Duarte, A. C. (2010). Extractability and mobility of mercury from agricultural soils surrounding industrial and mining contaminated areas. *Chemosphere*, 81(11), 1369–1377. <https://doi.org/http://dx.doi.org/10.1016/j.chemosphere.2010.09.030>
- Reis, N. W., Osborne, T. R., Holdsworth, G., & Hadden, C. (1989). Distribution of mercury species in soil from a mercury-contaminated site. *Water, Air, and Soil Pollution*, 45(1), 105–113. <https://doi.org/10.1007/BF00208581>
- Riedel, S., & Kaupp, M. (2009). The highest oxidation states of the transition metal elements. *Coordination Chemistry Reviews*, 253(5), 606–624. <https://doi.org/http://dx.doi.org/10.1016/j.ccr.2008.07.014>

- Rubio, R., & Rauret, G. (1996). Validation of the methods for heavy metal speciation in soils and sediments. *Journal of Radioanalytical and Nuclear Chemistry*, 208, 529–540.
- Sakamoto, H., Tomiyasu, T., & Yonehara, N. (1992). Differential Determination of Organic Mercury, Mercury(II) Oxide and Mercury(II) Sulfide in Sediments by Cold Vapor Atomic Absorption Spectrometry. *Analytical Sciences*, 8(1), 35–39. <https://doi.org/10.2116/analsci.8.35>
- Sakamoto, M., Kubota, M., Liu, X. J., Murata, K., Nakai, K., & Satoh, H. (2004). Maternal and Fetal Mercury and n-3 Polyunsaturated Fatty Acids as a Risk and Benefit of Fish Consumption to Fetus. *Environmental Science & Technology*, 38(14), 3860–3863. <https://doi.org/10.1021/es034983m>
- Sakamoto, M., Kubota, M., Matsumoto, S., Nakano, A., & Akagi, H. (2002). Declining risk of methylmercury exposure to infants during lactation. *Environmental Research*, 90(3), 185–198.
- Saniewska, D., & Beldowska, M. (2017). Mercury fractionation in soil and sediment samples using thermo-desorption method. *Talanta*, 168, 152–161. <https://doi.org/http://dx.doi.org/10.1016/j.talanta.2017.03.026>
- Sargent & Lundy. (2003). *Wet flue gas desulphurization technology evaluation*. Chicago, USA. Retrieved from http://www.graymont.com/sites/default/files/pdf/tech_paper/wet_flue_gas_desulfurization_technology_evaluation_0_1.pdf
- Schoefield, K. (2004). Elegant elusive oxidation mechanism of mercury. *Prepr. Pap. Am. Chem. Soc. Div. Fuel Chem*, 49(1), 294–295.
- Schroeder, K., & Kairies, C. (2005). Distribution of mercury in FGD byproducts. In *2005 World of Coal Ash (WOCA)* (p. 7). Lexington, Kentucky, USA.
- Schroeder, S. L. M., & Gottfried, M. (2002). Temperature-Programmed Desorption (TPD) Thermal Desorption Spectroscopy (TDS), 22.
- Schroeder, W. H., & Munthe, J. (1998). Atmospheric mercury—An overview. *Atmospheric Environment*, 32(5), 809–822. [https://doi.org/http://dx.doi.org/10.1016/S1352-2310\(97\)00293-8](https://doi.org/http://dx.doi.org/10.1016/S1352-2310(97)00293-8)
- Sedlar, M. (2014). *Temperature fractionation of mercury in solid samples*. Jožef Stefan international postgraduate school.
- Sedlar, M., Pavlin, M., Jaćimović, R., Stergaršek, A., Frkal, P., & Horvat, M. (2015). Temperature Fractionation (TF) of Hg Compounds in Gypsum from Wet Flue Gas Desulfurization System of the Coal Fired Thermal Power Plant (TPP). *American Journal of Analytical Chemistry*, Vol.6 No.1(November), 939–956.
- Sedlar, M., Pavlin, M., Popovič, A., & Horvat, M. (2015). Temperature stability of mercury compounds in solid substrates. *Open Chemistry*, 13, 404–419. <https://doi.org/10.1515/chem-2015-0051>
- Selin, N. E. (2009). Global Biogeochemical Cycling of Mercury: A Review. *Annual Review of Environment and Resources*, 34(1), 43–63. <https://doi.org/10.1146/annurev.enviro.051308.084314>

- Senior, C. (2004). *Oxidation of mercury across SCR catalysts in coal-fired power plants burning low rank fuels, Final Report*. Salt Lake City. <https://doi.org/DE-FC26-03NT41728>
- Senior, C. L., & Johnson, S. A. (2005). Impact of Carbon-in-Ash on Mercury Removal across Particulate Control Devices in Coal-Fired Power Plants. *Energy & Fuels*, 19(3), 859–863. <https://doi.org/10.1021/ef049861+>
- Senior, C. L., Sarofim, A. F., Zeng, T., Helble, J. J., & Mamani-Paco, R. (2000). Gas-phase transformations of mercury in coal-fired power plants. *Fuel Processing Technology*, 63(2), 197–213. [https://doi.org/http://dx.doi.org/10.1016/S0378-3820\(99\)00097-1](https://doi.org/http://dx.doi.org/10.1016/S0378-3820(99)00097-1)
- Serrano, S., Vlassopoulos, D., Bessinger, B., & O'Day, P. A. (2012). Immobilization of Hg(II) by Coprecipitation in Sulfate-Cement Systems. *Environmental Science & Technology*, 46(12), 6767–6775. <https://doi.org/10.1021/es202939v>
- Shah, P., Strezov, V., Prince, K., & Nelson, P. F. (2008). Speciation of As, Cr, Se and Hg under coal fired power station conditions. *Fuel*, 87, 1859–1869. <https://doi.org/10.1016/j.fuel.2007.12.001>
- Shuetze, J., Kunth, D., Weissbach, S., & Koeser, H. (2012). Mercury Vapor Pressure of Flue Gas Desulfurization Scrubber Suspensions: Effects of pH Level, Gypsum, and Iron. *Environmental Science and Technology*, 46, 3008–3013. Retrieved from <https://www.ncbi.nlm.nih.gov/pubmed/22324514>
- Shuvaeva, O. V, Gustaytis, M. A., & Anoshin, G. N. (2008). Mercury speciation in environmental solid samples using thermal release technique with atomic absorption detection. *Analytica Chimica Acta*, 621(2), 148–154. <https://doi.org/http://dx.doi.org/10.1016/j.aca.2008.05.034>
- Simpson, W. R., von Glasow, R., Riedel, K., Anderson, P., Ariya, P., Bottenheim, J., ... Wolff, E. (2007). Halogens and their role in polar boundary-layer ozone depletion. *Atmos. Chem. Phys.*, 7(16), 4375–4418. <https://doi.org/10.5194/acp-7-4375-2007>
- Skyllberg, U. (2010). Mercury Biogeochemistry in Soils and Sediments. *Developments in Soil Science*, 34, 379–410. [https://doi.org/http://dx.doi.org/10.1016/S0166-2481\(10\)34013-X](https://doi.org/http://dx.doi.org/10.1016/S0166-2481(10)34013-X)
- Skyllberg, U. (2012). Chemical speciation of mercury in soil and sediment. In G. Liu, Y. Cai, & N. O'Driscoll (Eds.), *Environmental Chemistry and Toxicology of Mercury* (First edit, pp. 219–258). John Wiley & Sons, Inc.
- Sladek, C., Gustin, M. S., Kim, C. S., & Biester, H. (2002). Application of three methods for determining mercury speciation in mine waste. *Geochemistry: Exploration, Environment, Analysis*, 2(4), 369 LP-375. Retrieved from <http://geea.lyellcollection.org/content/2/4/369.abstract>
- Smith M. (1987). *Trace elements from coal combustion. IEA Coal Research Report, IEA CR/01*.
- Smodiš, B., Jaćimović, R., Medin, G., & Jovanović, S. (1993). Instrumental neutron activation analysis of sediment reference materials using the k0-standardization method. *Journal of Radioanalytical and Nuclear Chemistry*, 169(1), 177–185.

- <https://doi.org/10.1007/BF02046792>
- Snoj Tratnik, J., Falnoga, I., Trdin, A., Mazej, D., Fajon, V., Miklavčič, A., ... Horvat, M. (2017). Prenatal mercury exposure, neurodevelopment and apolipoprotein E genetic polymorphism. *Environmental Research*, 152(Supplement C), 375–385. <https://doi.org/https://doi.org/10.1016/j.envres.2016.08.035>
- Somorjai, G. A. (1969). Studies of the Sublimation Mechanism of Solids. *Advances in High Temperature Chemistry*, 2, 203–234. [https://doi.org/http://dx.doi.org/10.1016/S0065-2741\(13\)70011-3](https://doi.org/http://dx.doi.org/10.1016/S0065-2741(13)70011-3)
- Somorjai, G. A., & Lester, J. E. (1967). Evaporation mechanism of solids. *Progress in Solid State Chemistry*, 4, 1–52. [https://doi.org/http://dx.doi.org/10.1016/0079-6786\(67\)90004-0](https://doi.org/http://dx.doi.org/10.1016/0079-6786(67)90004-0)
- Spears, D. A., & Martinez-Tarrazona, M. R. (2004). Trace elements in combustion residues from a UK power station. *Fuel*, 83, 2265–2270. <https://doi.org/10.1016/j.fuel.2004.06.025>
- Srivastava, R. K. (2002). *Controlling SO2 Emissions: A Review of Technologies*. Washington, D.C. Retrieved from [http://plainsjustice.org/files/ElkRun/Elk_Run_References/EPA Publications/EPA_600_R-00_093 controlling so2 emissions.pdf](http://plainsjustice.org/files/ElkRun/Elk_Run_References/EPA_Publications/EPA_600_R-00_093_controlling_so2_emissions.pdf)
- Srivastava, R. K., Hutson, N., Martin, B., Princiotta, F., & Staudt, J. (2006). Control of Mercury Emissions from Coal-Fired Electric Utility Boilers. *Environmental Science & Technology*, 40(5), 1385–1393. <https://doi.org/10.1021/es062639u>
- Stergaršek, A., Horvat, M., Frkal, P., Ribeiro Guevara, S., & Kocjančič, R. (2013). Removal of Hg⁰ in wet FGD by catalytic oxidation with air – A contribution to the development of a process chemical model. *Fuel*, 107, 183–191. <https://doi.org/10.1016/j.fuel.2012.08.001>
- Stergaršek, A., Horvat, M., Frkal, P., & Stergaršek, J. (2010). Removal of Hg⁰ from flue gases in wet FGD by catalytic oxidation with air – An experimental study. *Fuel*, 89(11), 3167–3177. <https://doi.org/10.1016/j.fuel.2010.04.006>
- Stergaršek, A., Horvat, M., Kotnik, J., Tratnik, J., Frkal, P., Kocman, D., ... Čujež, M. (2008). The role of flue gas desulphurisation in mercury speciation and distribution in a lignite burning power plant. *Fuel*, 87(17–18), 3504–3512. <https://doi.org/10.1016/j.fuel.2008.06.003>
- Stergaršek, A., Kocjančič, R., & Gerbec, M. (1996). Experimental determination and modelling of the absorption of SO₂ into a single drop based on pH measurement. *Chemical Engineering Science*, 51(23), 5081–5089. [https://doi.org/10.1016/S0009-2509\(96\)00346-6](https://doi.org/10.1016/S0009-2509(96)00346-6)
- Stern, A. H., & Smith, A. E. (2003). An assessment of the cord blood:maternal blood methylmercury ratio: implications for risk assessment. *Environmental Health Perspectives*, 111(12), 1465–1470. Retrieved from <http://www.ncbi.nlm.nih.gov/pmc/articles/PMC1241648/>
- Streets, D. G., Devane, M. K., Lu, Z., Bond, T. C., Sunderland, E. M., & Jacob, D. J.

- (2011). All-Time Releases of Mercury to the Atmosphere from Human Activities. *Environmental Science & Technology*, 45(24), 10485–10491. <https://doi.org/10.1021/es202765m>
- Streets, D. G., Horowitz, H. M., Jacob, D. J., Lu, Z., Levin, L., ter Schure, A. F. H., & Sunderland, E. M. (2017). Total Mercury Released to the Environment by Human Activities. *Environmental Science & Technology*, 51(11), 5969–5977. <https://doi.org/10.1021/acs.est.7b00451>
- Stropnik, B., Byrne, A. R., Smodiš, B., & Jačimović, R. (1994). Air pollution monitoring in the Šalek valley Part 2: Elemental composition of size-fractionated lignite coal-combustion particles during Šoštanj TPP peration. *Acta Chimica Slovenica*, 41(1), 65–82.
- Suárez-Ruiz, I., & Parra, J. B. (2007). Relationship between Textural Properties, Fly Ash Carbons, and Hg Capture in Fly Ashes Derived from the Combustion of Anthracitic Pulverized Feed Blends. *Energy & Fuels*, 21(4), 1915–1923. <https://doi.org/10.1021/ef060656z>
- Subir, M., Ariya, P. A., & Dastoor, A. P. (2012). A review of the sources of uncertainties in atmospheric mercury modeling II. Mercury surface and heterogeneous chemistry – A missing link. *Atmospheric Environment*, 46, 1–10. <https://doi.org/http://dx.doi.org/10.1016/j.atmosenv.2011.07.047>
- Sui, Z., Zhang, Y., Li, W., Orndorff, W., Cao, Y., & Pan, W.-P. (2015). Partitioning effect of mercury content and speciation in gypsum slurry as a function of time. *Journal of Thermal Analysis and Calorimetry*, 119(3), 1611–1618. <https://doi.org/10.1007/s10973-015-4403-9>
- Sun, M., Cheng, G., Lu, R., Tang, T., Baig, S. A., & Xu, X. (2014). Characterization of Hg⁰ re-emission and Hg²⁺ + leaching potential from flue gas desulfurization (FGD) gypsum. *Fuel Processing Technology*, 118, 28–33. <https://doi.org/http://dx.doi.org/10.1016/j.fuproc.2013.08.002>
- Sun, M., Hou, J., Cheng, G., Baig, S. A., Tan, L., & Xu, X. (2014). The relationship between speciation and release ability of mercury in flue gas desulfurization (FGD) gypsum. *Fuel*, 125, 66–72. <https://doi.org/http://dx.doi.org/10.1016/j.fuel.2014.02.012>
- Sun, M., Lou, Z., Cheng, G., Baig, S. A., Fang, L., Zhou, X., ... Xu, X. (2015). Process migration and transformation of mercury in simulated wet flue gas desulfurization slurry system. *Fuel*, 140, 136–142. <https://doi.org/http://dx.doi.org/10.1016/j.fuel.2014.09.094>
- Swaine, D. J. (1990). *Trace Elements in Coal*. London: Butterworths.
- Swanson, S. M., Engle, M. A., Ruppert, L. F., Affolter, R. H., & Jones, K. B. (2013). Partitioning of selected trace elements in coal combustion products from two coal-burning power plants in the United States. *International Journal of Coal Geology*, 113, 116–126. <https://doi.org/10.1016/j.coal.2012.08.010>
- Taerakul, P., Sun, P., Golightly, D. W., Walker, H. W., & Weavers, L. K. (2006).

- Distribution of Arsenic and Mercury in Lime Spray Dryer Ash. *Energy & Fuels*, 20(4), 1521–1527. <https://doi.org/10.1021/ef060029+>
- Talbot, R., Mao, H., Feddersen, D., Smith, M., Kim, S. Y., Sive, B., ... Russo, R. (2011). Comparison of Particulate Mercury Measured with Manual and Automated Methods. *Atmosphere*. <https://doi.org/10.3390/atmos2010001>
- Tang, Q., Liu, G., Yan, Z., & Sun, R. (2012). Distribution and fate of environmentally sensitive elements (arsenic, mercury, stibium and selenium) in coal-fired power plants at Huainan, Anhui, China. *Fuel*, 95, 334–339. <https://doi.org/10.1016/j.fuel.2011.12.052>
- Tang, Q., Liu, G., Zhou, C., & Sun, R. (2013). Distribution of trace elements in feed coal and combustion residues from two coal-fired power plants at Huainan, Anhui, China. *Fuel*, 107, 315–322. <https://doi.org/10.1016/j.fuel.2013.01.009>
- Tang, T., Xu, J., Lu, R., Wo, J., & Xu, X. (2010). Enhanced Hg²⁺ removal and Hg⁰ re-emission control from wet fuel gas desulfurization liquors with additives. *Fuel*, 89(12), 3613–3617. <https://doi.org/http://dx.doi.org/10.1016/j.fuel.2010.07.045>
- Tariq, S. A., & Hill, J. O. (1981). Thermal analysis of mercury(I) sulfate and mercury(II) sulfate. *Journal of Thermal Analysis*, 21(2), 277–281. <https://doi.org/10.1007/BF01914211>
- Templeton, D. M., Ariese, F., Cornelis, R., Danielsson, L.-G., Muntau, H., & Lobinski, R. (2000). *Guidelines for Terms Related to Chemical Speciation and Fractionation of Elements. Definitions, Structural Aspects, and Methodological Approaches (IUPAC Recommendations 2000)*. *Pure and Applied Chemistry* 72 (2000) (Vol. 72). <https://doi.org/10.1351/pac200072081453>
- Tewalt, S. J., Bragg, L. J., & Finkelman, R. B. (2001). *Mercury in U.S. coal; abundance, distribution, and modes of occurrence* (Online Ver). *Fact Sheet*. Retrieved from <http://pubs.er.usgs.gov/publication/fs09501>
- Tiffreau, C., Lützenkirchen, J., & Behra, P. (1995). Modeling the Adsorption of Mercury(II) on (Hydr)oxides. *Journal of Colloid and Interface Science*, 172(1), 82–93. <https://doi.org/http://dx.doi.org/10.1006/jcis.1995.1228>
- Tossell, J. A., & Vaughan, D. J. (1981). Relationships between valence orbital binding energies and crystal structures in compounds of copper, silver, gold, zinc, cadmium, and mercury. *Inorganic Chemistry*, 20(10), 3333–3340. <https://doi.org/10.1021/ic50224a038>
- U.S. EPA. (2003). *U.S. EPA-452/F-03-034, Air pollutant control technology fact sheet*.
- Uddin, M. A., Ozaki, M., Sasaoka, E., & Wu, S. (2009). Temperature-Programmed Decomposition Desorption of Mercury Species over Activated Carbon Sorbents for Mercury Removal from Coal-Derived Fuel Gas. *Energy & Fuels*, 23(10), 4710–4716. <https://doi.org/10.1021/ef801068z>
- Ullrich, S. M., Tanton, T. W., & Abdrashitova, S. A. (2001). Mercury in the Aquatic Environment: A Review of Factors Affecting Methylation. *Critical Reviews in Environmental Science and Technology*, 31(3), 241–293.

- <https://doi.org/10.1080/20016491089226>
- UNEP. (2002). *Global mercury assessment*. Geneva, Switzerland.
- UNEP. (2013a). *Global Mercury Assessment 2013: Sources, Emissions, Releases and environmental Transport*. Geneva, Switzerland.
- UNEP. (2013b). *Minamata Convention on Mercury*. Geneva, Switzerland. Retrieved from http://www.mercuryconvention.org/Portals/11/documents/Booklets/Minamata Convention on Mercury_booklet_English.pdf
- Uradni list 103/2011. Uredba o odpadkih (2011).
- Van Loon, L., Mader, E., & Scott, S. L. (2000). Reduction of the Aqueous Mercuric Ion by Sulfite: UV Spectrum of HgSO₃ and Its Intramolecular Redox Reaction. *The Journal of Physical Chemistry A*, 104(8), 1621–1626. <https://doi.org/10.1021/jp994268s>
- Vassilev, S. V., Eskenazy, G. M., & Vassileva, C. G. (2001). Behaviour of elements and minerals during preparation and combustion of the Pernik coal, Bulgaria. *Fuel Processing Technology*, 72(2), 103–129. [https://doi.org/10.1016/S0378-3820\(01\)00186-2](https://doi.org/10.1016/S0378-3820(01)00186-2)
- Vassilev, S. V., Kitano, K., & Vassileva, C. G. (1996). Some relationships between coal rank and chemical and mineral composition. *Fuel*, 75(13), 1537–1542. [https://doi.org/10.1016/0016-2361\(96\)00116-0](https://doi.org/10.1016/0016-2361(96)00116-0)
- Vejahati, F., Xu, Z., & Gupta, R. (2010). Trace elements in coal: Associations with coal and minerals and their behavior during coal utilization - A review. *Fuel*, 89(4), 904–911. <https://doi.org/10.1016/j.fuel.2009.06.013>
- Wagman, D. D., Evans, W. H., Parker, V. B., Haiow, I., Bailey, S. M., & Schumm, R. H. (1968). *Selected Values of Chemical Thermodynamic Properties*. U.S. Government Printing Office, Washington, D.C.
- Wang, J., Feng, X., Anderson, C. W. N., Qiu, G., Ping, L., & Bao, Z. (2011). Ammonium thiosulphate enhanced phytoextraction from mercury contaminated soil – Results from a greenhouse study. *Journal of Hazardous Materials*, 186(1), 119–127. <https://doi.org/http://dx.doi.org/10.1016/j.jhazmat.2010.10.097>
- Wang, J., & Yang, P. (2017). Potential flue gas desulfurization gypsum utilization in agriculture: A comprehensive review. *Renewable and Sustainable Energy Reviews*. <https://doi.org/http://dx.doi.org/10.1016/j.rser.2017.07.029>
- Wang, Q., Liu, Y., & Wu, Z. (2018). Laboratory Study on Mercury Release of the Gypsum from the Mercury Coremoval Wet Flue Gas Desulfurization System with Additives. *Energy & Fuels*. <https://doi.org/10.1021/acs.energyfuels.7b02088>
- Wang, S. X., Zhang, L., Li, G. H., Wu, Y., Hao, J. M., Pirrone, N., ... Ancora, M. P. (2010). Mercury emission and speciation of coal-fired power plants in China. *Atmospheric Chemistry and Physics*, 10(3), 1183–1192. <https://doi.org/10.5194/acp-10-1183-2010>
- Wang, X., Andrews, L., Riedel, S., & Kaupp, M. (2007). Mercury Is a Transition Metal: The First Experimental Evidence for HgF₄. *Angewandte Chemie International Edition*, 46(44), 8371–8375. <https://doi.org/10.1002/anie.200703710>

- Wang, Y., Liu, Y., Wu, Z., Mo, J., & Cheng, B. (2010). Experimental study on the absorption behaviors of gas phase bivalent mercury in Ca-based wet flue gas desulfurization slurry system. *Journal of Hazardous Materials*, 183(1), 902–907. <https://doi.org/http://dx.doi.org/10.1016/j.jhazmat.2010.07.114>
- Watling, R. J., Davis, G. R., & Meyer, W. J. (1972). Trace identification of mercury compounds as a guide to sulphide mineralization at Keel, Erie. In *4th International Geochemical Exploration Symposium* (pp. 59–69). London.
- WHO. (1990). *Methylmercury. Environmental Health Criteria 101*. Geneva, Switzerland.
- Windmüller, C. C., Wilken, R.-D., & Jardim, W. D. F. (1996). Mercury speciation in contaminated soils by thermal release analysis. *Water, Air, and Soil Pollution*, 89(3), 399–416. <https://doi.org/10.1007/BF00171644>
- Wo, J., Zhang, M., Cheng, X., Zhong, X., Xu, J., & Xu, X. (2009). Hg²⁺ reduction and re-emission from simulated wet flue gas desulfurization liquors. *Journal of Hazardous Materials*, 172(2–3), 1106–1110. <https://doi.org/10.1016/j.jhazmat.2009.07.103>
- Wong, J., Lytle, F. W., Messmer, R. P., & Maylotte, D. H. (1984). K -edge absorption spectra of selected vanadium compounds. *Physical Review B*, 30(10), 5596–5610. <https://doi.org/10.1103/PhysRevB.30.5596>
- Wu, S., Uddin, M. A., Nagano, S., Ozaki, M., & Sasaoka, E. (2011). Fundamental Study on Decomposition Characteristics of Mercury Compounds over Solid Powder by Temperature-Programmed Decomposition Desorption Mass Spectrometry. *Energy & Fuels*, 25(1), 144–153. <https://doi.org/10.1021/ef1009499>
- Xia, K., Weesner, F., Bleam, W. F., Helmke, P. A., Bloom, P. R., & Skyllberg, U. L. (1998). XANES Studies of Oxidation States of Sulfur in Aquatic and Soil Humic Substances. *Soil Science Society of America Journal*, 62, 1240–1246. <https://doi.org/10.2136/sssaj1998.03615995006200050014x>
- Xilei, L., Corte, F., Moens, L., Simonits, A., & Hoste, J. (1984). Computer-assisted reactor NAA of geological and other reference materials, using the k₀-standardization method: Evaluation of the accuracy. *Journal of Radioanalytical and Nuclear Chemistry*, 81(2), 333–343. <https://doi.org/10.1007/BF02135386>
- Xu, M., Yan, R., Zheng, C., Qiao, Y., Han, J., & Sheng, C. (2004). Status of trace element emission in a coal combustion process: A review. *Fuel Processing Technology*, 85, 215–237. [https://doi.org/10.1016/S0378-3820\(03\)00174-7](https://doi.org/10.1016/S0378-3820(03)00174-7)
- Xu, P., Zhang, B., Zeng, X., Xu, Y., Luo, G., & Yao, H. (2017). Influence of Hg occurrence in coal on accuracy of Hg direct measurement based on thermal decomposition. *International Journal of Coal Geology*, 170(Supplement C), 14–18. <https://doi.org/https://doi.org/10.1016/j.coal.2016.08.023>
- Yan, R., Gauthier, D., & Flamant, G. (2001). Partitioning of trace elements in the flue gas from coal combustion. *Combustion and Flame*, 125(1–2), 942–954. [https://doi.org/10.1016/S0010-2180\(00\)00239-X](https://doi.org/10.1016/S0010-2180(00)00239-X)
- Yokoyama, T., Asakura, K., Matsuda, H., Ito, S., & Noda, N. (2000). Mercury emissions from a coal-fired power plant in Japan. *Science of The Total Environment*, 259(1),

- 97–103. [https://doi.org/http://dx.doi.org/10.1016/S0048-9697\(00\)00552-0](https://doi.org/http://dx.doi.org/10.1016/S0048-9697(00)00552-0)
- Yudovich, Y. ., & Ketris, M. P. (2005a). Mercury in coal: a review: Part 1. Geochemistry. *International Journal of Coal Geology*, 62(3), 107–134. <https://doi.org/http://dx.doi.org/10.1016/j.coal.2004.11.002>
- Yudovich, Y. E., & Ketris, M. P. (2005b). Mercury in coal: a review Part 2. Coal use and environmental problems. *International Journal of Coal Geology*, 62(3), 135–165. <https://doi.org/http://dx.doi.org/10.1016/j.coal.2004.11.003>
- Zhang, L., Wang, S., Wu, Q., Wang, F., Lin, C.-J., Zhang, L., ... Hao, J. (2016). Mercury transformation and speciation in flue gases from anthropogenic emission sources: a critical review. *Atmospheric Chemistry and Physics*, 16(4), 2417–2433. <https://doi.org/10.5194/acp-16-2417-2016>
- Zhang, L., Wang, S. X., Wang, F. Y., Yang, H., Wu, Q. R., & Hao, M. J. (2013). Mercury transformation and removal in three coal-fired power plants with selective catalytic reduction systems. In *The 11th International Conference on Mercury as a Global Pollutant*.
- Zhang, Y., Yang, J., Yu, X., Sun, P., Zhao, Y., Zhang, J., ... Zheng, C. (2017). Migration and emission characteristics of Hg in coal-fired power plant of China with ultra low emission air pollution control devices. *Fuel Processing Technology*, 158, 272–280. <https://doi.org/http://dx.doi.org/10.1016/j.fuproc.2017.01.020>
- Zhao, S., Duan, Y., Tan, H., Liu, M., Wang, X., Wu, L., ... Tang, H. (2016). Migration and Emission Characteristics of Trace Elements in a 660 MW Coal-Fired Power Plant of China. *Energy & Fuels*, 30(7), 5937–5944. <https://doi.org/10.1021/acs.energyfuels.6b00450>
- Zheng, C., Wang, L., Zhang, Y., Zhang, J., Zhao, H., Zhou, J., ... Cen, K. (2017). Partitioning of Hazardous Trace Elements among Air Pollution Control Devices in Ultra-Low-Emission Coal-Fired Power Plants. *Energy & Fuels*, 31(6), 6334–6344. <https://doi.org/10.1021/acs.energyfuels.7b00894>
- Zheng, L., Liu, G., & Chou, C.-L. (2007). The distribution, occurrence and environmental effect of mercury in Chinese coals. *Science of The Total Environment*, 384(1), 374–383. <https://doi.org/http://dx.doi.org/10.1016/j.scitotenv.2007.05.037>
- Zhou, J., Zhongyang, L., Yanqun, Z., & Mengxiang, F. (2013). Mercury Emission and its Control in Chinese Coal-Fired Power Plants. In P. M. F. Prof. Jinsong Zhou, Prof. Zhongyang Luo, Dr. Yanqun Zhu (Ed.), *Advanced Topics in Science and Technology in China* (pp. 105–149). College of Mechanical and Energy Engineering, Zhejiang University, 310027, P.R. China: Springer Berlin Heidelberg. <https://doi.org/10.1007/978-3-642-37874-4>
- Zhu, Z.-W., Zhuo, Y.-Q., Fan, Y.-M., & Wang, Z.-P. (2017). Mechanism of mercury vapor release from flue gas desulfurization gypsum. *Fuel Processing Technology*, 156, 485–490. <https://doi.org/http://dx.doi.org/10.1016/j.fuproc.2016.10.015>
- Zhu, Z., Zhuo, Y., Fan, Y., & Wang, Z. (2016). Fate of mercury in flue gas desulfurization gypsum determined by Temperature Programmed Decomposition and Sequential

- Chemical Extraction. *Journal of Environmental Sciences*, *43*, 169–176.
<https://doi.org/http://dx.doi.org/10.1016/j.jes.2015.09.011>
- Zou, R., Zeng, X., Luo, G., Qiu, Y., Zhang, B., Xu, Y., ... Yao, H. (2016). Mercury stability of byproducts from wet flue gas desulfurization devices. *Fuel*, *186*, 215–221.
<https://doi.org/http://dx.doi.org/10.1016/j.fuel.2016.08.023>

Bibliography

Publications Related to the Thesis

Journal Articles

Pavlin, M., Popovič, A., Jaćimović, R., Horvat, M. (2018). Mercury fractionation in gypsum using temperature desorption and mass spectrometric detection. *Open Chemistry* (In press).

Sedlar, M., Pavlin, M., Jaćimović, R., Strgarsek, A., Frkal, P., Hovav, M. (2015). Temperature Fractionation (TF) of Hg compounds in gypsum from wet flue gas desulfurization system of the coal fired Thermal Power Plant (TPP). *American journal of analytical chemistry*, 6(12), 939-956. doi: 10.4236/ajac.2015.612090.

Sedlar, M., Pavlin, M., Popović, A., Horvat, M. (2014). Temperature stability of mercury compounds in solid substrates. *Open chemistry*, 13(1), 404-419, doi: 10.1515/chem-2015-0051.

Conference Paper

Pavlin, M., Popović, A., Jaćimović, R., Horvat, M. (2016). A study of the thermal release of mercury compounds in FGD gypsum from the Šoštanj Thermal Power Plant using mass spectrometry. In: *Pavlin, M. (ed.), et al. Zbornik: 1. del = Proceedings: part 1. Ljubljana: Mednarodna podiplomska šola Jožefa Stefana*, 91-95. http://ipssc.mps.si/2016/Proceedings8_IPSSC_2016_Part1.pdf.

Sedlar, M., Pavlin, M., Kocjančič, R., Bašič, S., Horvat, M. (2013). Development of the method for temperature fractionation of mercury in solid samples. In: *6th International Conference on Clean Coal Technologies, CCT2013, 12-16 May 2013, Thessaloniki, Greece*. London: IEA Clean Coal Centre.

Sedlar, M., Pavlin, M., Bašič, S., Horvat, M. (2013). Stability of mercury compounds at high temperatures. In: *Trdin, N. (ed.), et al. Zbornik = Proceedings, 5. študentska konferenca Mednarodne podiplomske šole Jožefa Stefana = 5th Jožef Stefan International Postgraduate School Students Conference*, 23. maj 2013, Ljubljana, Slovenija. Ljubljana: Mednarodna podiplomska šola Jožefa Stefana. 60-69.

Pavlin, M., Popović, A., Horvat, M. Thermal desorption of Hg compounds from the WFGD gypsum studied by mass spectrometric detection. In: *Abstracts, 13th International Conference on Mercury as a Global Pollutant*, Providence, ICMGP 2017, Rhode Island, July 16-21, 2017

Pavlin, M., Sedlar, M., Jaćimović, R., Frkal, P., Stergaršek, A., Horvat, M. (2016). Distribution of mercury and other trace elements in by-products of Šoštanj Thermal Power plant. In: Mihevc, S. (ed.), Prunk, M. (ed.), Pungerčar, J. (ed.). *10th Young researchers' day, 31 March, 2016, Ljubljana: program and abstract book*. Ljubljana: Institut Jožef Stefan. 2016, 39.

Pavlin, M., Popović, A., Jaćimović, R., Horvat, M. Properties of mercury in gypsum studied by mass spectrometry technique in support to safe disposal and/or use. In: *Abstract book, 18th International Conference on Heavy Metals in the Environment, ICHMET 2016, 12 to 15 September 2016, Ghent, Belgium. Gent: Universiteit Gent. 2016*, 561-562.

Horvat, M., Pavlin, M., Sedlar, M., Jaćimović, R., Popović, A., Frkal, P., Stergaršek, A., Gao, X. (2015). Mercury and other major and trace elements in gypsum samples from WFGD plants of the coal-burning power plants. In: *11th Mercury emission from coal and Energy efficiency workshops, 16-20 November 2015, Chennai Tamil Nadu, India*. [S. l.]: IEA Clean Coal Centre. http://www.lumexinstruments.com/images/news/final_mec_agenda.pdf.

Pavlin, M., Popović, A., Sedlar, M., Jaćimović, R., Horvat, M. (2015). Temperature stability and characterization of mercury compounds present in gypsum samples from various thermal power plants. In: Rotaru, A. (ed.), Cerc Korošec, R. (ed.). *Book of abstracts: CEEC-TAC3, 3rd Central and Eastern European Conference on Thermal Analysis and Calorimetry, 25-28 August 2015, Ljubljana, Slovenia*. [S. l.]: Central and Eastern European Committee for Thermal Analysis and Calorimetry, 200.

Pavlin, M., Sedlar, M., Popović, A., Frkal, P., Stergaršek, A., Jaćimović, R., Gao, X., Horvat, M. (2015). Mercury and other trace elements in gypsum samples from WFGD plants of the coal burning Power Plants (TPP). In: *ICMGP 2015 Korea, 12th International Conference on Mercury as a Global Pollutant, June 14-19, 2015, Jeju, Korea*. [S. l.: s. n.], 281.

Pavlin, M., Popović, A., Sedlar, M., Jaćimović, R., Horvat, M. (2015). Temperature desorption characterization of mercury compounds in WFGD gypsum samples from the coal-fired Thermo Power Plants (TPP). In: *ICMGP 2015 Korea, 12th International Conference on Mercury as a Global Pollutant, June 14-19, 2015, Jeju, Korea*. [S. l.: s. n.], 281.

Horvat, M., Sedlar, M., Pavlin, M., Stergaršek, A., Jaćimović, R., Gao, X. (2014). Temperature stability of mercury species in the FGD gypsum. In: *Conference proceedings, 5th China (Taiyuan) International Energy Industry Expo Low Carbon Development Summit-2014, BIT's 2nd Annual World Congress of EnergyWise-2014, BIT's 3rd Annual International Symposium of Clean Coal Technology-2014, BIT's 1st Annual World Congress of Geophysics-2014, September 16-18, 2014, Taiyuan, China*. [S. l.: s. n.], 120.

Pavlin, M., Sedlar, M., Horvat, M., Jaćimović, R., Popović, A. (2014). Identification of mercury compounds in gypsum samples from lignite burning thermo power plant. In: *Programme and abstracts, 7th Nordic Conference on Plasma Spectrochemistry, June 1-4, 2014, Loen. Loen: University of Oslo*. 5.

Pavlin, M., Sedlar, M., Horvat, M. (2013). Stability of mercury compounds at higher temperatures. In: Rotaru, A. (ed.), Matulis, D. (ed.). *Book of abstracts: CEEC-TAC2, 2nd Central and Eastern European Conference on Thermal Analysis and Calorimetry, 27-30 August 2013, Vilnius, Lithuania*. [S. l.]: Central and Eastern European Committee for Thermal Analysis and Calorimetry. PS2.35.

Begu, E., Pavlin, M., Sedlar, M., Horvat, M. (2013). Calibration of the method for temperature fractionation of mercury compounds in solid samples. In: *ICMGP 2013, The 11th International Conference on Mercury as a Global Pollutant, 28th July - 2nd August 2013, Edinburgh, Scotland*. [S. l.: s. n.]. <http://www.mercury2013.com/registration/>.

Stergašek, A., Horvat, M., Frkal, P., Kocjančič, R., Begu, E., Pavlin, M. (2013). Modified wet FGD chemistry features the removal of Hg(II) and Hg(0) from flue gas. In: *ICMGP 2013, The 11th International Conference on Mercury as a Global Pollutant, 28th July - 2nd August 2013, Edinburgh, Scotland*. [S. l.: s. n.]. <http://www.mercury2013.com/registration/>.

Sedlar, M., Pavlin, M., Kocjančič, R., Horvat, M. (2013). Temperature fractionation of mercury compounds in solid samples. In: Lisjak, D. (ed.), Dušak, P. (ed.), Kralj, S. (ed.). *[Program and abstract book], 7th Young Researchers' Day, 19 February, 2013, Ljubljana, Slovenia*. Ljubljana: Institut Jožef Stefan. 51.

Unpublished Invited Lecture

Pavlin, M., Horvat, M., Sedlar, M., Begu, E., Jaćimović, R., Frkal, P., Stergaršek, A. (2014). Removal of mercury in wet FGD by desulphurisation products. *10th Workshop on mercury emissions from coal, 22-24 April, Clearwater, Florida*.

Treatise, Preliminary Study, Study

Pavlin, M., Sedlar, M., Horvat, M. (2013). Total mercury and temperature fractionation of mercury in gypsum samples from different Chinese power plants. UNEP technical assessment, (IJS delovno poročilo, 11442).

Articles Related to the Thesis

- Pavlin, M., Jaćimović, R., Stergaršek, A., Frkal, P., Koblar, M., Horvat, M. (2018). Distribution and accumulation of major and trace elements in gypsum samples from lignite combustion power plant. Fuel processing. (Submitted).
- Pavlin, M., Popovič, A., Jaćimović, R., Horvat, M. (2018). Temperature stability of mercury compounds in WFGD gypsum samples from China (In preparation).
- Pavlin, M., Vogel-Mikuš, K., Kodre, A., Arčon, I., Czyżycki, M., Horvat, M. (2018). Artefacts present during identification of mercury species in the gypsum (In preparation).

Biography

Majda Pavlin graduated from the Faculty of Chemistry and Chemical Technology, University of Ljubljana, Slovenia, with a Bachelor of Science degree in chemistry. She finished her BSc study with a diploma thesis entitled “Thermodynamics of binding of cationic ligands to human telomeric DNA oligonucleotide” under supervision of prof. dr. Jurij Lah (Faculty of Chemistry and Chemical Technology, Chair of Physical Chemistry).

After graduation, she was a young researcher at the Department of Environmental Sciences, Jožef Stefan Institute for three and a half years. She enrolled the postgraduate study of Ecotechnology at the Jožef Stefan International Postgraduate School in 2012.

As a young researcher, she published one original scientific article as the first author, 8 articles as a co-author, among which two are related to the doctoral dissertation, and submitted one scientific articles as the first author. She actively participated in ten conferences in Slovenia and abroad. She spent one month at the Department of Energy Engineering, Zhejiang University (Hangzhou, China). During the period of her young researcher position, she gained expertise in the determination and measurements of mercury and its compounds in solid, liquid and gaseous phase by using CV-AAS, CV-AFS, and mass spectrometers with electron ionization. She has also introduced different sample preparation procedures. She will finish her Ph.D. study with the defense of her doctoral dissertation entitled “Mass spectrometric approach for identification of mercury compounds in solid samples.”