

ENVIRONMENTAL IMPACTS OF BUILDING
MATERIALS CONTAINING INDUSTRIAL
WASTE BY-PRODUCTS AND FLY ASH
FROM THERMAL POWER PLANTS

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Doctoral Dissertation
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OKOLJSKI VPLIVI GRADBENIH MATERIALOV Z
DODATKI INDUSTRIJSKIH ODPADNIH SNOVI IN
ELEKTROFILTRSKEGA PEPELA IZ
TERMOELEKTRARN

Doktorska disertacija

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Ljubljana, Slovenia, September 2018

Acknowledgments

The path toward this doctoral dissertation would not have been possible without the help and support of people who challenged, guided, encouraged and stuck with me all the way. I would like to take this opportunity to thank them all.

First, I would like to thank my supervisor Prof. Dr. Janez Ščančar for help and guidance during studies. Also, I want to thank Prof. Dr. Radmila Milačič for giving me the opportunity to accomplish my PhD study, for her dedicated help, continuous support, time and energy invested in helping me to achieve this work. All of this would not have been possible without their help and support.

Next, I want to express my special gratitude and appreciation to my co-mentors. Assist. Prof. Dr. Tea Zuliani for her scientific help and personal support, encouragement that went a long way in successfully completion of my work. For answering my enormous amount of questions and have patience with me. And to Assoc. Prof. Dr. Irena Nikolić, for her support, valuable comments, compressive advices and for providing me with material necessary for this work to come to existences. Above that, for believing in me and always available for nice talk.

I am especially thankful to Dr. Janja Vidmar, Dr. Petra Novak and Dr. Kelly Peeters for they friendship, help and useful comments and advices on my work. Together with Katarina Marković, Matic Bergant and Stefan Marković they made my work and living in Ljubljana enjoyable.

I want to thank the members of the evaluation board: Prof. Dr. Milena Horvat, Prof. Dr. Radmila Milačič and Prof. Dr. Ana Mladenovič for reviewing the manuscript and judging the work of my thesis.

I would like to thank to the Public Scholarship, Development, Disability and Maintenance Fund of the Republic of Slovenia – Ad Future, for the financial funding of this PhD thesis. This work has also been supported by the European Communities 7th Framework Programme Funding under Grant agreement no.603629-ENV-2013-6.2.1-Globaqua.

At the end, I would like to thank my family and friends, for their unconditional love and care. Especially, to my parents' for their sacrifice, patience and for teaching me good things that really matter in life. Their love and support has always been my strength.

To my sisters and brother who have been my best friends and the biggest support all my life. There are no words to express how much I love them and missed them during this time. I am deeply grateful for their faith in me and for sticking by my side and not letting me to give up when times are rough.

To Goca and Saša for being friend that someone can only wish for, for their love, moral support and making they home like my second one. They made my staying in Ljubljana fun, enjoying and not so far away from home.

Once again, I am so thankful and happy to have my family, for friends that turned into family and for dreams that turned into reality.

Abstract

For the evaluation of long-term environmental impacts caused by the release of contaminants from monolithic building and waste materials, the NEN 7375 test has been proposed. Over a period of 64 days, at specific points in time, the leaching solution (demineralised water) is replenished. By applying the NEN 7375 test, leaching of contaminants that is based mainly on diffusion is followed. In the Doctoral Dissertation, modified leaching protocols were applied and results evaluated against those obtained by the NEN 7375 test. In the modified protocols, synthetic sea, surface and MilliQ water were used for the leaching of selected elements and chromate, arsenate, molybdate and vanadate from compact and ground building composites (98% mixture of fly ash (80%) and cement (20%), and 2% of electric arc furnace (EAF) dust) over 6 months. The leaching solutions were not replenished, imitating both the diffusion and the dissolution of contaminants. The data revealed a larger extent of leaching when the leaching solution was not replenished. More extensive was also the leaching from ground composites, which simulated the disintegration of the material over time. The composition of the leaching solution influenced the release of the matrix constituents from the composites and, consequently, the amount of elements and their chemical species. Synthetic sea and surface water used as leaching solutions, without replenishing, were found to be suitable to simulate the conditions when the building material is immersed in stagnant environmental waters. Fly ash, cement and EAF dust are frequently mixed in building composites. The data revealed that chromate, molybdate, vanadate and arsenate may be leached in significant amounts, causing a potential environmental threat.

Next, a high performance liquid chromatography - inductively coupled plasma mass spectrometry (HPLC-ICP-MS) procedure was used for simultaneous speciation of chromate, arsenate, molybdate and vanadate. First, the behaviour of chromium (Cr), arsenic (As), molybdenum (Mo) and vanadium (V) species in different oxidation states was studied during their separation under acidic (pH 5) and alkaline (pH 12) conditions. At alkaline pHs chromate, arsenate, molybdate and vanadate were simultaneously separated and eluted at retention times from 390 to 450 s, 230 to 270 s, 340 to 430 s and 270 to 380 s, respectively, and detected on-line by ICP-MS, recording m/z 52, 75, 95 and 51, respectively. When V species were leached in significantly higher concentrations than Cr, Mo and As, simultaneous speciation analysis was particularly difficult. Therefore, the detection was possible at the low abundance (0.25%) ^{50}V isotope, which is also the mass of the ^{50}Cr isotope (abundance 4.345%), due to selective separation between V and Cr species. Good repeatability of the measurement (RSD better than $\pm 3.0\%$) and quantitative elution of elemental species (column recoveries 99–105%) were obtained.

Finally, sensitive and reliable analytical procedure for the determination of hazardous hexavalent Cr (Cr(VI)) in sediments of industrially exposed sites of the Sava River (stainless steel production and impact of metallurgic industry) was developed. An ultrasound-assisted extraction procedure (80 °C, using 2% NaOH + 3% Na₂CO₃ as the extraction solution) was found to be optimal to leach the total amount of Cr(VI) from sediments. The addition of 0.4 mol L⁻¹ MgCl₂ prevented oxidation of Cr(III) during the

extraction step. To control for species interconversion during the analytical procedure and for an accurate calculation of the Cr(VI) concentration by speciated isotope dilution (ID)-ICP-MS, the alkaline extract was doubly spiked with enriched $^{50}\text{Cr(VI)}$ and $^{53}\text{Cr(III)}$. The accuracy of the determination of Cr(VI) was verified by analysing the certified reference material CRM 041 (Cr(VI) in soil), and by spike recovery test. Low limits of detection (LOD) and quantification (LOQ) (1.25 and $4.0\text{ }\mu\text{g Cr(VI) kg}^{-1}$, respectively) and good repeatability of measurement (relative standard deviation better than $\pm 4.8\%$) were obtained. The use of isotopically enriched tracers importantly contributed to the validity of the obtained results. The analytical data revealed that Cr(VI) concentrations in sediments of the Sava River did not represent any known environmental hazard.

Povzetek

Pri oceni dolgoročnih vplivov, ki jih povzroča sproščanje onesnažil iz monolitnih gradbenih materialov in različnih odpadnih materialov, se v splošnem uporablja NEN 7375 test. V obdobju 64 dni se v določenih časovnih intervalih zamenja izlužitveno sredstvo (demineralizirana voda). Pri uporabi NEN 7375 testa sledimo izluževanju onesnažil na osnovi difuzije. V doktorski disertaciji smo uporabili modificirane izlužitvene teste in rezultate primerjali s tistimi, pridobljenimi z uporabo NEN 7375 testa. V modificiranih postopkih smo kot izlužitveno sredstvo uporabili sintetično morsko in površinsko vodo ali MilliQ vodo ter 6 mesecev sledili izluževanju izbranih elementov, kromata, arzenata, molibdata in vanadata iz kompaktnih in zdrobljenih gradbenih kompozitov iz mešanice 80 % letečega pepela (98 %) z dodatkom filterskega prahu iz elektroobločne peči (EAF prah) (2 %) in 20 % cementa. V času trajanja poskusa izlužitvenega sredstva nismo zamenjali, zaradi česar smo lahko sledili tako difuziji kot raztapljanju onesnažil. Rezultati so pokazali, da je obseg izluževanja večji, ko izlužitvenega sredstva ne zamenjamo. Nadalje se je izkazalo, da je izluževanje iz zdrobljenih kompozitov, ki so simulirali razpadanje materiala s časom, večje pri zdrobljenih kot pri kompaktnih kompozitih. Izkazalo se je tudi, da je obseg izluževanja elementov in njihovih kemijskih zvrsti bistveno odvisen od sestave matrice izlužitvenega sredstva. Rezultati so pokazali, da uporaba sintetične površinske vode in sintetične morske vode, ko v času poskusa izlužitvenega sredstva ne zamenjamo, ustrezno simulirata pogoje, ko gradbeni kompozit potopimo v stoječe vode. Leteči pepel, cement in EAF prah se pogosto uporabljajo kot mešanica v gradbenih kompozitih. Tovrstni gradbeni kompoziti so z okoljskega vidika lahko sporni, saj se iz njih lahko izlužujejo znatne množine kromata, molibdata, vanadata in arzenata.

V nadaljevanju smo razvili originalni speciacijski postopek za simultano določitev kromata, arzenata, molibdata in vanadata s tekočinsko kromatografijo, sklopljeno z masno spektrometrijo z induktivno sklopljeno plazmo (HPLC-ICP-MS). Najprej smo preučili obnašanje kromovih (Cr), arzenovih (As), molibdenovih (Mo) in vanadijevih (V) kemijskih zvrsti v različnih oksidacijskih stanjih, med njihovo ločbo pri kislih (pH 5) in alkalnih pogojih (pH 12). Pri alkalnih pogojih so se kromat, arzenat, molibdat in vanadat sočasno ločili in eluirali pri retencijskih časih med 390 do 450 s, 230 do 270 s, 340 do 430 s oziroma 270 do 380 s. Ločene kemijske zvrsti smo sledili z ICP-MS pri m/z 52, 75, 95 in 51. Kadar je bil V prisoten v bistveno višjih koncentracijah, kot so bile koncentracije Cr, Mo in As, je bila simultana speciacija vseh štirih elementov praktično nemogoča. Zato smo pri detekciji izkoristili možnost uporabe ^{50}V izotopa, ki je v naravi prisoten le v 0,25 %. Ker se masi izotopa ^{50}Cr (naravna prisotnost 4,345 %) in ^{50}V izotopa prekrivata, je bila simultana speciacijska analiza možna, ker sta bila kromat in vanadat na kromatografski koloni selektivno ločena. Z razvitim analiznim postopkom smo dosegli dobro ponovljivost merjenja (RSD boljši od $\pm 3,0$ %), kemijske zvrsti elementov pa so se kvantitativno eluirale iz kolone (izkoristki na koloni so bili med 99–105 %).

Razvili smo tudi zanesljiv analizni postopek za določitev strupenega šestvalentnega Cr (Cr(VI)) v sedimentih, ki smo jih vzorčili na industrijsko izpostavljenih območjih na reki Savi (jeklarska in metalurška industrija). Celotni Cr(VI) smo kvantitativno ekstrahirali iz

vzorca z ultrazvočno ekstrakcijo pri 80 °C in uporabo alkalnega ekstrakcijskega sredstva (2 % NaOH + 3 % Na₂CO₃). Z dodatkom 0,4 mol L⁻¹ MgCl₂ smo med postopkom ekstrakcije preprečili oksidacijo Cr(III). Za kontrolo pretvorb kemijskih zvrsti Cr med postopkom ekstrakcije in za točno določitev Cr(VI), s tehniko izotopskega redčenja v masni spektrometriji (ID-ICP-MS), smo v alkalne v ekstrakte dodali dvojni izotopski sledilec obogatenih stabilnih izotopov ⁵⁰Cr(VI) in ⁵³Cr(III). Točnost analiznega postopka smo preverili z določitvijo Cr(VI) v certificiranem referenčnem materialu CRM 041 (Cr(VI) v tleh) ter s testom, kjer smo k sedimentu pred analizo dodali znano množino Cr(VI) in izmerili izkoristek med dodano in določeno vrednostjo Cr(VI). Razvit analizni postopek je selektiven in občutljiv, z mejami zaznave (LOD) in kvantifikacije (LOQ) 1,25 oziroma 4,0 µg Cr(VI) kg⁻¹. Dosegli smo dobro ponovljivost merjenja (relativni standardni odklon meritev je bil boljši od ± 4,8 %). Uporaba obogatenih izotopskih sledilcev pomembno prispeva k zanesljivosti določanja Cr(VI) v sedimentih in točnosti analiznih rezultatov. Izsledki raziskave so pokazali, da je Cr(VI) v sedimentih reke Save prisoten v zelo nizkih koncentracijah, ki ne predstavljajo nevarnosti za okolje.

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Abbreviations

AAS	... Atomic absorption spectrometry
AB	... Arsenobetaine
AsC	... Arsenocholine
Al ₂ O ₃	... Aluminium oxide
Ar	... Argon
As(III)	... Trivalent Arsenic
As(V)	... Pentavalent Arsenic
BaCrO ₄	... Barium chromate
CaO	... Calcium oxide
CO ₂	... Carbon dioxide
Cr	... Chromium
Cr ₂ O ₃	... Cr(III) oxide
Cr(III)	... Trivalent chromium
Cr(VI)	... Hexavalent chromium
CRM	... Certified reference material
DMAA	... Dimethylarsinic acid
EDTA	... Ethylenediaminetetraacetic acid
EPA	... Environmental Protection Agency
ET-AAS	... Electrothermal atomic absorption spectrometry
Fe	... Iron
FeCr ₂ O ₄	... Fe(II) chromate
Fe ₂ O ₃	... Fe(III) oxide
FPLC	... Fast protein liquid chromatography
H ₃ BO ₃	... Boric acid
HECM	... High energy collision mode
HF	... Hydrofluoric acid
HCl	... Hydrochloric acid
HMI	... High matrix introduction
HNO ₃	... Nitric acid
HPLC	... High performance liquid chromatography
ICP-MS	... Inductively coupled plasma mass spectrometry
ID	... Isotope dilution
IDMS	Isotope dilution mass spectrometry
K ₂ HPO ₄	... Potassium hydrogen phosphate
LOD	... Limit of detection
LOQ	... Limit of quantification
MilliQ	... Ultrapure water
MMAA	... Monomethylarsonic acid
Mn	... Manganese
Mg	... Magnesium

MgO	...	Mg oxide
Mo	...	Molybdenum
Na ₂ CO ₃	...	Sodium carbonate
NaCl	...	Sodium chlorine
NIST	...	National Institute for Standards and Technology
NaOH	...	Sodium hydroxide
NH ₄ NO ₃	...	Ammonium nitrite
PFA	...	Perfluoroalkoxy
Ra/b	...	Ratio between isotope a and b
Rm	...	Measured ratio
RM	...	Reference material
SrCrO ₄	...	Strontium chromate
Se	...	Selenium
SIST	...	Slovenian Institute for Standardization
SIDMS		Speciated isotope dilution mass spectrometry
SiO ₂	...	Silicon dioxide
SO ₃	...	Sulphur trioxide
SPS-SW1	...	Surface water reference material
SRM	...	Standard reference material
QA	...	Quality assurance
QC	...	Quality control
TRIS	...	Tris(hydroxymethyl)aminomethane
V	...	Vanadium
XANES	...	X-ray Absorption Near Edge Structure

Chapter 1

Introduction

1.1 Industrial Wastes and Possibility of Their Reuse as Secondary Materials

As a consequence of intensive human activities and rapid industrial growth, huge quantities of different wastes are generated. In order to protect the environment, their safe disposal should be ensured, or alternatives of the reuse of wastes as secondary materials examined. Among various wastes from different industrial applications, building rubbles [1], waste glass [2], crumb rubber [3], quarry waste [4], shingle waste [5], sewage sludge [6], non-metallic automotive shredder residues [7] as well as wastes from steel-making industry (electric arc furnace (EAF) slag and ladle slag [8], [9], [10], [11], EAF dust [12], [13]) and coal fly ash ([14], [15], [16], [17], [18]) represent alternative secondary materials that may be used as a substitute for natural raw materials [19]. Since many industrial by-products own similar chemical and physical properties as ordinary building materials, they can be incorporated into building materials. With this, the quality of the product can even be improved, which significantly reduces exploration of natural resources and substantially decreases landfill loads. For instance, the use of coal fly ash integrated into mortar can enhance the strength and durability of concrete [15], [16], [17], [18], while the use of black steel slag can increase the durability of asphalts [11]. Since cement industry contributes to almost 5% of global anthropogenic CO₂ emissions, cement content in building materials can be substituted with waste materials, which leads to reduction of CO₂ emissions [20], [21]. For reducing cement content in building materials, different cementitious materials that contain waste by-products are being prepared and investigated regarding their physico-chemical properties as well as environmental impacts. Among them, EAF dust from steel making industry and coal fly ash from thermal power plants represent high potential to be incorporated into the building materials [12], [13], [17], [22], [23].

The reuse of waste materials helps us save natural resources, which is an essential part of green building, strongly supported by Directive 2008/98/ES on waste [24] and Construction Products Regulation No. 305/2011 [25].

Usage of materials that contain waste by-products is possible when such materials possess appropriate technical characteristics [13] and fulfil the requirements on hygiene, health and the environmental aspects, set by Construction Products Regulation [21]. To avoid environmental pollution, it is necessary to assure that contaminants in the final products are immobilized to prevent their possible release from the final products during their service life [10], [26], [27].

Waste by-products can be recycled in civil engineering in a variety of building materials or may be reused as composites for embankments.

In order to assess environmental impacts of new materials, the potential leaching of contaminants should be followed by the use of reliable analytical methods. Among pollutants in wastes from the steel making industry, metals and metalloids are the ones that may represent an environmental threat. For their accurate determination, element-specific detectors like inductively coupled plasma mass spectrometry (ICP-MS) are usually applied [28], [29]. Some waste by-products contain toxic components in concentrations that do not permit their direct incorporation into building composites. In such cases, toxic components must be first stabilised in a process that transforms them to stable, inert, non-hazardous forms [30], [31], [32], [33].

The amount of substances that can be leached from waste materials, e.g. EAF dust, EAF slag, ladle slag, or from secondary materials, e.g. asphalt and concrete mixes with waste by-products from the steel making industry, is estimated by applying different leaching tests. Commonly used are leaching tests where solid material is shaken with water (a liquid-to-solid ratio of 10:1) over 24 h. Based on the amount leached, the waste or secondary material is classified as inert, non-hazardous or hazardous. Before its actual application, a secondary material should fulfil the requirements of the relevant national regulation [34].

Leaching tests that classify secondary materials with regard to inertness cannot predict their possible long-term effects to the environment. In order to estimate long-term environmental impacts, leaching tests based on diffusion were proposed in the Netherlands NEN 7345 [35] standard and applied in the leaching protocol developed for concrete [36]. In these leaching tests the ratio between the volume of a testing composite and the volume of added leaching solution is 1:5.

Before the use of any alternative material, it is necessary to extensively investigate all the parameters that ensure the quality of such material as building product [37], [38], and to estimate the environmental impacts [10], [39], [40].

1.2 Steel Production

The reprocessing of scrap metal in the EAF is a common method in steel production (Fig. 1.1) [41]. Two classes of steel are produced in general: unalloyed steel, known as carbon steel, and alloyed steel, so-called stainless steel.

Unalloyed steel accounts for about 90% of steel production. It is widely used in civil engineering, car industry and shipping. When unalloyed carbon steel is produced, scrap steel and additives like CaO (lime) are added into the furnace. Then the graphite electrodes are immersed into the scrap and heated by electric power. During the heating, the carbon from the electrodes is released into the melting scrap, while the added lime and carbon maintain the reductive atmosphere. Simultaneously the oxygen is introduced, which raises the temperature up to about 1700 °C. Above the steel melt, EAF slag is formed, which has a lower density than the melted steel and is composed of metal oxides. It prevents heat loss and extracts impurities of undesired elements, such as phosphorous, manganese (Mn), silicon (Si) and sulphur (S) (in the form of oxides). During the melting process coke or charcoal is added. Carbon reduces FeO to elemental iron and the formed bubbles of carbon monoxide (CO) enhance the heat transfer. When the steel is completely melted, its chemical composition is examined. If it contains more impurities than desired, another portion of CaO is added by continuous introduction of the oxygen. The carbon content significantly influences the steel properties. In unalloyed steel its content is typically between 0.6 to 1.3%. 0.6% of carbon is crucial for obtaining the steel hardness, while raising the carbon content up to 1.3% significantly contributes to the increase of wear resistance and also slightly increases steel hardness [42].

During the steel production the dust particles are exhausted and collected in large bag filters. The collected EAF dust is a waste by-product, containing metals in high concentrations. After the melting process is completed, the layer of steel slag is removed from melted steel by decantation. During decantation, a minor amount of steel is mixed with steel slag. Steel slag is then deposited in slag yards for stabilisation. The pieces of steel are separated from steel slag by strong magnets and about 20% of steel slag is returned back to the primary process.

The process of alloyed stainless steel production is similar to the one of unalloyed carbon steel. In comparison to unalloyed steel, the stainless steel contains more additives, such as chromium (Cr) (11.5–18%), nickel (Ni) (up to 8%) and other alloy elements like titanium (Ti), molybdenum (Mo), lead (Pb), vanadium (V), manganese (Mn), aluminium (Al), boron (B), cobalt (Co), copper (Cu), phosphorus (P), silicone (Si), and tungsten (W). Cr in stainless steel prevents its corrosion by forming a thin layer of Cr oxide (Cr_2O_3). The properties of steel are influenced by alloying elements and heat treatment conditions. The most important element besides iron is carbon. The hardness of steel is related to the amount of carbon alloyed. In the production of alloyed steel, the oxidation process is governed under low pressure (100–200 mbar) (vacuum process), which enables the controlled low content of carbon (0.09–0.11%) and the formation of oxides (Mn, Cr, Si etc.) that are mostly transferred into slag. Since the slag contains high amounts of Cr_2O_3 , it is necessary to reduce Cr to obtain its desired content in the steel. The reduction of steel is carried out under low pressure by Fe, Si and Al. A part of Si and Al is alloyed into melted steel, while the newborn slag, which contains lower amounts of metal oxides than EAF slag, is called ladle slag. After that, boric acid is added to lower the melting temperature (and thus the energy consumption), to increase fluidity, strength of the steel and to reduce the corrosion of the refractory materials in the furnace. The ladle slag is removed from steel by decantation [43].

Among the most important waste materials from steel production are EAF slag, ladle slag and EAF dust [44]. Utilization of steel waste materials in civil engineering applications contributes to a reduction in the waste amount and thus alleviates the need for their disposal. By this, exploitation of natural resources is reduced, preserving them for future generations [45]. The possibility of using wastes from steel making industry is sometimes hampered due to the lack of adequate legislation. The technical and environmental obstacles for application of some slags in construction include volumetric expansion, disintegration and leaching of toxic substances (mainly metals) from the final products [46].

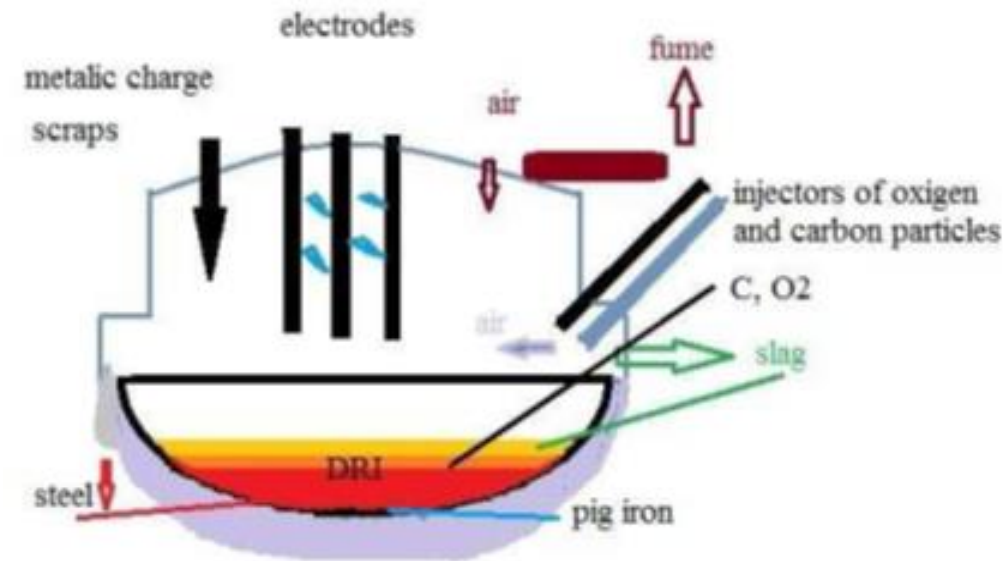


Figure 1.1: Schematization of the steel-making process (adapted from [41]).

1.2.1 Electric arc furnace dust

EAF dust is a fine powder which is formed from fumes upon a slag during the steel production. It is mainly composed of metals, with Zn oxide (23–24%) and Fe oxides (18–22%) as its prevailing components. Other metals like Pb, calcium (Ca), magnesium (Mg) and Mn are present in concentrations below 4%, while Cr concentration is about 0.3% [12]. The chemical composition of EAF dust varies from one plant to another and from one melt to the next. The type and amount of scrap material used in the EAF have a crucial influence on its chemical composition [47]. Due to chemical and physical properties, the EAF dust was categorized as hazardous waste [48]. Being treated as hazardous waste, it is either disposed at appropriate, by regulation-prescribed waste dumps, or being re-used in cement and construction products. It has already been successfully implemented in cementitious building composites [13],[47], [49] and asphalt mixes [12].

1.2.2 Fly ash from thermal power plants

Fly ash is generated during the combustion of coal in thermal power plants. Landfilling is undesirable from environmental and economic points of view. Therefore, there has been an increasing interest in order to establish suitable processes in which fly ash can be re-used efficiently. Fly ash is composed of ferro-aluminosilicate minerals. Its major constituents (95–99%) are oxides of Si, Al, Fe, Ca, and Mg, while as minor elements Ti, sodium (Na), potassium (K) and S are present (0.5–3.5%) [50]. Composition of fly ash depends mainly upon the geographical factors related to coal deposit, combustion conditions and the type of ash collection devices. Fly ash could be used as a prime component for a variety of construction materials and can increase the compressive strength of new products [18], [15], [16]. With the aim to reduce the landfilling of EAF dust, attempts were also made to prepare composites with fly ash, EAF dust and cement.

1.2.3 Cement

Cement is traditionally regarded as an energy and emission intensive construction material, generally used for production of concrete, the usage of which is growing in the last years [51], [52]. Construction cements are usually inorganic, lime or calcium silicate based, and can be divided into hydraulic and un-hydraulic, depending on their capability to adjust in the presence of water. Cement production is usually based on heating different raw materials, such as limestone, to clinker, which then combines with other additives. The resulting product is then ground to produce different kinds of cement [53]. Cement production contributes to almost 5% of global anthropogenic CO₂ emission [20]. An alternative for reducing CO₂ is to replace traditional Portland cement with alternative natural raw material, such as EAF dust, fly ash and blast furnace slag.

1.3 Disposal of Waste Materials: Environmental Concerns

During metal manufacturing and steel production, EAF slag, ladle slag, EAF dust and other waste by-products are disposed before being reused or recycled. Huge quantities of fly ash from coal burning in thermal power plants are also disposed before being reused. From the industrial waste disposals, contaminants may be released into the air, soil, water and sediments. To protect the environment, monitoring of contaminants' contents is needed to take necessary measures when they are released from wastes in elevated concentrations. In waste materials from steel production and coal burning processes, metals and metalloids like Cr, V, Mo, As, Zn and Pb represent the potential environmental threat. Among them, Cr in its highly toxic hexavalent form (Cr(VI)) is under the environmental scrutiny [12], [54]. To evaluate the potential environmental hazard of Cr(VI), it is necessary to understand Cr chemistry and to apply reliable speciation analysis [55], [56], [57], [58].

1.3.1 Chromium as a contaminant in the environment

Cr is a naturally occurring element present in different minerals, soils, volcanic dust and gases [59]. In the environment, Cr is mainly present in trivalent (Cr(III)) form and in very low concentrations as hexavalent (Cr(VI)) species. Most Cr(III) compounds are sparingly soluble and exhibit low mobility at environmentally relevant pH values. Conversely, alkali and alkaline earth chromates are highly soluble and highly mobile in the environmental compartments [60]. The toxicity, bioavailability and mobility of Cr depends not only on its total concentration, but primarily on the chemical forms in which Cr exists. Cr(III) compounds are essential for glucose and lipids metabolism, while Cr(VI) species are carcinogenic, mutagenic and can provoke contact dermatitis [54], [61].

Cr sources are geogenic and anthropogenic. Cr is produced mainly from chromite ore (FeCr₂O₄). About 90% of Cr is used in the metallurgical industry (steel, ferro- and nonferrous alloys), chemical industry, electroplating, in the production of Cr pigments and dyes, for leather tanning, in petroleum refining and wood treatment. Cr is also present in cement and cement products [61]. The extensive use of Cr and disposal of waste materials, which contain Cr, makes this element a common pollutant in the terrestrial and aquatic environments [60]. The main source of Cr in soil, water and sediments is from a variety of manufactured processes and disposal of Cr-rich waste materials [62], [63], [64].

Cr speciation depends on pH and the presence of reducing and oxidising agents. In anaerobic environments Cr(VI) is rapidly reduced to Cr(III) with reducing agents like sulphides, sulphites, iron(II) and organic matter, and also by different anaerobic bacteria [65], [66]. Since the redox potential of the Cr(VI)/Cr(III) couple is high, Mn(IV) oxides are the only oxidants present in environmental compartments that are able to oxidise Cr(III)

to Cr(VI). Oxidation is also possible by dissolved oxygen, but only at highly alkaline environmental conditions [66], [67], [54].

In recent years, analytical procedures for following the environmental fate of Cr and determination of toxic Cr(VI) in different sample matrices have been significantly improved. These procedures usually involve quantitative extraction of Cr species from the sample matrix, followed by speciation analysis [54], [68]. For Cr speciation analysis, ion-exchange chromatography coupled to ICP-MS is commonly applied [69], [70], [71]. Since Cr(VI) is of environmental concern, speciation analysis is mostly oriented to the determination of its hazardous hexavalent form. Cr(VI) was frequently investigated in environmental waters [63], [64], leachates from building composites [12], [13], [39] and solid matrices [56], [54].

As a consequence of different industrial activities, soils and sediments may also be contaminated with Cr. In soil samples treated with tannery waste, Cr(VI) was found in trace amounts even after 22 years from the last waste application [56]. At industrially exposed sites from steel-making and metallurgical industries, total Cr was found in elevated concentrations in sediments [64]. Cr was found present as a pollutant also in urban sediments due to contaminated wastewater receiving domestic and industrial sewage [55].

To follow the fate of Cr in the environmental compartments, reliable and sensitive analytical techniques for Cr speciation are needed.

1.4 Methods for Evaluation of Environmental Impacts of Building Materials Containing Waste Materials

For evaluating the environmental impacts of different waste materials and composites containing waste materials, short-term and long-term leaching tests are used.

1.4.1 Short-term leaching tests

Short-term leaching tests are applied for the characterization and estimation of the extent of leaching of contaminants from waste materials and from composites containing waste materials [72], [73], [49]. Several test methods have also been issued like the European test method for leaching aggregates SIST EN 1744-3 (2002) [74], CEN technical protocols (SIST-TS CEN/TS 15862, 2013 [75]; SIST-TS CEN/TS 14405: 2004) [76], the SW-846 test methods of the US guide for waste characterization (USEPA, 2012; [77]), the pH dependence test SIST EN 14429 (2013) [78], and short-term compliance tests for the leaching of granular waste materials and sludge (SIST EN 12457-4, 2004 [34]; SIST EN 12457-2, 2004) [79]. In the latter compliance tests (SIST EN 12457-4, 2004; SIST EN 12457-2, 2004) 90 g of sample is shaken with 900 mL of water (using liquid to solid ration 10:1) for 24 hours on a mechanical shaker at 10 rpm. Based on the results from these leaching tests, waste materials or composite materials containing waste materials are characterised as inert, non-hazardous or hazardous materials.

1.4.2 Long-term leaching tests

For evaluating the long-term environmental impacts and leaching characteristics of solid earthy and stony building and waste materials, the Dutch leaching test NEN 7345 [35] based on diffusion was established. NEN 7345 test was applied by Hohberg and co-workers (2000) [36] to evaluate the leaching of metals from concrete. Later, for evaluating the long-term environmental impacts caused by the release of contaminants from monolithic building and waste materials, the NEN 7375 (2004) [80] “tank test” was proposed. The

purpose of NEN 7375 diffusion test is to simulate the leaching of inorganic components from moulded and monolithic materials under aerobic conditions. Composite casts that are in a form of cylinders, 7 cm in height and 5 cm in diameter, were immersed into the leaching solution (demineralized water) in the period of 64 days. During 64 days, at specific time points the leaching solution must be replenished. This enables estimation of the diffusion of contaminants from the composite examined. The main difference between the two NEN tests is the extension of the applicability from stony building materials as prescribed by NEN 7345, to earthy and stony materials, as generalised in the NEN 7375 test. Further, the leaching in NEN 7375 test is conducted with neutral demineralized water, instead of acidified water, as proposed in NEN 7345 test. The neutral pH of water extended the applicability of NEN 7375 test to materials with a low buffer capacity.

A modified NEN 7375 protocol was also used to assess the long-term environmental impacts of asphalt mixes with the addition of electric arc furnace (EAF) dust [12] or EAF steel slag [11], cement composites with the addition of EAF dust [13] and cement composites with the addition of ladle slag [39]. To stimulate environmental conditions, the time period of 64 days was extended to 180 days, and as a leaching solution distilled water and salty water (3.8% NaCl) were used. The saline water was used to simulate a marine environment. Beside compact composites, in modified protocols ground composites (particle size below 0.5 cm) which represent the decomposition of material over time in the environment were also used. In the modified leaching test, leaching solution were not replenished at specified times executed, which enables following the diffusion and dissolution of contaminants in the stagnant environmental waters. In both, the NEN 7375 test and the modified NEN 7375 test, the material being investigated is placed into a plastic tank or a bucket and a leaching solution (distilled, salty water) is added. The ratio between the mass of investigated composite and the volume of added leaching solution is 1:5. At a specific time, samples were taken, filtered and the concentration of inorganic contaminants determined by element specific detectors.

1.5 Determination of Total Concentrations of Elements by Inductively Coupled Plasma Mass Spectrometry and Speciation Analysis

1.5.1 ICP-MS basics

For the determination of total elements concentrations in waste materials and building materials containing wastes, ICP-MS is commonly applied. It is the most versatile instrumental analytical technique, capable of simultaneous determination of over 90% of the elements in the periodic table at concentrations below $0.01 \mu\text{g L}^{-1}$ [81]. Moreover, ICP-MS allows simultaneous multielemental analysis and for elements with at least two isotopes, application of the isotope dilution (ID) technique. In ICP-MS the liquid sample is introduced into the inductively coupled plasma as an aerosol. Larger aerosol droplets are removed from the gas stream by a spray chamber and the remaining smaller droplets are swept into the central channel of the plasma, which is generated in a stream of argon contained in a quartz tube (torch). The torch is located in the centre of a cooled coil, through which a high power, high frequency electric current is passed. The intense magnetic field is created, which causes collisions between free electrons and argon atoms, producing ions and more electrons, until stable, high temperature plasma is formed (up to 10000 K). Aerosol droplets are rapidly dried, decomposed, vaporized and atomized, then ionized by the removal of one electron from each atom. The resulting ions (positively charged) are

extracted into the vacuum system through a pair of interface cones. Electrostatic lenses keep the ions focused in a compact ion beam as they pass through the vacuum system to the final chamber, where the mass spectrometer and detector are housed. In ICP-MS three types of mass analysers are used: magnetic sector, time-of-flight and the quadrupole analyser, which is the most common. The quadrupole uses a combination of direct (DC) and alternating current (AC) to separate ions based on their mass-to-charge ratio. The quadrupole comprises of two pairs of cylindrical rods, arranged in a square. The AC and DC give a hyperbolic electric field and allow only a narrow range of masses to be transmitted. The rest are lost from the beam. By altering the currents, but keeping the ratio between them constant, it is possible to control which masses are passed to detector [82].

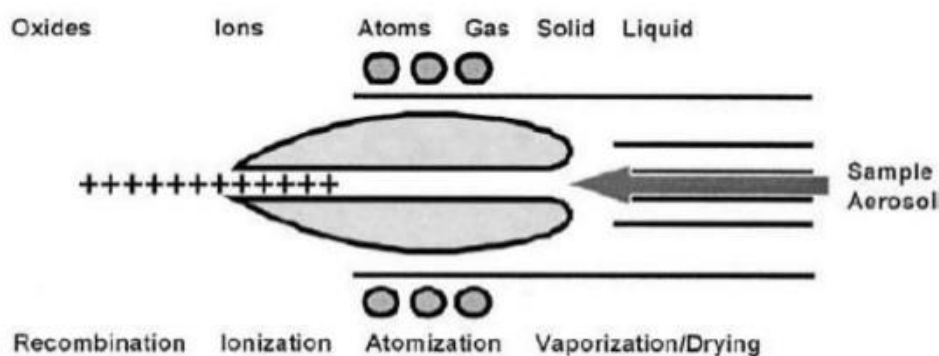


Figure 1.2: Generation of positively charged ions in the plasma (adopted from [83])

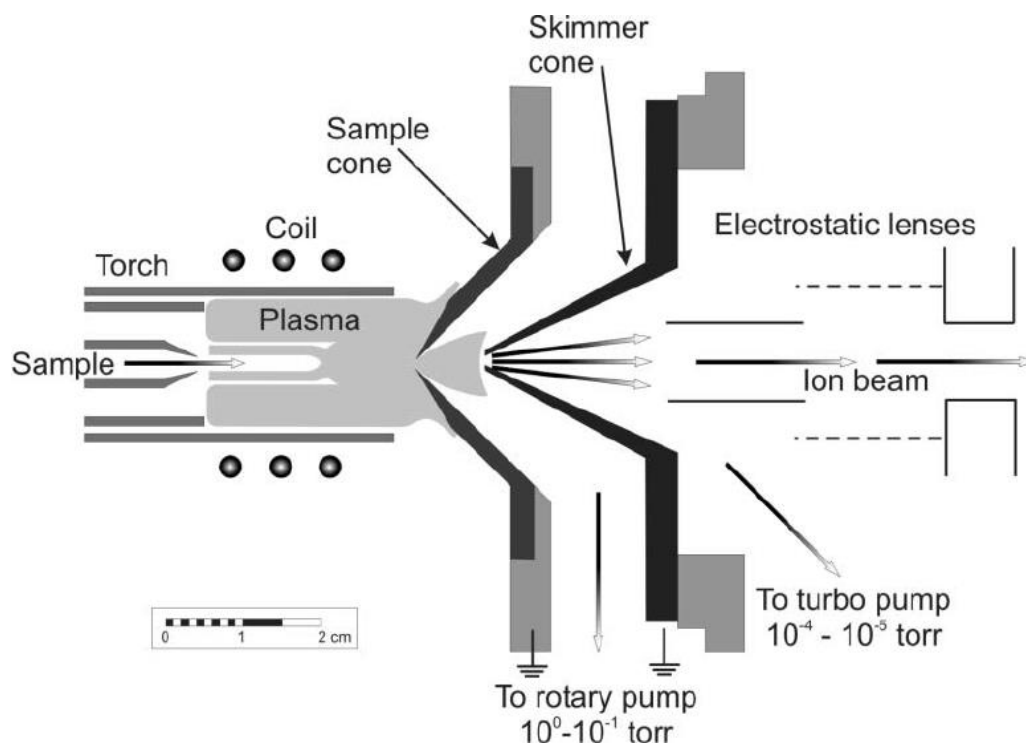


Figure 1.3: Schematic presentation of ICP-MS sample introduction area (adopted from [84]).

ICP-MS is very sensitive, mainly because of the electron multiplier, which can transform a single ion into a measurable signal pulse. As a positive ion reaches the detector, it is deflected to the first dynode, which releases free electrons that strike the next dynode. Each electron then again releases several new electrons and so on – hence the name. At the end of the cascade the pulse is strong enough to be measured. There are basically two detectors. The first one is for the so-called analogue detection used for higher concentrations, the second one is for the so-called pulse detection for lower concentrations. The analogue detector is placed in the middle of the electron multiplier and measures the current produced in the dynodes. The pulse detector uses the output of the analogue detector as its input, therefore amplifying the signal. To prevent damage to the pulse detector a protection circuit is placed between the detectors. For this reason, ICP-MS can operate in a dual or extended dynamic range, which greatly extends its linear range (up to 10⁹). The detector has high sensitivity, a wide linear dynamic range and low background noise. The background is affected by the plasma generator, lens configuration, analyser vacuum and the quality of the detector electronics [81].

ICP-MS offers several important advantages, e.g. simultaneous multielement capability, rapid quantitative analysis, wide dynamic range, high sensitivity, high selectivity, low detection limits and simple hyphenation with chromatography techniques for speciation analysis [81], [85].

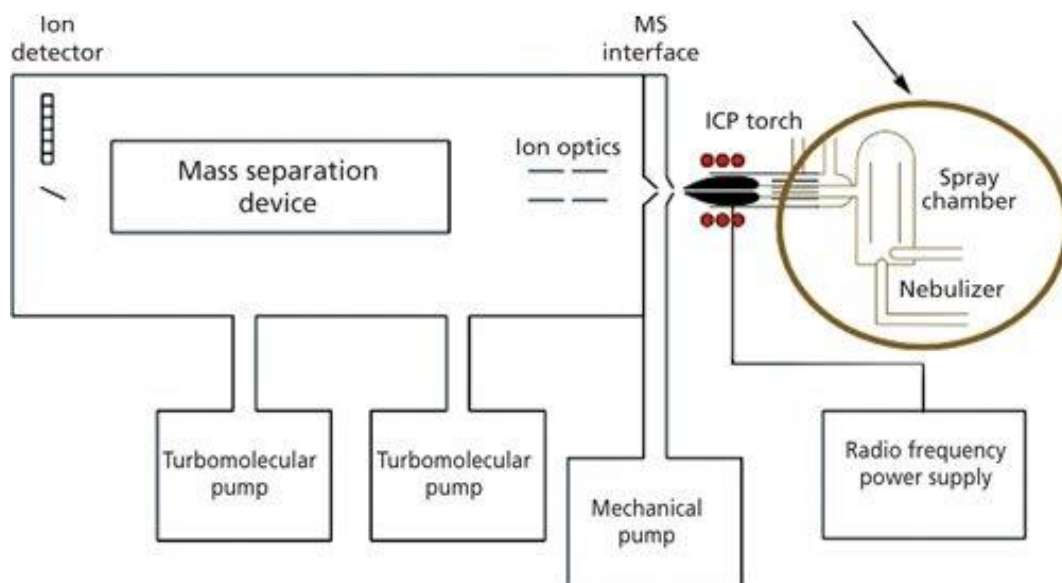


Figure 1.4: Major instrumental components of an ICP-MS system (adopted from [86]).

1.5.1.1 Spectral interferences in ICP-MS

Although quadrupole-based ICP-MS is a very powerful analytical technique, it suffers from spectral interferences such as:

- Isobaric interferences: Isobaric interferences appear when there is an overlap from a different element with an isotope at the same nominal mass like for instance ^{114}Sn and ^{114}Cd .
- Polyatomic interferences: In polyatomic interferences there is an overlap of ions of a measured element with those, which can be formed as a combination of species from the sample matrix, solvents and plasma gas ($^{40}\text{Ca}^{16}\text{O}$ overlaps with ^{56}Fe).
- Interferences by doubly-charged species: These species are formed when two electrons are lost instead of one. Because the quadrupole separates species based

on the mass-to-charge ratio, the doubly charged species will be separated at $m/2$ and cause an overlap with a singly charged species of another element. For instance, doubly charged $^{136}\text{Ba}^{2+}$ will interfere with $^{68}\text{Zn}^{+}$ [85].

- Interferences of oxides: When rare earth or refractory-type elements are present in the sample, which readily form molecular species, in particular oxides, these can create spectral overlap problems on other elements that are being determined by ICP-MS. An example is determination of Fe, which is hindered by the overlap of Ca oxide with the major isotope of Fe at m/z 56.

1.5.1.2 Removal of spectral interferences in ICP-MS

One of the most common forms of spectral interferences is polyatomic or molecular spectral interference, which is formed by the combination of two or more atomic ions. Their occurrence initiated many factors, but mostly they are associated with either the plasma/nebulizer gas used, matrix components in the solvent/ sample, other elements in the sample, or entrained oxygen/nitrogen from the surrounding air [85]. So it is necessary to optimize the chromatographic condition in order to avoid polyatomic interferences. Also, the use of high resolution ICP-MS instrument lately increasingly decreased the existence of interferences. Cr is one of the elements whose detection can be compromised by polyatomic interference, especially carbon and chlorine interferences, since natural samples as surface water and solids samples contain a high carbon concentration. Recent development of ICP-MS instruments enables the use of a high matrix introduction (HMI) system, which appreciably decreases the introduction of salts to ICP, and removes interferences due to high salt content. Also, the use of High Energy Collision Mode instead of He collision mode revealed better reduction of polyatomic interferences. Novotnik et al. [87] made a comparison of He and HECM mode for the minimization of chlorine and carbon polyatomic interferences and used HMI system to reduce the sample aerosol transport in the Cr speciation analysis. Their study showed that the use of HECM mode efficiently reduced polyatomic interferences at m/z 53 and m/z 52. The combined use of HECM and HMI system is today an indispensable speciation analysis where the eluent composition and matrix constituents can cause undesirable polyatomic interferences and salt deposition on sampler and skimmer cones.

1.5.2 High performance liquid chromatography

High performance liquid chromatography (HPLC) is a high resolving chromatographic separation technique, which is usually applied for separation of individual chemical species of elements present in a solution. HPLC instruments consist of a mobile phase reservoir, a high pressure pump, an injector, an analytical column, which can be temperature controlled, and a detector [87]. A schematic presentation of HPLC system is presented in Figure 1.5.

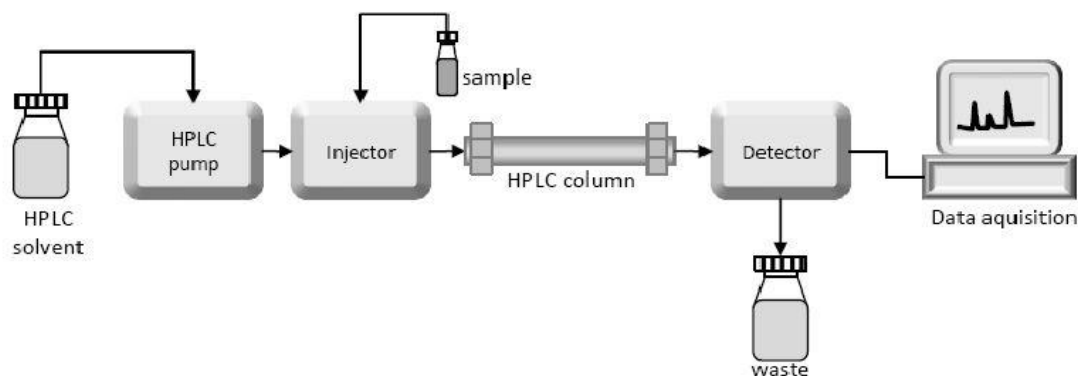


Figure 1.5: Schematic presentation of a HPLC system (adopted from [88]).

HPLC offers easy coupling with ICP-MS, which serves as an element-specific detector. However, it is important to stress that the eluents used in HPLC should be compatible with ICP-MS and the flow rate of the mobile phase from the column should be tolerable by the ICP-MS, typically between 0.5 and 1.5 mL min⁻¹ [89], [90], [91], [87]. HPLC is widely employed for separating the species of interest in a variety of environmental and biological samples [92], [93], [94], from acidic to alkaline pH [95], [96], [97]. Depending on chemical properties of the species analysed, different chromatographic columns are applied for their separation.

Size exclusion chromatographic columns are used to separate elemental species according to their size. Different chemical compounds can be separated using size. In speciation exclusion columns with various exclusion ranges from 1000 up to 200000 Da. Larger species pass through the column with the eluent faster than the smaller ones, which are retained for a longer time in the channels of the column support and are later eluted from the column resin.

Ion exchange columns are used to separate charged elemental species. Cation exchange resins, which bear negatively charged functional groups (e.g. sulphonate) retain cationic species, while anion-exchange resins, which bear positively charged functional groups (e.g. quaternary amines) retain anionic species. The retained negatively charged species are eluted with a solvent of high ionic strength, which is usually a salt. If sodium chloride is used as an eluent, chloride ions exchange the negatively charged species, while sodium cations positively charged species.

Separation of neutral chemical species of elements is possible on reverse phase columns. If the analyte is present in negatively or positively charged species, selective reagents are used to form ion pairs, which are neutral, and then retained on the column resin. For negatively charged species tetrabutyl ammonium phosphate may be used as an ion-pairing reagent, while for positively charged species sodium dodecyl sulfonate.

Separation can be achieved also by the affinity chromatography, where the specific antibody selectively retains the species of interest.

If samples are not in liquid form, the analyte should be extracted prior to the separation step.

1.5.3 Quantification of separated species by isotope dilution ICP-MS

For accurate quantification of separated chemical species of an element by ICP-MS, the isotope dilution (ID) technique can be applied in speciation analysis. To perform ID, the

element needs to have at least two stable isotopes, which are free of spectral interferences. The principle of ID mass spectrometry (IDMS) is very simple. To a sample with an unknown amount of an element, a known amount of the same element with altered isotopic composition (spike) is added. Isotopic composition of the element and spike is either known or can be determined. In the mixture, a new ratio between isotopes is established. The ideal ratio between the spike and the analyte is 1:1, but ratios between 0.1:1 and 10:1 are also acceptable. This means that prior to the ID analysis, the sample should be analysed by a conventional technique to estimate the analyte concentration. Once equilibration of the spike and analyte isotopes has been achieved, the total recovery of the analyte is not required, because the determined value is based on measuring the ratio between the analyte and the isotopic analogue (spike) [98], [99].

Two different modes of spiking can be applied in speciation analysis: species-specific and species-unspecific (Figure 1.6 [100]). In the species-specific ID, the species of the added isotopically enriched element have to be known and the same as the analyte. On the other hand, the species-unspecific mode is used when an unknown species in the sample is analysed or when isotopically enriched isotope in the chemical form of the analyte cannot be prepared. In the species-unspecific spiking mode, the addition of the isotope spiking solution is carried out after the complete separation of the naturally occurring species in the sample (post-column spiking).

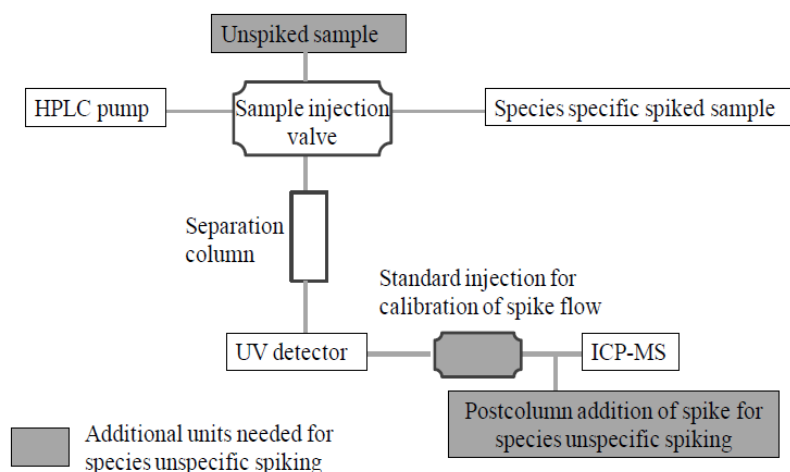


Figure 1.6: Schematic diagram of the species-specific and the species-unspecific isotope dilution (adopted from reference [100]).

The use of IDMS technique provides precision, accuracy and provision of definable uncertainty values. Since IDMS requires only isotope ratio and mass measurements, the possibility of a mistake is minimal. The uncertainty of measurements of elemental species concentrations depends only on the uncertainty of the measurement of the isotope ratio of the element.

When the species-specific mode is applied, the concentration of the element in the sample is calculated using Equation (1), adapted from reference [100], where s stands for sample and s_p for isotopically enriched spike. C_s and C_{sp} are the concentrations of the element in the sample and the spike, respectively. m_s and m_{sp} are the mass taken from the sample and the spike in the mixture, respectively. M_s and M_{sp} are the elemental atomic weights of the element in the sample and the spike, respectively. The concentration of the analyte, A_a is the abundance of the isotope a , A_b is the abundance of the isotope b , R_m

is the isotope ratio a/b in the mixture, R_s is the isotope ratio b/a in the sample, R_{sp} is the isotope ratio a/b in the spike.

$$C_s = C_{sp} \frac{m_{sp}}{m_s} \frac{M_s}{M_{sp}} \frac{A_{sp}^b}{A_s^a} \left(\frac{R_m - R_{sp}}{1 - R_m R_s} \right) \quad (1)$$

The use of ID technique enables also the verification of the accuracy of the analytical procedure. The accuracy of the analytical procedure can also be checked by the analysis of the certified reference materials (CRM) and by the spike recovery tests.

1.5.4 Speciation procedures used for evaluation of the environmental impacts of waste materials

During the process of steel production, operation of metal works and thermal power plants, huge quantities of waste are generated, which are before re-use collected on industrial disposals. From the disposed materials, different contaminants (metals and metalloids) can be released into the air, soil, surface waters and sediments. Among them, Cr is frequently present in elevated concentrations. Since the hexavalent form of Cr is of environmental concern, Cr speciation is needed for the evaluation of its environmental impacts.

For Cr speciation, numerous analytical methods have been developed to determine extractable and total Cr(VI) in soils and sediments. Zuliani et al. [56] applied extraction with 0.1 M K_2HPO_4 (pH 8) for the determination of exchangeable Cr(VI) content in soil samples.

To extract total Cr(VI) from solid matrices, including soluble, adsorbed, and precipitated, as well as sparingly soluble chromates, such as $PbCrO_4$, $BaCrO_4$ or $SrCrO_4$, the United States Environmental Protection Agency (US EPA, 1996) suggested an alkaline digestion procedure (Method 3060A) using a 3% Na_2CO_3 –2% NaOH extraction solution, and heating the extract to 90–95 °C for 60 min (US EPA, 1996). The addition of $/^{2+}$ in a phosphate buffer to the extraction solution is recommended to suppress Cr(III) oxidation under the highly alkaline pH of the extraction reagent. The 3060A method was commonly used to extract total Cr(VI) from solid matrices [101], [102], [103], including sediments [104]. As an alternative to the Na_2CO_3 –NaOH extraction agent, the use of ethylenediaminetetraacetic acid (EDTA) has been reported to recover Cr(VI) from soils [105] and sediments [106].

For quantification of Cr(VI) in water and solids matrices speciated ID-ICP-MS has been applied as a sensitive and accurate analytical method. Use of double isotopically enriched tracers, e.g. $^{50}Cr(VI)$ and $^{53}Cr(III)$, allows evaluation of, and correction for species-interconversion during the analytical procedure [107], [105], [56], [108].

Determination of Cr(VI) in sediments impacted by the industrial activities is important, since contaminated sediments can be a source of pollution of surface and ground waters [109]. Regardless of this fact, the occurrence of Cr(VI) in sediments and its potential impact to groundwater has not been commonly investigated. Mills and co-workers [110] studied a potential source of geogenic Cr(VI) in groundwater generated in vadose zone soils and alluvial sediments. Although contents of Cr(VI) extractable in 5 mM $CaSO_4/MgSO_4$ in soils and sediments did not exceed 0.042 mg kg^{-1} , the leaching of Cr(VI) into groundwater reservoirs was possible. Mädler and co-workers [104] analysed trace concentrations of Cr(VI) in 38 lake sediments collected in a pristine region in the Northern Ontario, Canada. Cr(VI) was determined by the ion chromatography-tandem mass spectrometry (IC-MS/MS) procedure after alkaline digestion of samples. Concentrations of Cr(VI) (wet weight) ranged from 0.03 to 0.2 mg kg^{-1} , while in 8 out of the sediment samples analysed, the Cr(VI) content was below the limit of detection (0.014 mg kg^{-1} , wet weight). Trace

Cr(VI) concentrations in sediments from geogenic origin in general do not represent an environmental hazard, but at industrially exposed sites, the Cr(VI) content may be of environmental concern. Rosales et al. [111] investigated Cr speciation in river sediments (Guadalentin River, SE Spain) contaminated by tannery effluents. The data revealed that Cr was present almost exclusively in the trivalent oxidation state (around 96%), but since total Cr concentrations were extremely high (up to 10000 mg kg⁻¹), concentrations of Cr(VI) were also very high (around 400 mg kg⁻¹), indicating severe anthropogenic contamination of the riverbed sediments. Byrne et al. [57] investigated the fate of Cr in urban sediments from historically contaminated wastewater from Salford Quays, UK, which received domestic and industrial sewage and road runoff prior to the remediation process that started in the late 1980s. By using X-ray Absorption Near Edge Structure (XANES) geochemical analyses, it was demonstrated that Cr(III), associated with aluminosilicate glass grains prevailed and existed in iron oxides, while only trace amounts of Cr(VI) were detected. Geochemical analyses additionally suggested low environmental mobility and limited bioavailability of Cr under anoxic conditions and neutral pH of sediments.

When Cr speciation is investigated, the use of isotopically enriched Cr(VI) and Cr(III) tracers importantly contributes to the validity of obtained results and enables Cr(VI) quantification with ID-ICP-MS [54].

The analytical procedures for the determination of Cr(VI) in sediments and soils are summarized in Table 1.1.

Table 1.1: Analytical procedures for the determination of Cr(VI) in sediments and soils.

If reported, LODs and or LOQs are provided.

Analyte and sample matrix	Purpose of work	Sample preparation	Detection technique	Reference
Leachable Cr(VI) in soils	Investigation of biogenic formation of Cr(VI) from serpentine soil by Mn(III/IV) oxides and Cr(VI) transport from soil to water reservoirs.	Extraction with deionized water	1,5-diphenylcarbazide spectrophotometry	[112]
Leachable Cr(VI) in artificial soil and sediment aggregates	Study of Cr(VI) generation from indigenous Cr(III) by Mn(III/IV) oxides under fluctuating hydrologic and redox conditions.	Extraction with deionized water	1,5-diphenylcarbazide spectrophotometry	[113]
Leachable Cr(VI) in soils, sediments and groundwater	Study of occurrence of Cr(VI) in soils, sediments and groundwater, originating from Cr-bearing serpentine minerals and anthropogenic influence from fly ash disposal.	Extraction with deionized water	1,5-diphenylcarbazide spectrophotometry LOD Cr(VI) in soil, sediment: 10 µg kg ⁻¹ LOD Cr(VI) in water: 1.5 µg L ⁻¹	[114]
Leachable Cr(VI) and Cr(III) in sediments	Development of analytical procedure for the determination leachable Cr forms in bottom sediment (Pławniowiec reservoir, Poland).	Extraction with deionized water, Extraction with 5 mM Na ₂ HPO ₄ and 50 mM KH ₂ PO ₄ , pH 6	HPLC-ICP-MS Chromatographic column: anion-exchange Dionex IonPac AG7; LOD Cr(III): 0.11 µg L ⁻¹ ; LOD Cr(VI): 0.17 µg L ⁻¹	[115]
Leachable Cr(VI) in soils and sediments	Study of the potential source of geogenic Cr(VI) in groundwater, generated in vadose zone soils and alluvial sediments.	Extraction with 5mM CaSO ₄ /MgSO ₄	1,5-diphenylcarbazide spectrophotometry	[116]

Analyte and sample matrix	Purpose of work	Sample preparation	Detection technique	Reference
Leachable Cr(VI) and Cr(III) in sediments	Investigation of the potential of Cr(III) oxidation by Mn(III/IV) oxides in Baltimore Harbour sediments	Extraction with 10 mM NaCl	Ion pairing RP-HPLC-ICP-MS Chromatographic column: reversed phase silica based Brownlee C8; LOQ (Cr(VI) and Cr(III): 0.5 $\mu\text{g L}^{-1}$	[117]
Exchangeable Cr(VI) in soils	Optimization of the analytical method by the use of Cr enriched stable isotopic tracers to assure minimal species interconversions during the extraction procedure.	Extraction with 100 mM K_2HPO_4 , pH 8	HPLC-ID-ICP-MS; Chromatographic column: anion-exchange FPLC Mono Q HR 5/5 LOD Cr(VI): 0.05 $\mu\text{g kg}^{-1}$; LOQ Cr(VI): 0.16 $\mu\text{g kg}^{-1}$	[56]
Total Cr(VI) in sediments	Speciation of Cr in sediments and pore water collected from the Baltimore Harbor.	Extraction with 0.28 M Na_2CO_3 /0.5 M NaOH	Ion pairing RP-HPLC-ICP-MS Chromatographic column: Brownlee C8; LOQ Cr(VI): 40 $\mu\text{g Cr kg}^{-1}$	[58]
Total Cr(VI) in sediments	Determination of trace amounts of Cr(VI) in sediments from pristine region in Northern Ontario. To control for species interconversion during the digestion procedure, the sample was doubly spiked with isotopically enriched $^{50}\text{Cr(III)}$ and $^{53}\text{Cr(VI)}$.	Extraction with 0.28 M Na_2CO_3 /0.5 M NaOH, Extraction with 50 mM EDTA, pH 10	IC-MS/MS Chromatographic column: Dionex, AS20; LOD Cr(VI): 14 $\mu\text{g kg}^{-1}$, wet weight	[118]
Total Cr(VI) and Cr(III) in soils	Development of analytical method for quantification of Cr(III) and Cr(VI) in candidate SRMs NIST 2700 and NIST 2701 (Cr(VI) in contaminated soil). Cr enriched isotopes were used to study Cr interconversion reactions.	Microwave-assisted extraction with 50 mM EDTA	HPLC-ID-ICP-MS Chromatographic column: anion-exchange Dionex Ion pack AS9-HC	[105]
Total Cr(VI) in soils	Quantification of Cr(VI) in soils from Lombardia, contaminated by polluted water plumes. The extent of Cr(VI) reduction during the analytical procedure was evaluated by the use of Cr enriched stable isotopic tracers.	Microwave-assisted extraction with 50 mM EDTA	HPLC-ID-ICP-MS Chromatographic column: anion-exchange Dionex Ion pack AS9-HC	[119]
Total Cr(VI) and Cr(III) in soils and sediments	Development of analytical methodology for speciation of Cr in soils and sediments.	Microwave-assisted extraction with 100 mM EDTA, 1% TBAB and HF	HPLC-ICP-OES Chromatographic column: anion-exchange Dowex-1, pH 4.5; LOD Cr(VI): 5000 $\mu\text{g kg}^{-1}$	[106]
Total Cr(VI) in sediments	Study of Cr speciation in Guadalentin river sediments contaminated by tannery effluents.	Extraction with 0.28 M Na_2CO_3 /0.5 M NaOH	1,5-diphenylcarbazide spectrophotometry	[111]
Cr(VI) and Cr(III) in sediments	Study of the solid-phase chemical speciation of Cr in urban sediment particulates from historically contaminated wastewater from Salford Quays, to evaluate the long-term fate of Cr in the urban sediment cascade.	Air-dried sediment samples impregnated with epoxy resin and polished surface blocks produced for XANES analysis.	XANES	[57]
Total Cr(VI) in soil and sediments	Determination of Cr(VI) in soils and sediments.	Extraction with 100 mM Na_2CO_3	ETAAS, no speciation procedure applied	[120]

1.5.5 Speciation procedures used for evaluation of the environmental impacts of building composites containing waste materials

To study the release of toxic substances from building composites, leaching tests were usually applied in which total concentrations of elements were determined in leachates from for evaluation of their environmental impacts [59], [34], [35], [63]. Since the mobility and toxicity of elements depends of their chemical forms, speciation analysis provide more relevant information [64]. To evaluate the potential environmental hazard of Cr, Cr(VI) was determined in leachates from building composites containing EAF dust [12], [13], EAF slag [11] and ladle slag [39] by 1,5 diphenylcarbazide spectrophotometry or HPLC-ETAAS procedure. Although ICP-MS offers hyphenation with HPLC and on-line analysis of separated Cr species, it was not applied as a detector for quantification of Cr species in leachates from building composites.

In wastes and building composites containing wastes from thermal power plants and steel-making industry, the pH is highly alkaline. Therefore, the leaching of elements such as Cr, As, V and Mo is expected to occur in the form of oxoanions, in their highest oxidation state [14], [39], [40], [11]. It is well known that Cr, Mo and V are more toxic as Cr(VI), Mo(VI) and V(V), respectively), while As(V) is less toxic than As(III) [121], [122], [123], [124]. Oxoanions of Cr(VI), As(V), Mo(VI) and V(V) are highly mobile in the form of alkali chromates, arsenates, molybdates and vanadates. However, there were no literature reports on their determination in building composites containing waste materials.

ICP-MS offers simultaneous determination of elements. However, there are only few literature reports on simultaneous speciation analysis using ICP-MS as a detector of separated elemental species. Ščančar et al. [125] developed an analytical procedure for the simultaneous speciation analysis of chromate, molybdate, tungstate and vanadate by anion-exchange HPLC-ICP-MS. At highly alkaline conditions single CrO_4^{2-} , MoO_4^{2-} and WO_4^{2-} were present and eluted in sharp chromatographic peaks, while VO_4^{3-} species, which predominates at pH 12, was eluted in a slightly broadened peak. Eluted species were simultaneously detected on-line by ICP-MS recording m/z 52, 95, 182 and 51. The developed procedure was successfully applied to the analysis of leachable concentrations of chromate, molybdate, tungstate and vanadate in alkaline extracts of manual metal arc (MMA) welding fumes loaded on filters. Morita et al. [92] applied a sensitive method for the simultaneous speciation of As and Sb in hot spring water and fish samples by HPLC-ICP-MS using C30 reversed-phase column. After careful optimization of the chromatographic conditions, it was possible to separate eight As (As(III), As(V), monomethylarsonic acid (MMAA), dimethylarsinic acid (DMAA), arsenobetaine (AB), arsenocholine (AsC), trimethylarsine oxide (TMAO) and tetramethylarsonium (TeMA)) and two antimony species (Sb(III) and Sb(V)). Bednar et al. [93] performed separation of oxoanions of tungsten (W), Mo and P on an anion-exchange Dionex AS-11 chromatographic column. Coupling of this column to ICP-MS enabled simultaneous speciation analysis of tungstate, molybdate, and phosphate at the sub mg L^{-1} concentration levels in ground water and aqueous soil extracts. Wolf et al. [94] modified the analytical method that was previously developed for the determination of Cr(III) and Cr(VI) by HPLC-ICP-MS. The usage of a silica-based Brownlee C8 column and the same chromatographic conditions as for the Cr speciation allowed the simultaneous determination of As(III), As(V), Se(IV), Se(VI), Cr(III), and Cr(VI) in leachates from ash and soil affected by wildfires. Simultaneous speciation analysis of As, Sb and thallium (Tl) species (As(III), As(V), Sb(III), Sb(V), Tl(I), and Tl(III)) in river water samples was reported, in which an anion-exchange Dionex IonPac AS-7 column coupled to ICP-MS was used [126]. The analytical procedure was also optimized for the simultaneous speciation of

As(III), As(V), monomethylarsenic acid (MMA), dimethylarsenic acid (DMA), Cr(III) and Cr(VI), and Cd(II) in water samples on an anion-exchange Hamilton PRP-X100 column with ICP-MS detection [91].

ICP-MS offers great potential to be used as detector in simultaneous speciation analysis of oxoanions of chromate, arsenate, molybdate and vanadate in leachates from building composites containing different wastes, but for the time being, it was not applied.

Chapter 2

Aims and Hypothesis

During the operation of the thermal power plants vast amounts of fly ash are generated. The alloying of steel through various refining processes also leads to generation of waste materials, like EAF dust, EAF slag and ladle slag. The disposal of these waste materials represents an environmental burden.

The alternative to landfilling is the re-use of such waste by-products in cementitious building materials. Reduction of the cement content in building materials significantly contributes to the reduction of CO₂ emissions, and also lowers the landfill loads. When industrial wastes are re-used, it is necessary to assure the immobilization of contaminants, and to estimate the environmental hazard due to their possible release from the final cementitious products during their service life.

For understanding the mechanisms of contaminants' immobilization in new composites, it is essential to know the chemical speciation of elements. To follow the long-term environmental impacts of building composites, the NEN 7375 test is prescribed, considering diffusion of contaminants from monolithic building materials. However, in the environment, processes of diffusion and dissolution of contaminants simultaneously occur.

The landfilling of waste materials cannot be completely omitted, because it is not possible to re-use all the waste materials generated. In addition, EAF slag and ladle slag should be stabilised before they are incorporated into new materials. From such waste disposals, contaminants may be leached into the terrestrial and aquatic surroundings. To evaluate their environmental impacts, reliable analytical procedures are needed, which include chemical speciation analysis.

The aims of the Doctoral Dissertation were:

- To develop new leaching protocols based on diffusion and dissolution of elements and their chemical species from building composites prepared from fly ash, cement and EAF dust for the long-term assessment of environmental impacts.
- To critically evaluate the results from new leaching protocols against those obtained by the NEN 7375 test.
- To develop an analytical procedure for simultaneous speciation of chromate, arsenate, molybdate and vanadate in leachates from building composites from fly ash, cement and EAF dust by the HPLC-ICP-MS.
- To develop a reliable and sensitive analytical procedure for the determination of total Cr(VI), which is based on speciated ID-ICP-MS, and to determine Cr(VI) content in the sediments from industrially exposed sites of the Sava River influenced by the stainless steel production and activities of the metallurgic industry.

Chapter 3

Materials and Methods

3.1 Materials

All the reagents used were of analytical-reagent grade. Ultrapure 18.2M Ω cm water obtained from a Direct-Q 5 Ultrapure water system (Millipore Watertown, MA, USA) was used for all aqueous solutions. Individual standards of the chromate, molybdate and vanadate were prepared from K_2CrO_4 and $(NH_4)_6Mo_7O_{24}$ in water (1000 ± 2 mg L^{-1} of Cr and Mo, respectively), and from NH_4VO_3 salt dissolved in alkaline buffer (2% NaOH + 3% Na_2CO_3) (1000 ± 2 mg L^{-1} of V), all purchased from Merck. Arsenate stock solution was prepared from $Na_2HAsO_4 \cdot 7H_2O$ salt in water (1000 ± 2 mg L^{-1} of As) from Sigma-Aldrich. Other working standard solutions were prepared daily in water or in alkaline buffer and were purchased from Merck.

Suprapur nitric acid (65% HNO_3), hydrochloric acid (30% HCl), hydrofluoric acid (40% HF), boric acid (H_3BO_3) and ammonium peroxo disulphate ($(NH_4)_2S_2O_8$) supplied from Merck Millipore (Darmstadt, Germany) were used for microwave-assisted digestion of fly ash, cement, EAF dust and sediment.

Enriched ^{50}Cr and ^{53}Cr isotopes in the form of Cr_2O_3 were obtained from Oak Ridge National Laboratory (Oak Ridge, TN, USA) and were used for the preparation of $^{50}Cr(VI)$ and $^{53}Cr(III)$ isotopic spike solutions. The determined composition of enriched ^{50}Cr isotope was $96.04 \pm 0.05\%$ for isotope 50, $3.40 \pm 0.02\%$ for isotope 52, $0.25 \pm 0.01\%$ for isotope 53 and $0.03 \pm 0.01\%$ for isotope 54. The determined composition of enriched ^{53}Cr isotope was $0.040 \pm 0.005\%$ for isotope 50, $2.81 \pm 0.02\%$ for isotope 52, $95.58 \pm 0.02\%$ for isotope 53 and $0.160 \pm 0.005\%$ for isotope 54. SRM 979-Cr (isotopic) for isotope ratio measurements was purchased from NIST (National Institute of Standards & Technology, Gaithersburg, USA). A natural abundance Cr(III) solution ($Cr(NO_3)_3$ in 2–3% HNO_3) containing 1000 mg L^{-1} of Cr was purchased from Merck (Darmstadt, Germany).

For the extraction of Cr(VI) from sediments, extracting buffer solution was prepared daily from Merck suprapur sodium hydroxide monohydrate and suprapur sodium carbonate. Sodium chloride of suprapur quality used in HPLC separations and analytical grade magnesium chloride, tris(hydroxymethyl)aminomethane (Tris) and ethylenediaminetetraacetic acid (EDTA) were also obtained from Merck. Anhydrous sodium sulphite (Na_2SO_3) from Acros Organics (Geel, Belgium) was used as a reducing agent. For the filtration of leachates, Minisart membrane filters (Sartorius, Göttingen, Germany) were used.

Certified reference materials were purchased from BCR, Geel, Belgium (CRM 320 Trace Elements in River Sediment and CRM 544, Cr(VI) in a lyophilised solution) and from NRC, Ottawa, Ontario, Canada (SLRS-5, River water reference material). The certified

reference material CRM 041, Chromium VI – Soil, which was used to check the accuracy of the method for the determination of Cr(VI), was obtained from Merck.

3.2 Instrumentation

The total concentrations of the elements in leachates of the composites from fly ash, cement and EAF dust and those after microwave-assisted digestion were determined by ICP-MS on an Agilent 7700x ICP-MS instrument from Agilent Technologies (Tokyo, Japan). The HPLC speciation analyses were performed on Agilent series 1200 quaternary pump equipped with a model 7725i Rheodyne sample valve (Cotati, Ca, USA) fitted with a 0.2 mL injection loop. For the separation of Cr, Mo, As and V species, a strong anion-exchange fast protein liquid chromatography (FPLC) Mono Q HR 5/5 column (Pharmacia, Uppsala, Sweden) (column dimensions 5 x 50 mm, matrix polystyrene/divenyl benzene, pH stability 2-12, particle size 10µm) connected to ICP-MS was used. The data processing was based on the peak area. The control and operation of the coupled system was performed by using an Agilent MassHunter software.

Ultrasonic-assisted extraction of samples was performed on a 550D VWR International ultrasonic bath (West Chester, PA, USA). A CEM MARS 5 (CEM Corporation, USA) Microwave Acceleration Reaction System equipped with temperature and pressure feedback controls operating at 1600W was used for the digestion of samples.

A sensIONTM+ EC5 Portable Conductivity Meter (HACH, USA) was employed to determine the pH and conductivity of the samples. A Mettler AE 163 (Mettler Toledo, Zürich, Switzerland) analytical balance was used for all weighing.

3.3 Methods

3.3.1 Sampling and sample preparation

3.3.1.1 Building composites from fly ash, cement and EAF dust

In order to investigate the parameters that influence the leachability of elements from building materials with the addition of waste by-products, composites from fly ash, cement and EAF dust were prepared and left for 30 days at ambient conditions for the stabilization. Fly ash and EAF dust were obtained from the coal-red power station Pljevlja and the steel mill Nikšić in Montenegro, while ordinary Portland cement CEM II/B-M (SLL) 42.5 N was used. The composite casts were cylinders, 7 cm in height and 5 cm in diameter, with a volume of approximately 0.137 L. Various types of composites were examined: 99.5% mixture of fly ash (70%) and cement (30%) and 0.5% EAF dust, 99.5% mixture of fly ash (80%) and cement (20%) and 0.5% EAF dust, 100% mixture of fly ash (70%) and cement (30%), and 98% mixture of fly ash (80%) and cement (20%) and 2% EAF dust. The composites were immersed into MilliQ water, synthetic surface and sea water and leachates taken at different time periods. In addition to compact composites, ground composites were also prepared. The specimens were ground (disc-mill from tungsten carbide) to a particle size below 0.5 cm. The ground composites simulated the disintegration of the material in the environment over time (Figure 3.1).



Figure 3.1: Compact and ground building composites.

3.3.1.2 Sediment samples

Sediment samples were collected in 2 L plastic bottles from the river bank (grab sampling, top 10 cm layer) along the Sava River at locations presented. Ten samples were collected from different sampling locations. Sampling points are presented in Figure 3.1. Prior to analysis samples were stored at room temperature. The unpolluted site Mojstrana was chosen as a reference location. Sediments from the Jesenice site were taken from six locations below the black and ladle slag disposals from the steel works Acroni Jesenice. The potential influence of the steel-making industry was also followed downstream of Jesenice at the Radovljica and Gobovce sampling sites, while in Croatia and Serbia, Cr(VI) was determined in sediments contaminated as a consequence of the heavy metal industry and metallurgical activities.

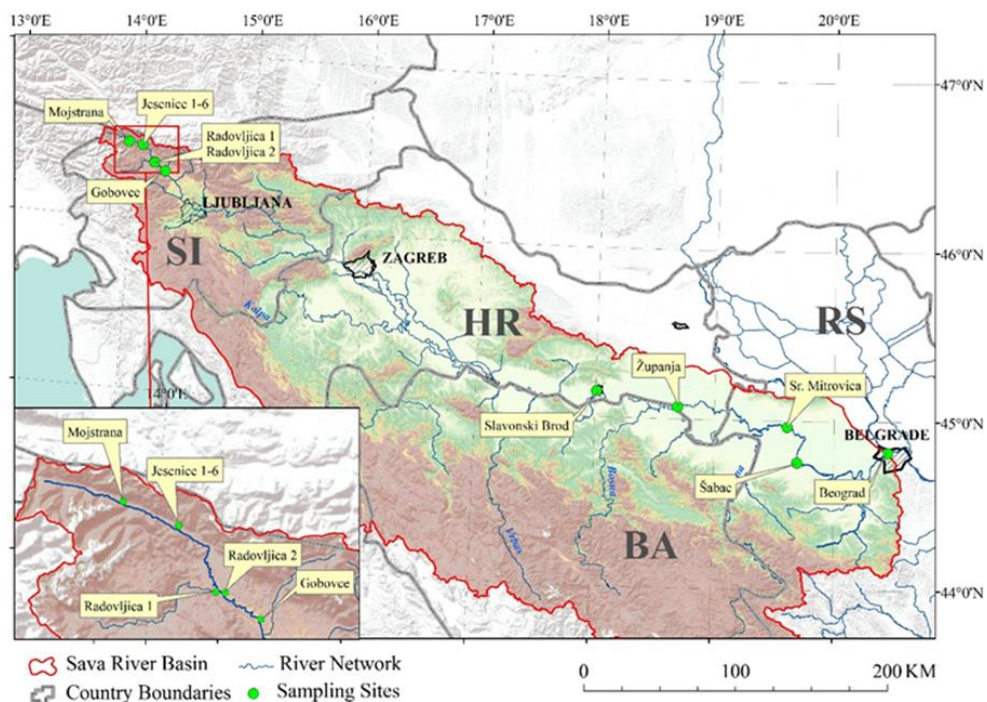


Figure 3.2: The Sava River sampling sites.

3.3.2 Optimized analytical procedures

3.3.2.1 Leaching tests

To assess the long-term environmental impacts of building composites, the leachability tests based on diffusion as set by the NEN 7375 test and its modified leaching procedures were performed over a period of 64 days. The compact specimens were immersed in MilliQ water (pH 7) and samples taken at 0.25, 1, 2.25, 4, 9, 16, 36 and 64 days as specified in the NEN 7375 test. In addition to compact composites, ground composites were also prepared in the modified protocols. The samples were taken at the same times as for the NEN 7375 test, and also at 120 and 180 days (to see trends of contaminants leaching). The specimens were ground (disc-mill from tungsten carbide) to a particle size below 0.5 cm. The ground composites simulated the disintegration of the material in the environment over time. Along with MilliQ water (pH 7), synthetic sea water composed of 3.8% NaCl, MgCl_2 ($1500 \text{ mg L}^{-1} \text{ Mg}$), CaCl_2 ($600 \text{ mg L}^{-1} \text{ Ca}$) and KCl ($420 \text{ mg L}^{-1} \text{ K}$) and synthetic surface water composed of CaCO_3 ($5 \text{ mg L}^{-1} \text{ Ca}$) and MgCO_3 ($1 \text{ mg L}^{-1} \text{ Mg}$), which were not replenished during the course of the experiment, were also used as leaching solutions. The experiments were carried out in 1 L polyethylene flasks. The volume ratio of the tested composites to the added leaching solution was 1:5, as specified by the NEN 7375 test. To each compact and/or ground composite, 0.687 L of the leaching solution was added, and the flasks covered. Blank samples of the leaching solutions were also analyzed along with the samples. Prior to each sampling, the solution was mixed with a glass rod. 0.7 mL of the sample was taken with a plastic syringe and filtered ($0.45 \mu\text{m}$). After each sampling, the same amount of the leaching solution that was taken was then added. In the leaching solutions collected, the pH and conductivity were measured. The total elemental concentrations were determined in 10-times diluted samples by ICP-MS. When the modified NEN 7375 protocols were applied, the concentrations of chromate, vanadate and molybdate were also determined by HPLC-ICP-MS, from 2-times diluted samples. A schematic presentation of the leaching protocols is given in Figure 3.2.

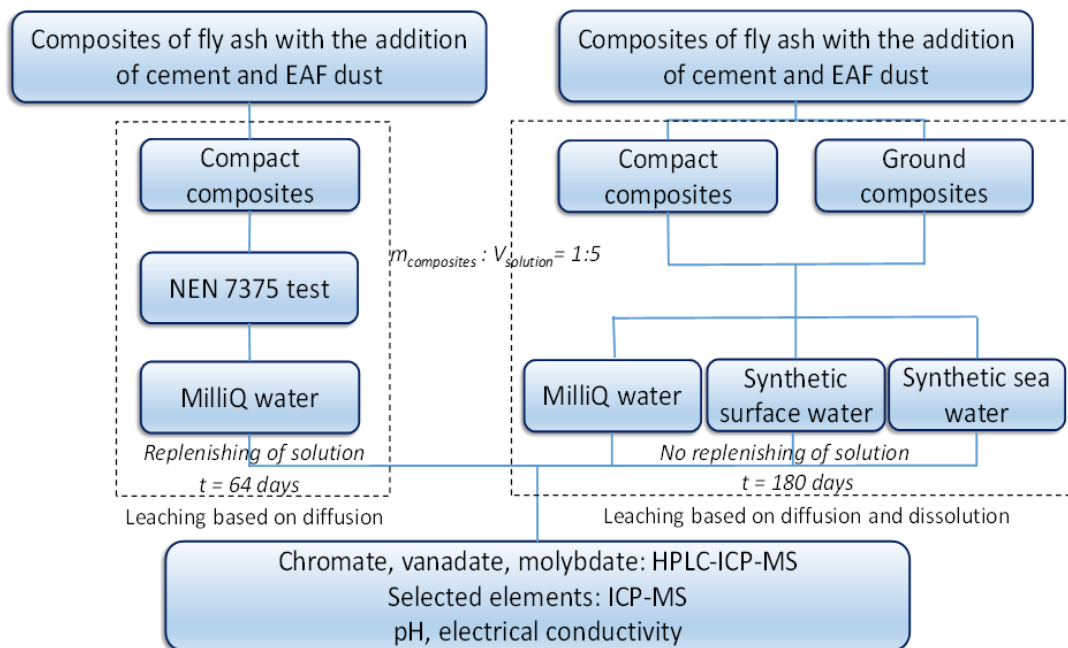


Figure 3.3: A schematic presentation of the leaching protocol.

3.3.2.2 Microwave-assisted digestion

For the determination of total elements concentrations in building composites and sediments, a two-step microwave-assisted digestion procedure, previously developed in our group, was performed [127]. 0.1 g of waste material or 1 g of sediments were weighed into 100 mL high-pressure Teflon vessel. Into a vessel 4 mL of supra pure HNO_3 , 2 mL of supra pure HF , 1 mL of supra pure H_2O_2 and 1 mL of supra pure HCl were added. The Teflon vessels were covered and subjected to microwave-assisted digestion at a maximal power of 1200 W ramp to temperature 200 °C in 30 min, pressure 50 bar, hold at 200 °C for 60 min and cooling the contents in the following 30 min. After that, the Teflon vessel was vented and the vessel cap removed. 12.5 mL of supra pure H_3BO_3 (4% aqueous solution) was then added for complexation of fluorides and in the second step the contents digested again by ramping the temperature to 200 °C in 15 min, holding the same temperature for the next 30 min and cooling the contents in the following 30 min [56]. After digestion the clear solution was obtained. The content was quantitatively transferred to a 30 mL graduated perfluoroalkoxy (PFA) flask and filled to mark with water. Prior to ICP-MS analysis, samples were appropriately diluted with MilliQ water. Blank samples were prepared under the same analytical protocol with the exception that no samples were added.

3.3.2.3 Ultrasound-assisted extraction

For the extraction of total Cr(VI) content from sediments, an alkaline extraction procedure was applied. To a 50 mL flat bottom glass beaker, 2 g of wet sediment was weighed and 9 mL of 2% NaOH + 3% Na_2CO_3 extraction solution added. Then, 1 mL of 4 mol L^{-1} MgCl_2 was added in order to prevent oxidation of Cr(III) during the extraction procedure. To control for species interconversion during the extraction procedure and for the calculation of Cr(VI) concentration by speciated isotope dilution (ID)-ICP-MS, 100 μL of ^{53}Cr (III) and 100 μL of ^{50}Cr (VI) enriched Cr stable isotopic solution with a concentration of 10000 $\mu\text{g L}^{-1}$ of Cr were added. The sample was transferred to an ultrasonic bath at 80 °C, and the contents were sonicated for 1 hour at maximal power of 700 W. The sample was then cooled to room temperature, filtered through a 0.45 μm membrane filter and diluted 10 times prior to speciation analysis.

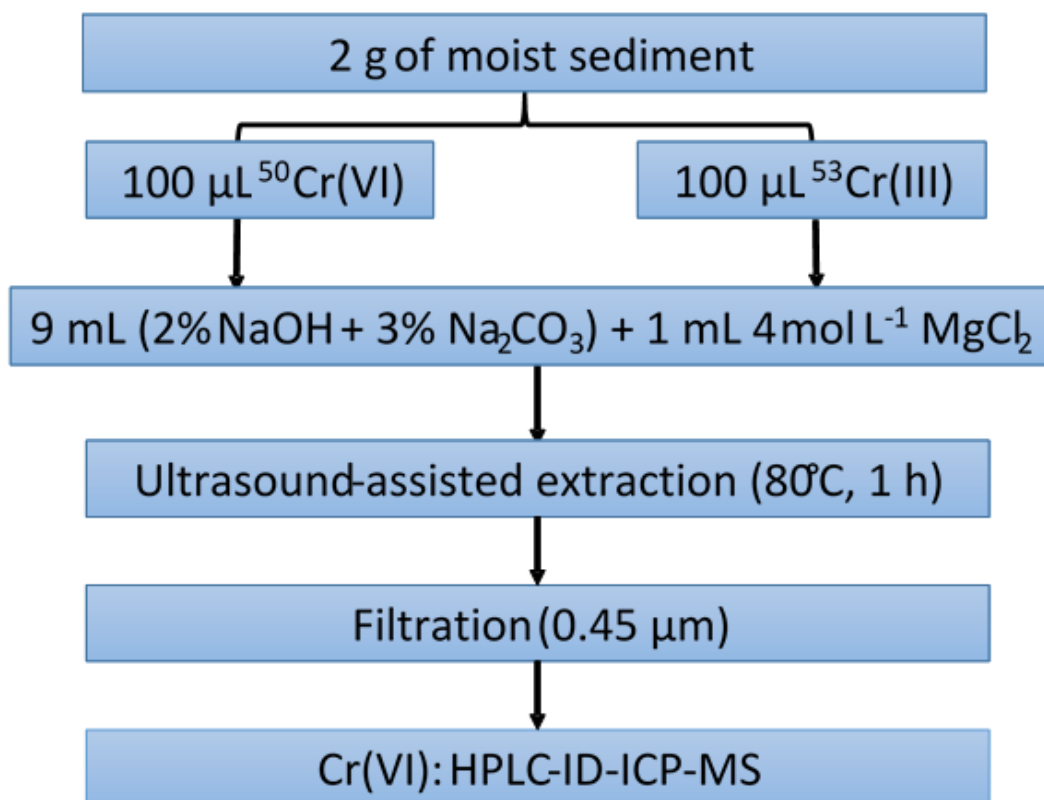


Figure 3.4: Flow chart of the analytical procedure for the determination of Cr(VI) in sediments.

3.3.2.4 Chromatographic separation of elements species by anion-exchange HPLC

A volume of 0.2 mL of sample was injected onto the column. To reduce the blank arising from the stainless steel needle, the sample was drawn with the syringe in the opposite direction through the plastic tube of the waste exit from the injector (reverse injection) [87]. A linear gradient elution from water to 0.7 M NaCl (0 to 100%) was applied for 10 min at a flow rate of 1.5 mL min⁻¹. After separation, the column was regenerated with 2 mol L⁻¹ NaCl for 3 min and equilibrated with water for 7 min. The eluate from the column was directed to the ICP-MS during the separation step, while it was directed to waste through a software-controlled six-port valve during the regeneration step. Cleaning of the Mono Q column was performed by 0.5 mL of 1 mol L⁻¹ sodium hydroxide which was injected onto the column resin, and the chromatographic procedure was applied. The cleaning procedure was repeated twice. Before each new series of experiments, two blank samples were first injected.

All the experiments were performed in two or three replicates.

3.3.3 Preparation of enriched isotopic standard solutions

Cr(VI) standard solution was prepared by alkaline melting from Cr₂O₃, enriched by a ⁵⁰Cr isotope, while the ⁵³Cr(III) standard solution was prepared from Cr₂O₃ enriched by a ⁵³Cr isotope, applying microwave-assisted digestion [128]. Natural abundance Cr(III) and Cr(VI) solutions were prepared from ^{nat}Cr(III) and ^{nat}Cr(VI) standards purchased from Merck. Possible species interconversions were calculated according to the procedure

proposed by Tirez et al. [129]. Determination of the concentrations of enriched $^{53}\text{Cr}(\text{III})$ and $^{50}\text{Cr}(\text{VI})$ standard solutions was performed by reverse ID-ICP-MS [130], [131].

$^{50}\text{Cr}(\text{VI})$ standard solution:

0.0029 g of Cr_2O_3 (^{50}Cr enriched isotope) was transferred to a platinum beaker and 0.4 g of NaKCO_3 and 0.1 g of NaOH were added. The contents were melted by a Bunsen burner until a yellow-orange melt was obtained. During the melting procedure quantitative oxidation of Cr by air oxygen was achieved only in an alkaline media. The melt was cooled to a room temperature and 0.7 mL of concentrated HCl was carefully added to dissolve the deposit. The clear solution was transferred to a Teflon tube and diluted to 10 mL with water. The concentration of Cr in the stock isotopic spike solution was determined by reverse ID-ICP-MS.

$^{53}\text{Cr}(\text{III})$ standard solution:

0.0029 g of Cr_2O_3 (^{53}Cr enriched isotope) was transferred to a Teflon vessel and 4 mL of concentrated HNO_3 was added. The Teflon vessel was subjected to microwave-assisted digestion performed at maximal power of 1200 W, ramp to temperature 20 min, 190 °C, pressure 10 bar, holding 20 min, cooling 20 min. The clear solution was quantitatively transferred to a platinum beaker and the contents carefully evaporated to approximately 0.2 mL. Then 0.7 mL of concentrated HCl was added, the solution transferred to a Teflon tube and diluted to 10 mL with water. The concentration of Cr in the stock isotopic spike solution was determined by reverse ID-ICP-MS.

3.3.4 Instrumental parameters for the determination of element concentrations by ICP-MS and chemical species of elements by HPLC-ICP-MS

The total element concentrations in the fly ash, cement and EAF dust were determined by ICP-MS after microwave-assisted digestion. In the leaching solutions collected at specific times, total element concentrations were determined in 10-times diluted samples by ICP-MS.

Concentrations of chromate, arsenate, vanadate and molybdate were determined in two-times diluted samples by HPLC-ICP-MS. The instrumental operating parameters of the ICP-MS and HPLC-ICP-MS are presented in Table 3.1 and Table 3.2.

Table 3.1: ICP-MS operating parameters for determining element concentrations.

Parameter	Type/Value	Helium mode	HECM mode	No gas mode
<i>Sample introduction</i>				
Nebuliser	Miramist			
Spray chamber	Scott			
Skimmer and sampler	Ni			
<i>Plasma conditions</i>				
Forward power	1550 W			
Plasma gas flow	15.0 L min ⁻¹			
Carrier gas flow		1.05 L min ⁻¹		0.75 L min ⁻¹

Parameter	Type/Value	Helium mode	HECM mode	No gas mode
Dilution gas flow		0.10 L min ⁻¹		0.45 L min ⁻¹
He gas flow		4.5 mL min ⁻¹	10 mL min ⁻¹	
QP bias		-15.0 V	-97 V	-3.6 V
Oct bias		-18.0 V	-100 V	-8.0 V
Cell entrance		-40 V	-130 V	-40 V
Cell exit		-60 V	-150 V	-50 V
Deflect		-2.2 V	-80 V	13.4 V
Plate bias		-60 V	-150 V	-40 V
Sample uptake rate	0.3 mL min ⁻¹			
<i>Data acquisition parameters</i>				
Isotopes monitored		⁵¹ V, ⁵² Cr, ⁵⁵ Mn, ⁵⁶ Fe, ⁵⁹ Co, ⁶⁰ Ni, ⁶³ Cu, ⁶⁶ Zn, ⁷⁵ As, ⁹⁵ Mo	⁷⁸ Se	¹¹¹ Cd, ¹²³ Sb, ¹³⁷ Ba, ²⁰¹ Hg, ²⁰⁸ Pb
Isotopes of internal standards		⁴⁵ Sc, ⁷² Ge, ⁸⁹ Y, ¹⁰³ Rh, ¹¹⁵ In	⁴⁵ Sc, ⁷² Ge, ⁸⁹ Y, ¹⁰³ Rh, ¹¹⁵ In	⁴⁵ Sc, ⁷² Ge, ⁸⁹ Y, ¹⁰³ Rh, ¹¹⁵ In

Table 3.2: ICP-MS operating parameters for speciation analysis.

Parameter	Value
<i>Plasma conditions</i>	
Forward power	1550 W
Plasma gas flow	15.0 L min ⁻¹
Carrier gas flow	0.64 L min ⁻¹
Dilution gas flow	0.53 L min ⁻¹
Total carrier gas flow	1.17 L min ⁻¹
He gas flow	10 mL min ⁻¹
QP bias	- 97 V
Oct bias	-100 V
Cell entrance	-130 V
Cell exit	-150 V
Deflect	-80 V
Plate bias	-150 V
Nebuliser type	Miramist
Sample uptake rate	1.5 mL min ⁻¹
<i>Data acquisition parameters</i>	
<i>m/z</i> isotopes monitored in V, Cr and Mo speciation	⁵¹ V, ⁵⁰ V, ⁵² Cr, ⁹⁵ Mo,

Parameter	Value
m/z isotopes of internal standards	^{45}Sc , ^{72}Ge , ^{103}Rh , ^{209}Bi
Total acquisition time	599 s

Chapter 4

Results and Discussion

4.1 Long-Term Environmental Impacts of Building Composites Containing Waste Materials: Evaluation of the Leaching Protocols

For evaluating long-term environmental impacts of different waste and building materials, NEN 7375 test or its various modifications are frequently applied. However, information about the extent of the leaching of contaminants from the materials tested when applying different leaching protocols is scarce. Therefore, the NEN 7375 test and its different modified leaching procedures were compared using building composites that were 98% composed of a mixture of fly ash (80%) and cement (20%), with the remaining 2% being EAF dust. The experiments were performed at specified times, as set out in the NEN 7357 test, and in the modified protocols over a period of 6 months.

4.1.1 Total concentrations of elements in the fly ash, cement and EAF dust

First, the total concentrations of selected elements in the fly ash, cement and EAF dust were analysed. Samples were decomposed using microwave-assisted digestion (paragraph 3.3.2.2) and determined by ICP-MS. Results are presented in Table 1. As evident, the concentrations of the elements in the fly ash and the EAF dust are comparable to reported values by Nikolić et al. [17], while concentrations in Portland cement CEM I 52.5R are similar to those found by Zalar Serjun et al. [39]. Since EAF dust is a by-product of the steel-making industry, it contains high concentrations of Zn (250000 mg kg⁻¹) and Fe (210000 mg kg⁻¹). Pb and Cr are present in moderate concentrations (32000 and 4200 mg kg⁻¹, respectively), while the content of As, Mo and V is appreciably lower (180, 65 and 70 mg kg⁻¹, respectively). In comparison to the EAF dust, the concentrations of these elements determined in the cement and fly ash were substantially lower, about 2000, 300, 10, 20 to 40, and 3 to 6 times for Zn, Pb, Fe, Cr, and for As, respectively. The concentrations of V are slightly higher in the cement and about 2.5 times higher in the fly ash than in the EAF dust.

Table 4.1: Total element concentrations in the fly ash, cement and EAF dust determined by ICP-MS after microwave-assisted digestion of the samples. Results indicate the mean value obtained from two parallel samples (RSD of measurement better than $\pm 2\%$).

Element	Fly ash (mg kg ⁻¹)	Cement (mg kg ⁻¹)	EAF dust (mg kg ⁻¹)
As	30.0	15.0	178
Se	4.95	2.50	9.0
Ba	630	420	680
Fe	37000	14800	213450
Mn	278	750	18555
Co	27.0	15.0	30.0
Ni	150	90	385
Cu	90	135	3510
Zn	26.0	120	293330
Cd	65.4	74.5	980
Sb	2.65	2.45	302
Hg	<15	<15	<15
Pb	52.7	110	31860
Cr	160	91	4170
Mo	3.32	22.4	64.6
V	180	107	69.2

4.1.2 Investigations of the long-term environmental impacts of building composites containing waste materials

The NEN 7375 test based on diffusion or its different modifications, which combine both the diffusion and dissolution of the contaminants, were applied in order to compare the extent of the leaching of the elements and their species from the building composite. The experiments were performed as described in paragraph 3.3.2.1. The building composite comprising a 98% mixture of the fly ash (80%) and cement (20%), and 2% of EAF dust was chosen. It was hypothesised that the elements which are present in the form of oxoanions (e.g., As, Cr, Mo and V) will be leached over time to a substantial extent, allowing us to observe the differences in the extent of their leaching during the course of the experiments performed, and to critically appraise the potential of different leaching protocols compared for the evaluation of the long-term environmental impacts of building composites.

The leachability of the selected elements and chromate (Cr(VI)), molybdate (Mo(VI)) and vanadate (V(V)) was monitored at specified time intervals in the compact and ground composites in synthetic sea water, synthetic surface water and MilliQ water. Due to the presence of soluble $\text{Ca}(\text{OH})_2$ and CaCO_3 arising from the building composite, the pH and electrical conductivity of the leachates were gradually increased over time to an extent that was much greater when the leaching solutions were not replenished as compared to when the NEN 7375 test was applied (replenishing the solution). These results are summarized in Table 4.2. It is clear that in the ground composites the pH was slightly higher than in the compact composites (higher specific surface area and thus higher leachability of $\text{Ca}(\text{OH})_2$ and CaCO_3). The pH of the leachates of the synthetic surface water was also

higher than that of the aqueous leachates (as a consequence of the higher ionic strengths of the surface water, the leachability of $\text{Ca}(\text{OH})_2$ and CaCO_3 from the building composite was increased, leading to an increase in the pH). At alkaline pHs, the MgCl_2 present in the synthetic sea water is precipitated. This phenomenon initially hindered the solubilisation of the $\text{Ca}(\text{OH})_2$ and CaCO_3 from the building composite. Consequently, the pH of the sea water leachates was lower in the first 10 days than in the MilliQ or surface water leachates. After this period, the pH of the leachates from the sea water started to approach the values for the MilliQ and the surface water, since due to the higher ionic strength of the sea water, larger amounts of $\text{Ca}(\text{OH})_2$ and CaCO_3 were leached from the building composite.

Table 4.2: pH and electrical conductivity (EC) of aqueous and saline water leachates during the course of the experiment for 180 days. RSD for pH measurements is 1% and EC better than 5%.

Sample	Parameter	Time(days)									
		0.25	1	2.25	4	9	16	36	64	120	180
Synthetic sea water											
Compact	pH										
	EC	9.5	9.6	10.0	10.9	11.3	12.4	12.7	12.9	13.0	13.1
	($\mu\text{S cm}^{-1}$)	6950	7150	7200	7400	7520	7700	7800	8010	9850	9950
Ground	pH										
	EC	9.5	10.0	10.5	11.8	12.0	12.5	12.9	12.9	13.0	13.1
	($\mu\text{S cm}^{-1}$)	7000	7150	7210	7300	7800	8185	8220	8300	9700	9960
Synthetic surface water											
Compact	pH										
	EC	9.9	10.8	11.6	11.7	12.1	12.4	12.9	13.0	13.1	13.1
	($\mu\text{S cm}^{-1}$)	42	215	295	1090	1580	1970	2200	2330	3080	3110
Ground	pH										
	EC	10.0	10.9	11.7	11.8	12.3	12.6	13.0	13.1	13.1	13.2
	($\mu\text{S cm}^{-1}$)	215	390	410	1240	1880	2190	2300	2370	3280	3450
MilliQ water											
Compact	pH										
	EC	9.5	9.8	10.5	11.6	12.0	12.5	12.8	13.0	13.1	13.1
	($\mu\text{S cm}^{-1}$)	52	125	205	1040	1670	1980	2270	2310	3000	3060
Ground	pH										
	EC	10.0	11.0	11.5	12.0	12.2	12.6	12.9	13.0	13.1	13.1
	($\mu\text{S cm}^{-1}$)	270	320	360	1320	1920	2200	2250	2360	3060	3260
NEN 7375test											
Compact	pH										
	EC	9.5	9.5	9.8	10.0	10.0	11.5	12.0	12.5	/	/
	($\mu\text{S cm}^{-1}$)	45	55	35	225	265	445	445	455	/	/
Ground	pH										
	EC	/	/	/	/	/	/	/	/	/	/
	($\mu\text{S cm}^{-1}$)	/	/	/	/	/	/	/	/	/	/

4.1.3 Leachability of selected elements by applying NEN 7375 test and its modified leaching protocols

From the data gathered on the leachability of selected elements it is clear that the concentrations of Ba, Fe, Mn, Co, Ni, Cu, Zn, Cd, Sb, Hg and Pb in all the investigated samples, in general, remained below, or were close to their respective limits of detection with ICP-MS (Table 4.3). This phenomenon is related to the precipitation of the majority

of the elements at highly alkaline pHs and their effective immobilization in a lattice of aluminosilicate geopolymers [15], [17], [132]. In contrast, As, Cr, Mo and V, which are present in the form of highly soluble oxoanions at these pHs, were leached in larger amounts from the building composites. When the NEN 7375 test was applied (replenishing the solution), the highest determined As concentration in the leachate was 55 $\mu\text{g L}^{-1}$, while in experiments, where the leaching solution was not replenished, much higher concentrations were determined in the sample leachates taken during the course of the experiment.

Table 4.3: Concentration ranges of the elements in the leachates from the compact and ground composites during the course of the experiments. Concentrations of the elements were determined by ICP-MS (RSD of measurements better than $\pm 2\%$).

Element	Synthetic sea water ($\mu\text{g L}^{-1}$)		Synthetic surface water ($\mu\text{g L}^{-1}$)		MilliQ water ($\mu\text{g L}^{-1}$)		MilliQ water: NEN 7375 test ($\mu\text{g L}^{-1}$)	
	Compact	Ground	Compact	Ground	Compact	Ground	Compact	Ground
As	20–1660	6–1680	45–1720	185–1800	45–1745	290–1835	45–55	/
Se	4–290	10–300	2–315	16–340	3–370	17–480	0.7–24	/
Ba	0.4–67	7–87	<0.01–2	<0.01–3	<0.01–2	<0.01–3	<0.01–1	/
Fe	<0.02–17	<0.09–19	1–16	11–26	2–15	6–29	1–13	/
Mn	<0.007–7	<0.03–2	<0.03–4	<0.03–5	<0.03–2	<0.07–2	<0.07–3	/
Co	<0.006–0.6	<0.006–0.2	<0.006–0.2	<0.05–0.5	<0.006– 0.2	<0.006– 0.1	<0.06–0.02	/
Ni	<0.005–190	<0.005–6	<0.005–7	<0.005–12	<0.005–92	<0.005–2	<0.005–8	/
Cu	<0.04–13	<0.04–13	<0.08–2	<0.08–3	<0.04–2	<0.08–3	<0.04–2	/
Zn	<0.02–1	<0.02–2	<0.05–46	<0.2–21	<0.05–39	0.08–22	<0.05–12	/
Cd	<0.007–0.5	<0.007–1	<0.007–1	<0.04–0.8	<0.01–0.4	<0.02–0.5	<0.007–0.2	/
Sb	0.1–9	0.3–9	0.2–16	0.5–14	0.3–15	0.2–12	<0.005–4	/
Hg	<0.03–0.8	<0.02–1	<0.03–1.4	<0.02–3	<0.03–1	<0.03–1.4	<0.07–0.7	/
Pb	<0.03–0.02	<0.03–0.04	<0.004–0.7	<0.004–0.7	<0.007–6	<0.004– 0.4	<0.03–0.1	/
/non applicable								

The maximum amounts of As (1835 $\mu\text{g L}^{-1}$) were released from the ground composite applying MilliQ water as a leaching solution, while in a slightly lesser extent, the As was leached with synthetic surface and sea water. Regarding the leachability of Cr, Mo and V, the maximal released concentrations applying the NEN 7375 test were 55 $\mu\text{g L}^{-1}$, 100 $\mu\text{g L}^{-1}$ and 1360 $\mu\text{g L}^{-1}$, respectively. In the experiments where the leaching solution was not replenished, the maximal amounts of Cr, Mo and V were leached from ground composites using MilliQ water as a leaching solution (590 $\mu\text{g L}^{-1}$, 1000 $\mu\text{g L}^{-1}$ and 14,480 $\mu\text{g L}^{-1}$, respectively). In a slightly lesser extent Cr, Mo and V were released when the synthetic surface and sea water were applied as leaching solutions. Based on the data from Table 4.1, it can be concluded that the As present in the leachates originated mainly from the EAF dust, which is a constituent of the composite investigated. The leaching of Cr was, to a large extent, a consequence of the addition of EAF dust and, to a lesser extent, the addition of fly ash to the building composite. The leaching of Mo from the examined building composite came mainly from the EAF dust and much less from cement, while the leaching of V originated from the EAF dust, cement, and fly ash.

4.1.4 Comparison of data on leachability of the total arsenic, chromium, molybdenum and vanadium from compact building composite into MilliQ water by applying NEN 7375 test and the modified protocol without replenishing the leaching solution

To evaluate the range of leaching of As, Cr, Mo and V when the NEN 7375 test is applied (replenishing of the leaching solution) against the extent of leaching when the leaching solution was not replenished, compact building composites were immersed into MilliQ water and samples taken over a period of 64 days, at points in time specified by the NEN 7375 test (NEN 7375, 2004). Concentrations of elements leached from the surface were calculated per time unit and the results summarized in Table 4.4.

Table 4.4: Total concentrations of As, Cr, Mo and V released into MilliQ water from the compact building composite over a period of 64 days of applying replenishing of the leaching solution (NEN 7375 test), and concentrations of these elements in the leachates without replenishing the leaching solution. Concentrations of elements were determined by ICP-MS (RSD of measurements better than $\pm 2\%$).

Element / Concen- tration	Sampling mode	Points in time when samples were taken (days)								
		0.25	1	2.25	4	9	16	36	64	
As (mg/m ² day)	Replenishing of solution	8.0	0.40	0.48	3.4	2.0	1.6	0.50	0.18	
	(NEN 7375 test)	8.0	3.0	1.8	8.8	5.5	3.8	2.4	1.3	
	No replenishing of solution									
Cr (mg/m ² day)	Replenishing of solution	1.2	0.13	0.40	1.1	0.48	0.15	0.07	0.04	
	(NEN 7375 test)	1.2	0.90	0.98	3.8	2.2	1.2	0.58	0.28	
	No replenishing of solution									
Mo (mg/m ² day)	Replenishing of solution	4.0	0.13	0.16	1.2	0.8	0.71	0.10	0.03	
	(NEN 7375 test)	4.0	1.5	1.8	4.0	3.7	2.3	1.2	0.70	
	No replenishing of solution									
V (mg/m ² day)	Replenishing of solution	24	5.3	7.2	17	10	9.2	3.0	1.6	
	(NEN 7375 test)	24	15	18	55	40	26	17	10	
	No replenishing of solution									

It is evident that at the first sampling (after 0.25 day) the surface wash-off of As, Cr, Mo and V initially occurs, followed by a substantial decrease in elemental concentrations in the second sampling (after 1 day). Then, concentrations of elements tend to increase until the 4th day, and afterwards start to decrease slowly until the end of the experiment (64 days). When the solution was replenished, the extent of leaching was three to ten times lower than in the experiments without replenishing of the leaching solution. These observations are related to the leaching mechanisms. In the case when the NEN 7375 test was applied (replenishing of solution), diffusion was the key process which governed the leaching of elements from the building composite, while in the experiments performed without replenishing the solution, diffusion and dissolution were involved in the leachability of elements. The decrease in elemental concentrations after the 4th day from the start of the experiment indicates that beside diffusion and dissolution, other processes, which contribute to the stabilization of contaminants, also take place. A crucial role in the

stabilization processes is played by the dissolution of the composite's constituents with the leaching solution. From the data in Figure 4.1 it is evident that in the case when the solution was not replenished, $\text{Ca}(\text{OH})_2$ and CaCO_3 were leached in a much higher extent as compared to when the solution was not replenished. As a consequence of appreciably higher ionic strength (conductivity), also the pH of the leaching solution was higher. The oxoanionic species of As, Cr, Mo and V dissolved more readily in the medium with the higher alkalinity, which is also evident from the data in Table 4.4.

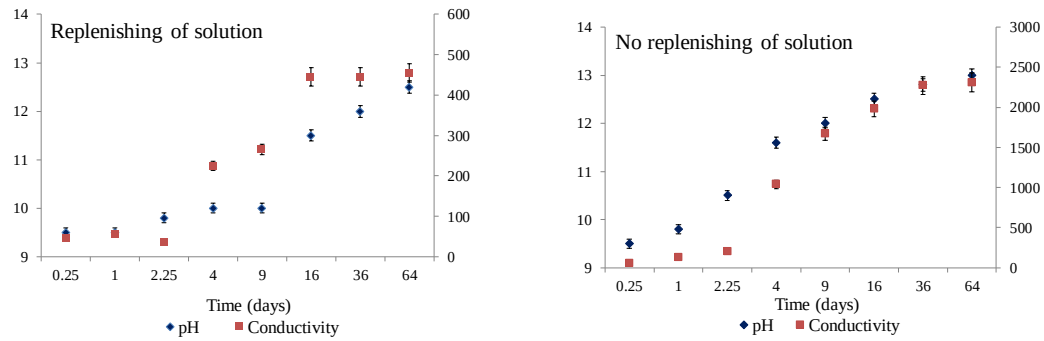


Figure 4.1: pH and electrical conductivity of leachates from the tested compact composites (fly ash with the addition of cement and EAF dust) immersed into MilliQ water over time by applying replenishing of the solution (NEN 7375 test) and no replenishing of the solution.

To better understand these processes and to simulate the environmental conditions in stagnant environmental waters, compact and ground building composites were further investigated using MilliQ water, synthetic surface and synthetic sea water without replenishing the leaching solutions. Since the chemical speciation plays an important role in the behaviour of elements in a given matrix, concentrations of total Cr and Cr(VI), total Mo and Mo(VI) and total V and (V) were followed in the leachates, collected in a time span of 6 months. Speciation analyses were performed by the procedure described in paragraph 3.3.2.4.

4.1.5 Leachability of the total chromium and chromate from compact and ground building composites by applying modified leaching protocols without replenishing the leaching solution

The leachability of the total Cr and Cr(VI) with time, applying modified leaching protocols in which the leaching solution was not replenished, is presented in Figure 4.2.

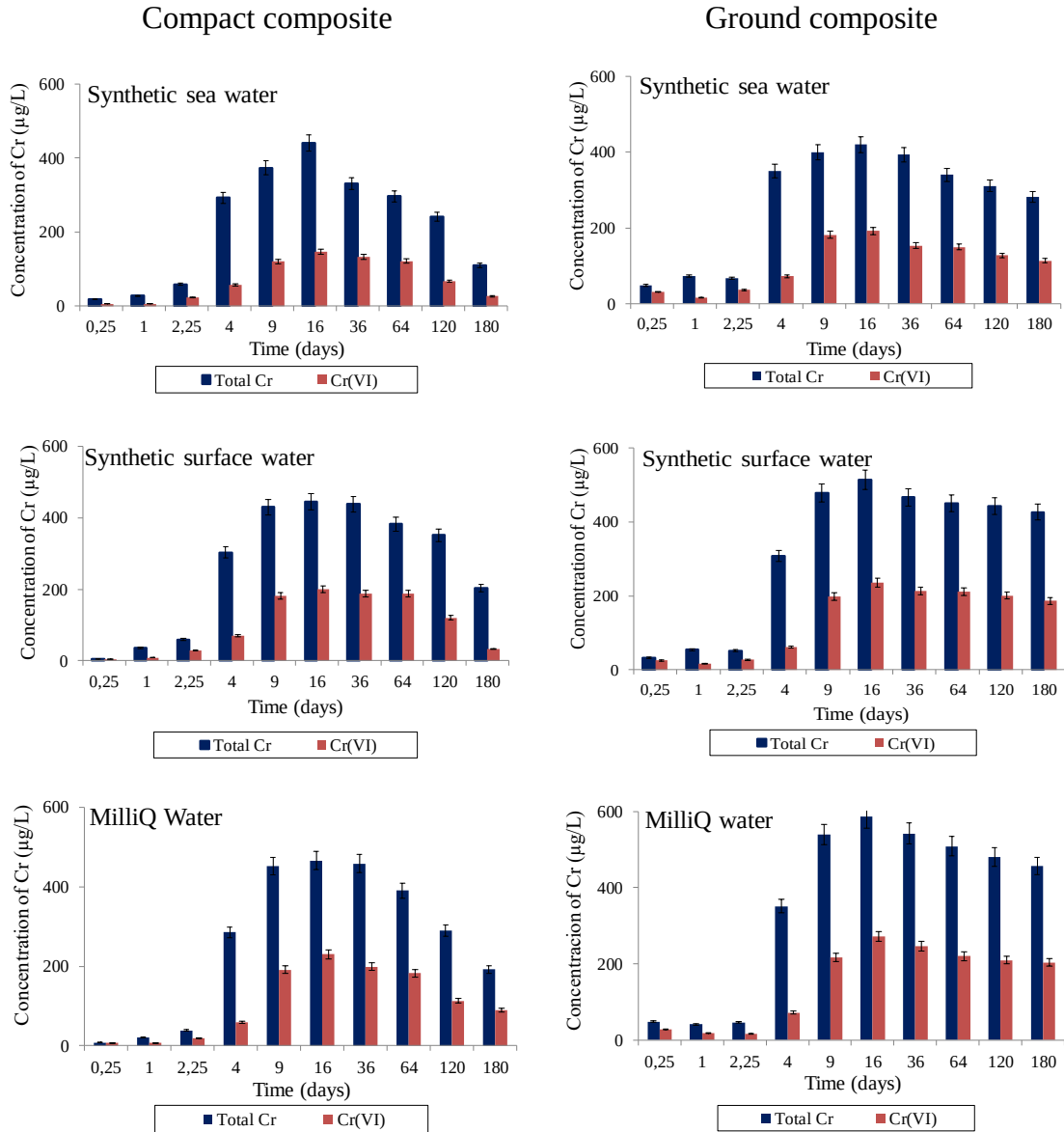


Figure 4.2: Leaching of Cr and Cr(VI) in synthetic sea water, synthetic surface water and MilliQ water over time (without replenishing the solution), from the tested compact and ground composites (fly ash with the addition of cement and EAF dust). The results represent the average of three parallel samples (the error bars indicate the deviations from the mean value concentrations).

The data indicate that at the beginning of the experiments the amounts of Cr and Cr(VI) leached were low and were progressively increased after 4 days, reaching their maximum values on the 16th day. Afterwards, the concentrations gradually dropped due to the adsorption and immobilization of the released Cr species in the building composite. The highest leached Cr and Cr(VI) concentrations (590 and 270 $\mu\text{g L}^{-1}$, respectively) were observed from the ground building composite into MilliQ water. Despite the fact that the Cr in the cement and EAF dust is present primarily in its hexavalent form [12], [13], [39], sulphites arising from the fly ash [133], which are strong reducing agents [134], reduced the

Cr(VI). Consequently, its concentration in the leachates did not exceed 50% of the total Cr content. It can be also seen that larger amounts of Cr and Cr(VI) were leached from the ground than from the compact composites. This phenomenon is related to the higher surface area of the ground composites. Despite the higher ionic strength of the synthetic sea water (see the data for electrical conductivity in Table 2), the extent of the leaching was slightly lower than in the synthetic surface or MilliQ water. Namely, at an alkaline pH, the $MgCl_2$ present in the synthetic sea water is precipitated, which inhibited the release of the soluble Cr(III) and hindered its oxidation to Cr(VI). In addition, Friedel's salt is formed by the hydration of the cement from the building composite. It is a double-layered hydroxide and a good adsorbent for the immobilization of Cr(VI) [135]. The extent of the leaching of Cr and Cr(VI) depends on the composition of the leaching solution, which governs the dissolution of the alkaline constituents and the reducing agents from the building composite. Hence, despite the higher pHs that favour oxidation processes, the sulphite leached from the building composite controls the extent of Cr(VI) reduction.

4.1.6 Leachability of the total molybdenum and molybdate from compact and ground building composites by applying modified leaching protocols without replenishing the leaching solution

The leachability of the total Mo and Mo(VI) with time, applying modified leaching protocols in which the leaching solution was not replenished, is presented in Figure 4.3.

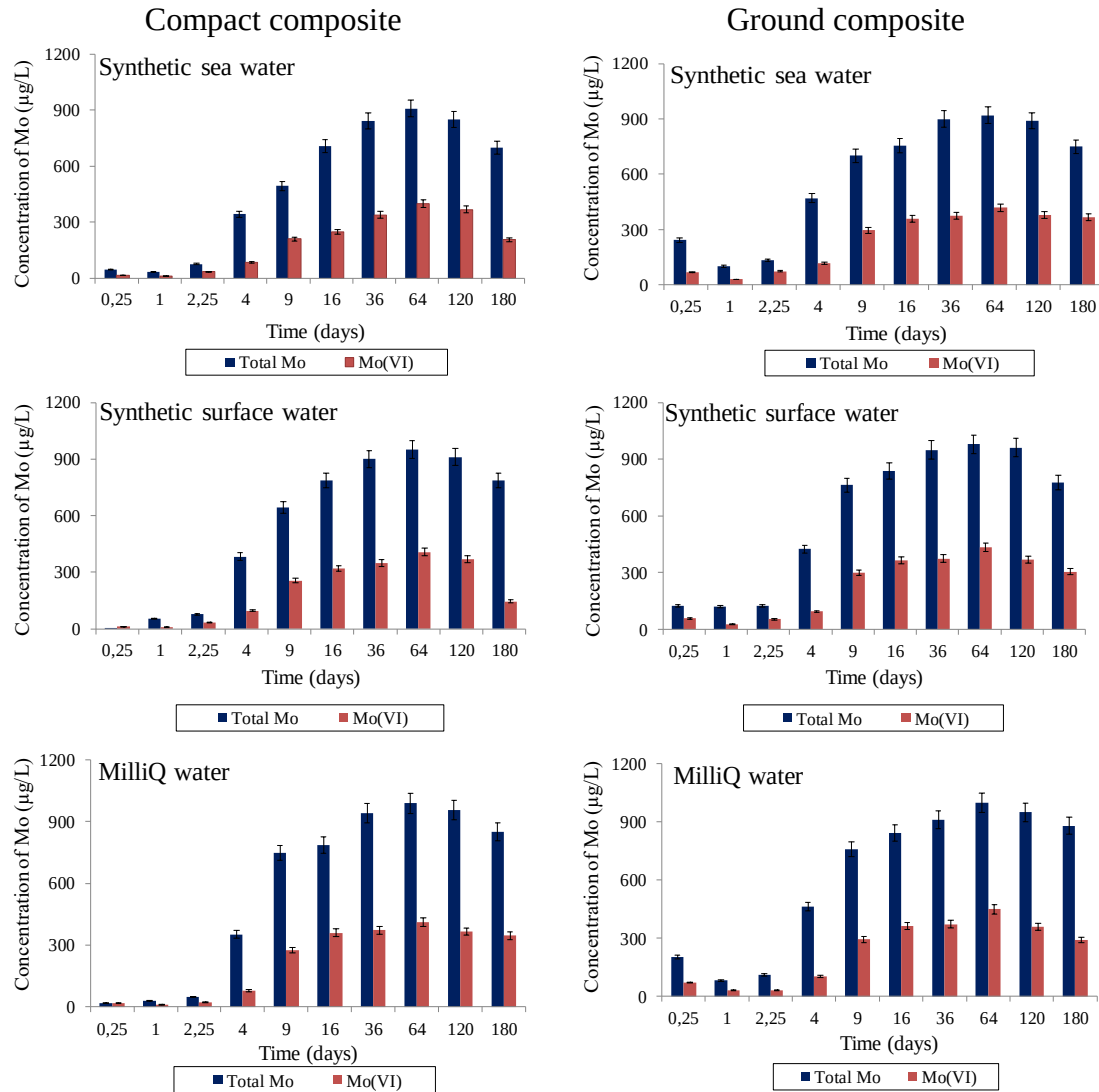


Figure 4.3: Leaching of Mo and Mo(VI) in synthetic sea water, synthetic surface water and water over time (without replenishing the solution), from the tested compact and ground composites (fly ash with the addition of cement and EAF dust). The results represent the average of three parallel samples (the error bars indicate the deviations from the mean value concentrations).

For Mo, a greater extent of leaching than that of the Cr was observed. It can be seen that at the beginning, the leaching of Mo and Mo(VI) was negligible, but from the 4th day it rapidly increased up to the 64th day, followed by a progressive decrease over time. The decrease in Mo and Mo(VI) concentrations is mainly related to the adsorption and immobilization of Mo species in the building composite. The extent of leaching is similar when applying synthetic sea, synthetic surface and MilliQ water from compact or ground composites. The highest concentrations of Mo and Mo(VI) (1000 and 450 $\mu\text{g L}^{-1}$, respectively) were leached from the ground building composite into MilliQ water. Similar to Cr(VI), the reducing agents originating from the fly ash triggered the Mo(VI) reduction and its release from the building composite. The Mo(VI) concentration represented less than 40% of the total Mo content leached.

4.1.7 Leachability of the total vanadium and vanadate from compact and ground building composites by applying modified leaching protocols without replenishing the leaching solution

The leachability of the total V and V(V) with time, applying modified leaching tests without replenishing the leaching solutions is presented in Figure 4.4.

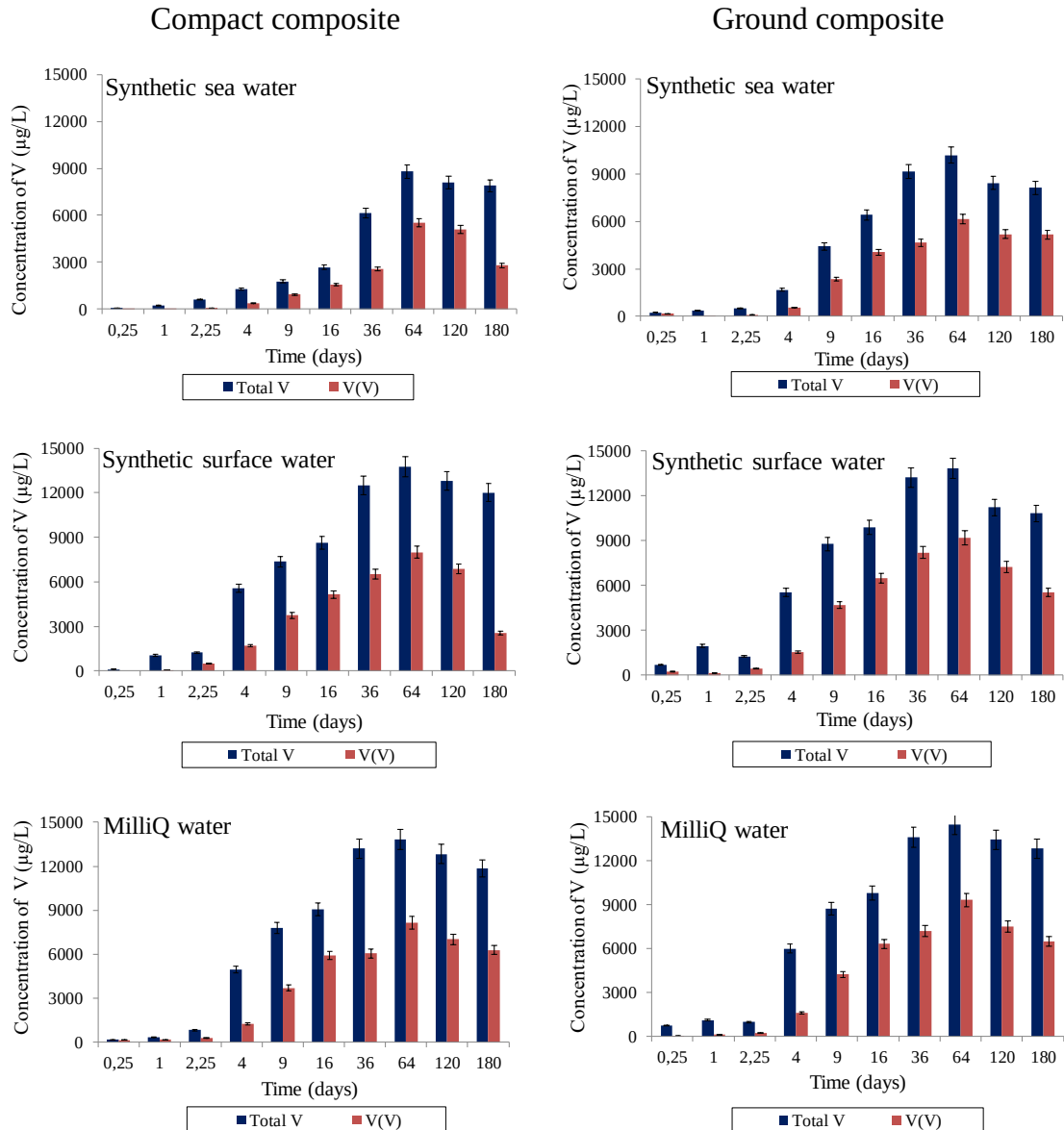


Figure 4.4: Leaching of V and V(V) in synthetic sea water, synthetic surface water and water over time (without replenishing the solution), from the tested compact and ground composites (fly ash with the addition of cement and EAF dust). The results represent the average of three parallel samples (the error bars indicate the deviations from the mean value concentrations).

Under highly alkaline conditions and in the presence of dissolved oxygen, the V was oxidised to its pentavalent oxidation state. However, as in the case of Cr and Mo, the sulphite released from the fly ash reduced the V(V) content by up to 50% of the total V leached from the building composites examined. The V was leached in much larger amounts than the Cr and Mo, since the complexes of V oxoanions are highly soluble under alkaline conditions. Similarly, to Cr and Mo, the leaching of V and V(V) is progressively increased till 64 days, followed by a gradual decrease over time (due to adsorption and immobilization of V and V(V) on the surface of the building composite). The maximum V and V(V) concentrations leached (14480 and 9320 $\mu\text{g L}^{-1}$, respectively) were observed from the ground building composite into MilliQ water, 64 days after the start of the experiment. As it is evident, the composition of synthetic sea water significantly influenced the leachability of V and V(V) from compact and ground composite. The extent of leaching is lower than in synthetic surface and MilliQ water, which is most probably related to co-precipitation of V species with MgCl_2 precipitate.

The results presented in Chapter 4.1 are based on the data of the published article by Drinčić et al. [40].

4.2 Simultaneous Speciation of Chromate, Arsenate, Molybdate and Vanadate in Building Composites Containing Waste Materials by HPLC - ICP-MS

In leachates from building composites containing fly ash, cement and EAF dust, Cr, As, Mo and V were leached in elevated concentrations. Since properties of elements, like toxicity towards living organisms, behaviour and fate in the environment, etc. depend primarily on the chemical forms in which they are present in a given environment. Cr, Mo and V are more toxic in their highest oxidation states (Cr(VI), Mo(VI) and V(V), respectively), while As(V) is less toxic than As(III) [121], [124], [122], [123]. Oxoanions of Cr(VI), As(V), Mo(VI) and V(V) are highly mobile in the form of alkali chromates, arsenates, molybdates and vanadates and can be present in leachates from building composites of fly ash, cement and EAF dust. To reduce the time and cost of analysis, the applicability of the HPLC-ICP-MS procedure was investigated for the simultaneous speciation of chromate, arsenate, molybdate and vanadate in highly alkaline leachate samples.

4.2.1 Separation of single element species on the HPLC column followed by ICP-MS detection

First, the behaviour of single elemental species in their highest and lower oxidation states was examined on an anion-exchange HPLC column applying the speciation procedure as described in paragraph 3.3.2.4. The study was performed using working standard solutions containing 20 ng mL^{-1} of a particular elemental species, prepared at pH 5 and 12. The results are presented in Figures 4.5–4.8.

For the study of Cr speciation, aqueous standard solutions of chromate and Cr(III)-nitrate were used. In aqueous solutions more acidic than pH 5, Cr(III) exists mainly as the positively charged $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ complex, while Cr(VI) as the negatively charged $\text{Cr}_2\text{O}_7^{2-}$ species. At pH 12, Cr(III) is mainly present in the form of sparingly soluble $\text{Cr}(\text{OH})_3$, and to a smaller extent also as the soluble $\text{Cr}(\text{OH})_4^-$ complex, whereas Cr(VI) exists as the CrO_4^{2-} species [54]. Separation of Cr(VI) and Cr(III) species at pH 5 and pH 12 is presented in Figure 4.5.

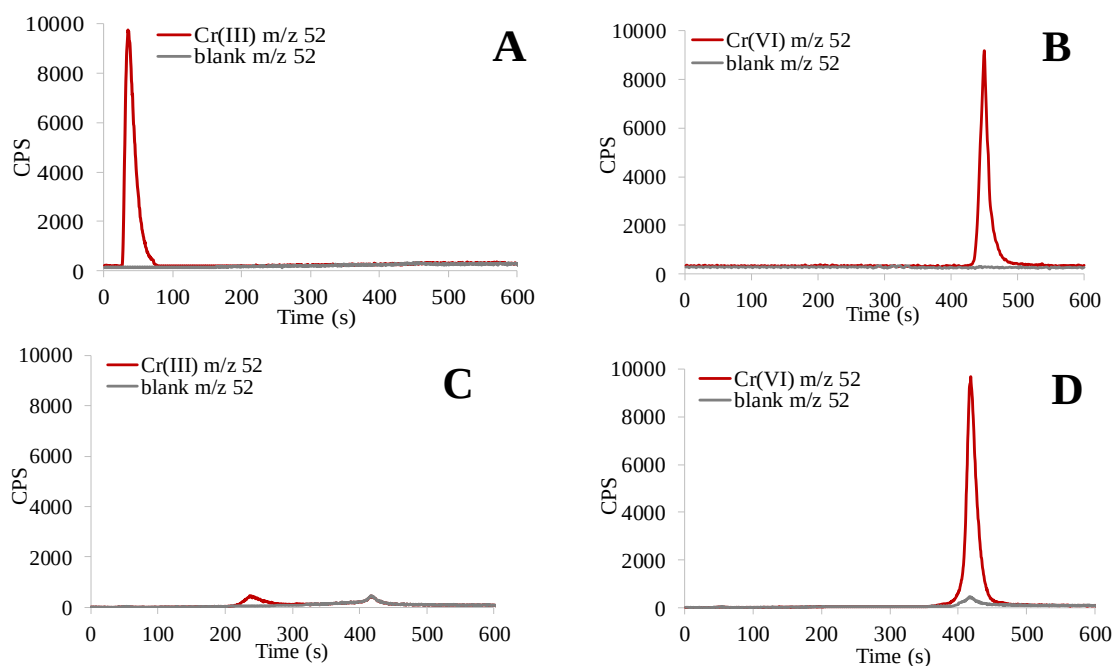


Figure 4.5: Separation of A: Cr(III) solution (pH 5), B: Cr(VI) solution (pH 5), C: Cr(III) solution in 0.2% NaOH + 0.3% Na₂CO₃ buffer (pH 12) and D: Cr(VI) solution in 0.2% NaOH + 0.3% Na₂CO₃ buffer (pH 12) applying the HPLC-ICP-MS procedure (20 ng mL⁻¹ of Cr).

Data from Figure 4.5A show that Cr(III) at pH 5 is eluted with a solvent front, while Cr(VI) from 430 to 490 s (Figure 4.5B). At pH 12, Cr(III) is mostly precipitated as Cr(OH)₃, which is strongly adsorbed on the column resin, while a small peak that eluted from 220 to 240 s corresponds to the Cr(OH)₄⁻ complex (Figure 4.5 C). Cr(VI) is eluted from 390 to 450 s (Figure 4.5D), and is separated from Cr(III) species. The small peak of the blank solution, which corresponds to Cr(VI) (Figure 4.5C and D) arises from the alkaline buffer solution, in which Cr(III) and Cr(VI) standards were prepared at pH 12.

For the investigation of As speciation, aqueous standard solutions of arsenite (As(III)) and arsenate (As(V)) were used. At a pH of 5, As(III) is present as H₃AsO₃ and As(V) as H₂AsO₄⁻ species [136]. Separation of As(III) and As(V) species at pH 5 and pH 12 is presented in Figure 4.6.

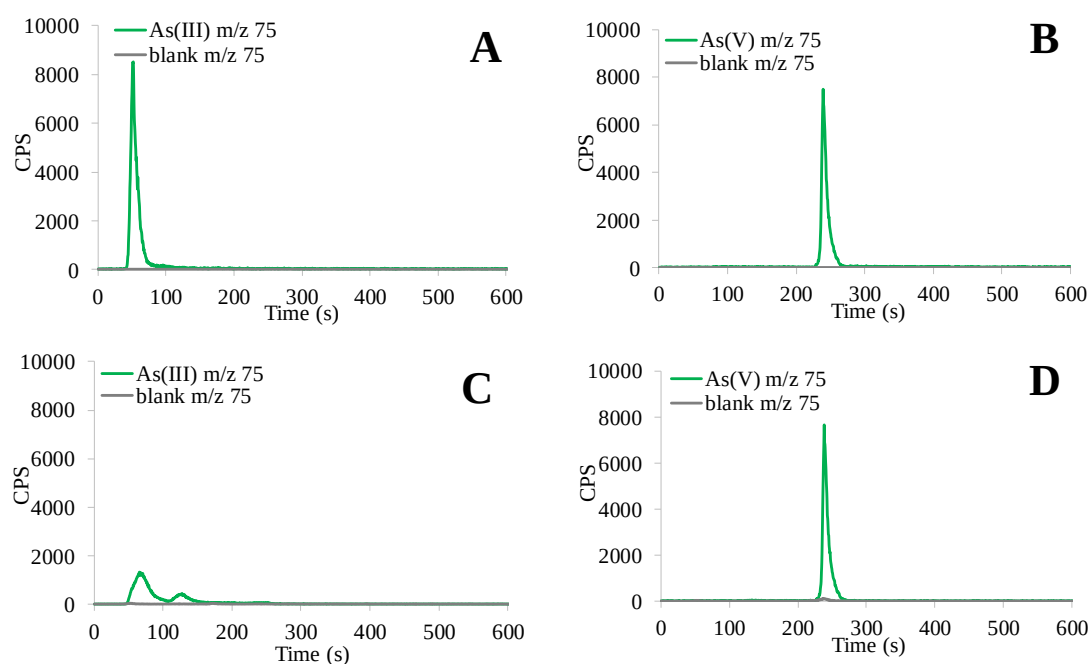


Figure 4.6: Separation of A: As(III) solution (pH 5), B: As(V) solution (pH 5), C: As(III) solution in 0.2% NaOH + 0.3% Na₂CO₃ buffer (pH 12) and D: As(V) solution in 0.2% NaOH + 0.3% Na₂CO₃ buffer (pH 12) applying the HPLC-ICP-MS procedure (20 ng mL⁻¹ of As).

The data in Figure 4.6A and B indicate that in acidic solutions As(III) and As(V) species are well separated. At pH 12 As(III) exists mainly as As(OH)₃ [137] and to a smaller extent as soluble HAsO₃²⁻ and AsO₃⁻ species [136]. At highly alkaline pHs, the only As(V) species is AsO₄³⁻ [136]. The data in Figure 4.6C show that As(OH)₃ is strongly adsorbed on the column resin, while HAsO₃²⁻ and AsO₃⁻ As(III) species are eluted as two small peaks from 50 to 150 s. From Figure 4.6D it can be seen that As(V) species is eluted as a sharp peak from 230 to 270 s and is separated from As(III).

In the study of Mo(VI) speciation, molybdate standard solution was used. Mo compounds in lower oxidation states are not soluble in water and can be dissolved by alkaline digestion, which induces oxidation to Mo(VI), and thus changes the speciation. To prepare Mo species in the lower oxidation states, Na₂SO₃ was added as a reducing agent to a standard solution of molybdate and the pH adjusted to 5 and 12. This reducing agent was chosen since it is present in the samples of alkaline leachates from fly ash, EAF dust and cement [40]. From acidic to alkaline pHs Mo(VI) prevails as MoO₄²⁻ species [138]. In lower oxidation states, Mo species in aqueous solutions are stable only at acidic pHs, in the form of the positively charged trivalent Mo(H₂O)₆³⁺, tetravalent Mo₃O₄⁴⁺ and pentavalent Mo₂O₄²⁺ complexes [139], [140]. The aqua monomeric trivalent, tetravalent and pentavalent Mo species tend to polymerise, forming di- or trinuclear oxo Mo species [139]. The speciation of Mo(VI) and Mo species formed after the reduction of Mo(VI) at pH 5 and pH 12 is presented in Figure 4.7.

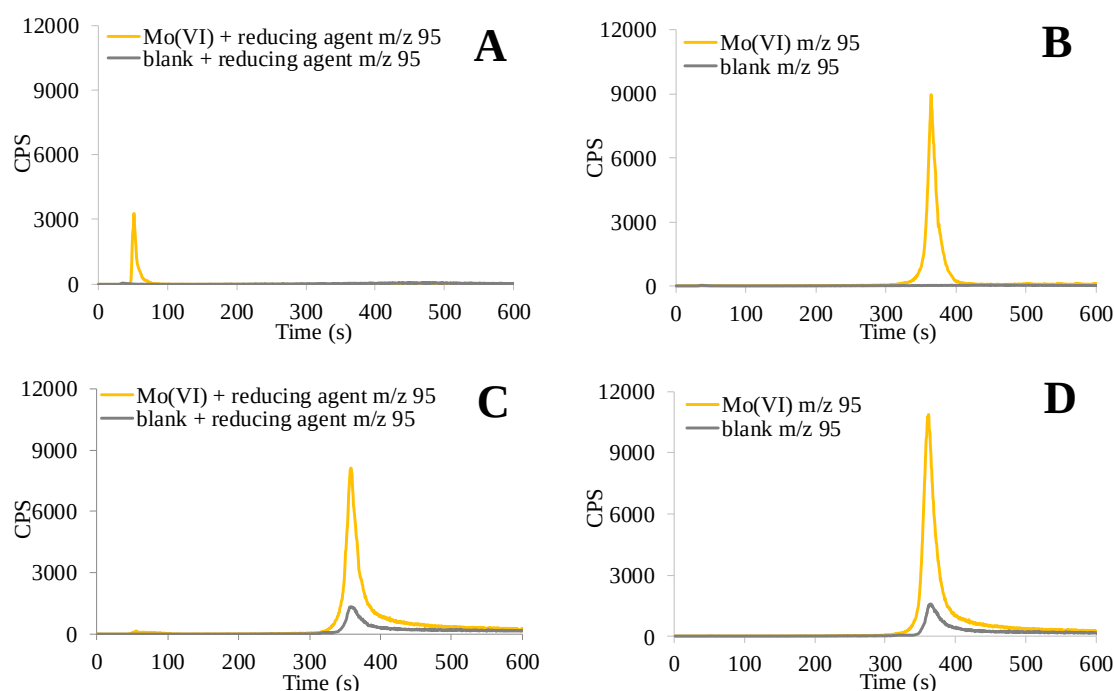


Figure 4.7: Separation of A: Mo(VI) solution (pH 5) in the presence of reducing agent $0.0002 \text{ g L}^{-1} \text{ Na}_2\text{SO}_3$, B: Mo(VI) solution (pH 5), C: Mo(VI) solution in $0.2\% \text{ NaOH} + 0.3\% \text{ Na}_2\text{CO}_3$ buffer (pH 12) in the presence of reducing agent $0.0004 \text{ g mL}^{-1} \text{ Na}_2\text{SO}_3$ and D: Mo(VI) solution in $0.2\% \text{ NaOH} + 0.3\% \text{ Na}_2\text{CO}_3$ buffer (pH 12) applying HPLC-ICP-MS procedure (20 ng mL^{-1} of Mo).

As can be seen from Figure 4.7A, at pH 5 the monomeric Mo species formed after the reduction of Mo(VI) are eluted with the solvent front, while polymeric Mo(V), Mo(IV) and Mo(III) species are adsorbed on the column resin. Mo(VI) is eluted from 330 to 420 s (Figure 4.7B) and is separated from species in lower oxidation states. At pH 12, the separated Mo(VI) species are eluted from 340 to 430 s (Figure 4.7C and D). The addition of the reducing agent ($0.0004 \text{ g mL}^{-1} \text{ Na}_2\text{SO}_3$) to Mo(VI) solution resulted in 20% decrease of the Mo chromatographic signal. Reduced Mo species were adsorbed on the column resin and were separated from Mo(VI). A peak of the blank solution at pH 12, which represents about 12% of the analytical signal of Mo(VI), arises mainly from the metallic parts of the HPLC and injector and to a smaller extent also from the alkaline extract.

To study the speciation of V(V), vanadate solution was used. Since tetravalent and trivalent V compounds are sparingly soluble in water, Na_2SO_3 (0.0002 g mL^{-1}) was added as a reducing agent to a standard solution of vanadate to prepare the V species in the lower oxidation states. Then the pH was adjusted to 5 and 12. In aqueous solutions with acidic pHs, H_2VO_4^- is a prevailing pentavalent monomeric V species [138], [141], [142], which co-exists with the polyoxovanadate $\text{V}_4\text{O}_{12}^{4-}$ and $\text{HV}_{10}\text{O}_{28}^{5-}$ ions. The latter decavanadate anion is the predominant polymeric V species in the pH range between 3 and 6 [142], [143]. At pH 12, VO_4^{3-} species prevails [138], [141], [142]. The main V species in lower oxidation states in aqueous solutions are tetravalent VOOH^+ and VO_2^+ , and trivalent $\text{V}(\text{H}_2\text{O})_6^{3+}$ aqua complex and VOH^+ species, which are stable at acidic pHs [138],[141]. The speciation of V(V) and V species formed after the reduction of V(V) at pH 5 and pH 12 are presented in Figure 4.8.

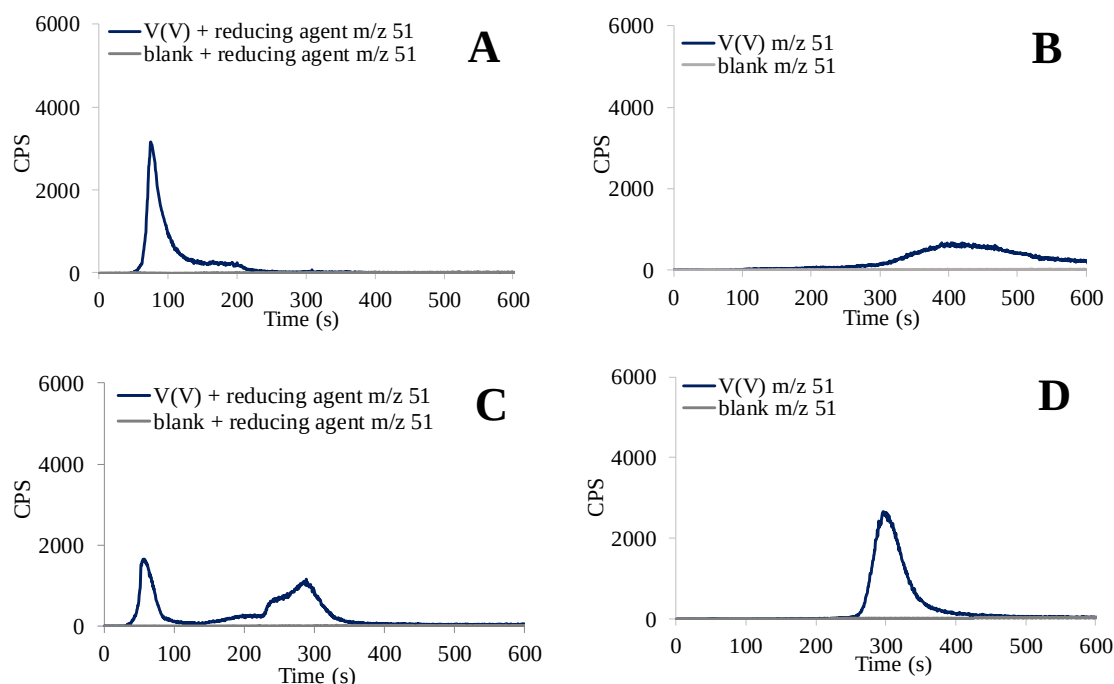


Figure 4.8: Separation of A: V(V) solution (pH 5) in the presence of reducing agent $0.0002 \text{ g L}^{-1} \text{ Na}_2\text{SO}_3$, B: V(V) solution (pH 5), C: V(V) solution in $0.2\% \text{ NaOH} + 0.3\% \text{ Na}_2\text{CO}_3$ buffer (pH 12) in the presence of reducing agent $0.0002 \text{ g mL}^{-1} \text{ Na}_2\text{SO}_3$ and D: V(V) solution in $0.2\% \text{ NaOH} + 0.3\% \text{ Na}_2\text{CO}_3$ buffer (pH 12) applying HPLC-ICP-MS procedure (20 ng mL^{-1} of V).

From the data presented in Figure 4.8A and B it can be seen that at pH 5, V(V) is separated from V species in the lower oxidation states. The positively charged V complexes formed after the reduction of V(V) are eluted with the solvent front, whereas negatively charged pentavalent polyoxovanadate complexes are eluted as a broad peak from 300 to 600 s. At pH 12, the pentavalent VO_4^{3-} species is eluted from 270 to 380 s (Figure 4.8D). The addition of a reducing agent to V(V) solution resulted in about 50% decrease of the V(V) chromatographic signal, while V species in the lower oxidation states are eluted with the solvent front (Figure 4.8C). From the data in Figures 4.5–4.8 it can be concluded that under the chromatographic conditions applied, speciation of chromate, arsenate, molybdate and vanadate is possible at highly alkaline pHs.

4.2.2 Simultaneous speciation of chromium, arsenic, molybdenum and vanadium species by the HPLC-ICP-MS method

To demonstrate the capability of the HPLC-ICP-MS analytical procedure for simultaneous speciation analysis, a multiple working standard solution containing 20 ng mL^{-1} of chromate, arsenate, molybdate and vanadate was prepared in alkaline buffer (pH 12). Separated elemental species of Cr, As, Mo and V were simultaneously detected by ICP-MS recording m/z 52, 75, 95 and 51, respectively. A typical chromatogram is presented in Figure 4.9.

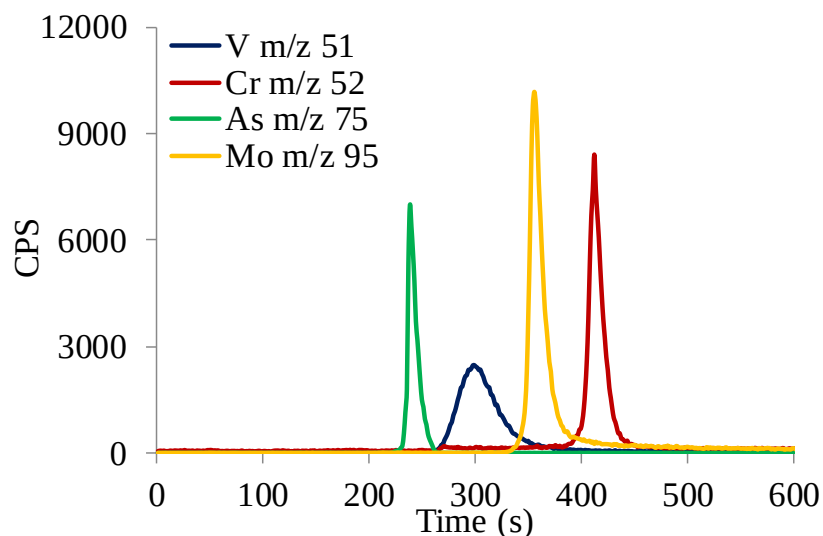


Figure 4.9: Simultaneous separation of chromate, arsenate, molybdate and vanadate in 0.2% NaOH + 0.3% Na₂CO₃ buffer (pH 12) applying HPLC-ICP-MS procedure (20 ng mL⁻¹ of Cr, As, Mo and V).

As evident, at pH 12, chromate, arsenate, molybdate and vanadate were eluted from 390 to 450 s, 230 to 270 s, 340 to 430 s and 270 to 380 s, respectively. Different elution times are related to different affinities of species for their retention on the anion-exchange resin. Since elution profiles were recorded at different m/z by ICP-MS, simultaneous speciation analysis of chromate, arsenate, molybdate and vanadate can be performed in a single chromatographic run, although the molybdate peak partially overlapped vanadate and chromate peaks.

If samples contain significantly higher concentrations of vanadate compared to those of chromate, arsenate and molybdate, detection of V species is possible even at its low abundance (0.25%) ⁵⁰V isotope [144]. Since ⁵⁰V isotope shares the same mass with ⁵⁰Cr isotope (abundance 4.345%), [144] simultaneous speciation analysis of V at m/z 50 is possible only if V and Cr species are selectively separated to avoid isobaric interferences in ICP-MS measurements. An example of simultaneous separation of chromate and vanadate at m/z 50 in alkaline (pH 12) solution containing 100 ng mL⁻¹ of Cr and 1000 ng mL⁻¹ of V is presented in Figure 4.10. As can be seen, chromate and vanadate are well separated and can be simultaneously recorded at m/z 50.

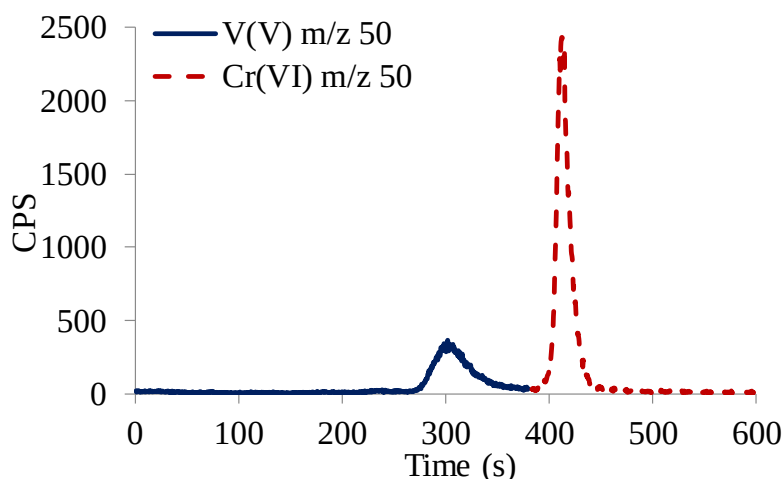


Figure 4.10: Simultaneous separation of chromate and vanadate in 0.2% NaOH + 0.3% Na₂CO₃ buffer (pH 12) applying the HPLC-ICP-MS procedure (100 ng mL⁻¹ of Cr and 1000 ng mL⁻¹ of V). Chromatograms were recorded at m/z 50.

4.2.3 Figures of merit of the HPLC-ICP-MS analytical method used for simultaneous speciation of chromate, arsenate, molybdate and vanadate in alkaline samples

4.2.3.1 Column recoveries

Possible interactions between the column resin and chromate, arsenate, molybdate and vanadate were checked by calculating column recoveries. For this purpose, single standard solutions of chromate, arsenate, molybdate and vanadate (20 ng mL⁻¹ as the element) were prepared in alkaline buffer (pH 12) and injected onto the column. Fractions eluted under the elution time typical for a particular species investigated were collected and the total elemental concentration was determined “off line” by ICP-MS. Column recoveries were calculated as the ratio between those concentrations of elemental species eluted and injected. The results are presented in Table 4.5. As can be seen, for all the elemental species investigated column recoveries ranged between 99 and 105%, indicating that chromate, arsenate, molybdate and vanadate are quantitatively eluted and did not interact with the column resin.

Table 4.5: Column recoveries for separation of single elemental species of chromate, arsenate, molybdate and vanadate in 0.2% NaOH + 0.3% Na₂CO₃ buffer (pH 12) applying the HPLC-ICP-MS procedure. Results represent the mean value of three replicate determinations of the selected element with the standard deviation of the measurements.

Species	Concentration of element added (ng mL ⁻¹)	Concentration of element found (ng mL ⁻¹)	Recovery (%)
Cr(VI) m/z 52	20.0 ± 0.2	19.8 ± 0.2	99

Species	Concentration of element added (ng mL ⁻¹)	Concentration of element found (ng mL ⁻¹)	Recovery (%)
As(V) <i>m/z</i> 75	20.0 ± 0.2	19.8 ± 0.2	99
Mo(VI) <i>m/z</i> 95	20.0 ± 0.2	21.0 ± 0.2	105
V(V) <i>m/z</i> 51	20.0 ± 0.2	20.0 ± 0.2	100

4.2.3.2 Repeatability of measurements

The repeatability of measurements was tested for six consecutive simultaneous speciation analyses of a standard solution of chromate, arsenate, molybdate and vanadate, containing 20 ng mL⁻¹ of Cr, As, Mo and V in alkaline buffer solution (pH 12). From results presented in Table 4.6 it is evident that the repeatability of measurements for the elemental species studied was found to be better than $\pm 3\%$.

Table 4.6: Repeatability of measurement tested for six consecutive speciation analyses of a standard solution of chromate, arsenate, molybdate and vanadate, containing 20 ng mL⁻¹ of Cr, As, Mo and V.

Species	Peak area						Average	RSD %
	1.	2.	3.	4.	5.	6.		
Cr(VI) <i>m/z</i> 52	103518	110234	110873	104262	107832	105342	107010	2.9
As(V) <i>m/z</i> 75	13138	12959	13359	13483	13101	13408	13241	1.6
Mo(VI) <i>m/z</i> 95	133624	134412	134320	136870	134482	131434	134190	1.3
V(V) <i>m/z</i> 51	84034	82286	84585	82317	81145	85777	83357	2.1

4.2.3.3 Limits of detection

Limits of detection (LODs) and limits of quantification (LOQs) for the determination of chromate, molybdate, arsenate and vanadate by HPLC-ICP-MS were calculated as the concentration that provides a signal (peak area) equal to 3s and 10s, respectively, of the blank sample in the chromatogram. To calculate LODs and LOQs, 8 blank samples of the alkaline buffer solution (0.2% NaOH + 0.3% Na₂CO₃) were injected and Cr, As, Mo and V recorded at *m/z* 52, 75, 95 and 51, respectively. By the use of ICP-MS operating parameters summarized in Table 3.2, the LODs and LOQs for chromate (*m/z* 52) were 0.2 and 0.67 ng Cr mL⁻¹, arsenate (*m/z* 75) 0.4 and 1.33 ng As mL⁻¹, molybdate (*m/z* 95) 1 and 3.33 ng Mo mL⁻¹, vanadate (*m/z* 51) 2 and 6.66 ng V mL⁻¹ and vanadate (*m/z* 50) 100 and 333 ng V mL⁻¹. The method was proved to be of adequate sensitivity for the simultaneous speciation analysis of chromate, arsenate, molybdate and vanadate in leachates from building composites.

4.2.3.4 Linearity

The linearity of measurement for chromate (*m/z* 52), arsenate (*m/z* 75), molybdate (*m/z* 95) and vanadate (*m/z* 51) by the HPLC-ICP-MS was obtained over the concentration range from LOQ to 1500 ng mL⁻¹ while for vanadate recorded at *m/z* 50, from LOQ to 50

000 ng mL⁻¹. The correlation coefficients were better than 0.998 for all the elements investigated.

4.2.3.5 Accuracy check

As there is no certified reference material for the simultaneous determination of chromate, arsenate, molybdate and vanadate available, the accuracy of the analytical procedure was checked by the spike recovery test. For this purpose, multiple standard solution of chromate, arsenate, molybdate and vanadate (pH 12), containing 50 ng mL⁻¹ of Cr, 100 ng mL⁻¹ of As, 50 ng mL⁻¹ of Mo and 500 ng mL⁻¹ of V was added to the leachate sample, composed of 99.5% mixture (70% fly ash + 30% cement) and 0.5% EAF dust, one day after immersion into MilliQ water. The sample was diluted 1:2 with alkaline buffer before the analysis. The recoveries were calculated as a ratio between found and added element concentration. The results are presented in Table 4.7. Data from Table 4.7 indicate that recoveries for chromate, arsenate, molybdate and vanadate of the spiked leachate sample lay between 98 and 102%, which confirmed the accuracy of the analytical procedure.

Table 4.7: Spike recovery test for chromate, arsenate, molybdate and vanadate for leachate sample (building composite from a 99.5% mixture of fly ash (70%) and cement (30%), and 0.5% of EAF dust), 1 day after immersion into MilliQ water) determined by simultaneous HPLC-ICP-MS speciation analysis. Results represent the mean value of three replicate determinations of the selected element with the standard deviation of the measurements.

Species	Concentration of element in leachate (ng mL ⁻¹)	Concentration of element added (ng mL ⁻¹)	Concentration of element found (ng mL ⁻¹)	Recovery (%)
Cr(VI) <i>m/z</i> 52	29.0 ± 0.3	50.0 ± 0.5	77 ± 2	98
As(V) <i>m/z</i> 75	175 ± 2	100 ± 1	280 ± 8	98
Mo(VI) <i>m/z</i> 95	38.0 ± 0.4	50 ± 0.5	90 ± 3	102
V(V) <i>m/z</i> 51	1100 ± 10	500 ± 5	1580 ± 50	99

4.2.4 Simultaneous speciation analysis of chromate, arsenate, molybdate and vanadate in leachates from building composites by HPLC-ICP-MS at different concentration levels of vanadate

The analytical procedure developed for the simultaneous speciation analysis of chromate, arsenate, molybdate and vanadate was applied to the analysis of alkaline leachates from building composites. In this experiment, different building composites from fly ash, EAF dust and cement were prepared and immersed into MilliQ water for two different times (1 day or 9 months). Due to the presence of soluble Ca(OH)₂ and CaCO₃ arising from the building composites, the pH values of the leachates were highly alkaline [40]. In samples immersed for 1 day into MilliQ water the pH was 11, while in those immersed for 9 months, it was 13. To perform speciation analysis within the linear concentration range, leachate samples obtained 1 day after immersion into MilliQ water were diluted 1 : 2 with alkaline buffer. Sample aliquots were injected onto the column and the simultaneous speciation analysis performed following the procedure described in paragraph 3.3.2.4. In samples immersed into MilliQ water for 9 months, concentrations of vanadate were significantly higher than those of chromate, arsenate and molybdate, so V detection was followed at

m/z 50. The total concentrations of elements and elemental species in leachates are presented in Table 4.8, while their corresponding chromatograms in Figure 4.11.

Table 4.8: Total concentrations of Cr, As, Mo and V determined by ICP-MS and concentrations of chromate, arsenate, molybdate and vanadate in leachates from building composites determined by HPLC-ICP-MS. (A1-A3) leachates 1 day after immersion and (B1-B3) leachates 9 months after immersion into MilliQ water. Results represent the mean value of three replicate determinations of selected element or elemental oxoanion species. Standard deviation of the measurements by ICP-MS is better than 1% and of the HPLC-ICP-MS better than 3%.

Sample/ Element	Concentra tion	Cr <i>m/z</i> 52 (ng/mL)	As <i>m/z</i> 75 (ng/mL)	Mo <i>m/z</i> 95 (ng/mL)	V <i>m/z</i> 50 (ng/mL)	V <i>m/z</i> 51 (ng/mL)
A1	Total	65	220	130	/	1635
99.5% (70% fly ash + 30% cement) + 0.5% EAF dust	Oxoanion	47	173	80	/	1120
A2	Total	49	230	97	/	1570
99.5% (80% fly ash + 20% cement) + 0.5% EAF dust	Oxoanion	28	139	40	/	795
A3	Total	60	193	132	/	1477
100% (80% fly ash + 20% cement) + 0% EAF dust	Oxoanion	37	140	68	/	900
B1	Total	82	2030	820	/	9080
98% (80% fly ash+ 20% cement) + 2% EAF dust	Oxoanion	42	1085	338	4445	/
B2	Total	85	2080	830	/	7110
98% (80% fly ash+ 20% cement) + 2% EAF dust	Oxoanion	39	1130	325	4500	/
B3	Total	86	2090	840	/	9970
98% (80% fly ash+ 20% cement) + 2% EAF dust	Oxoanion	44	1265	378	5290	/

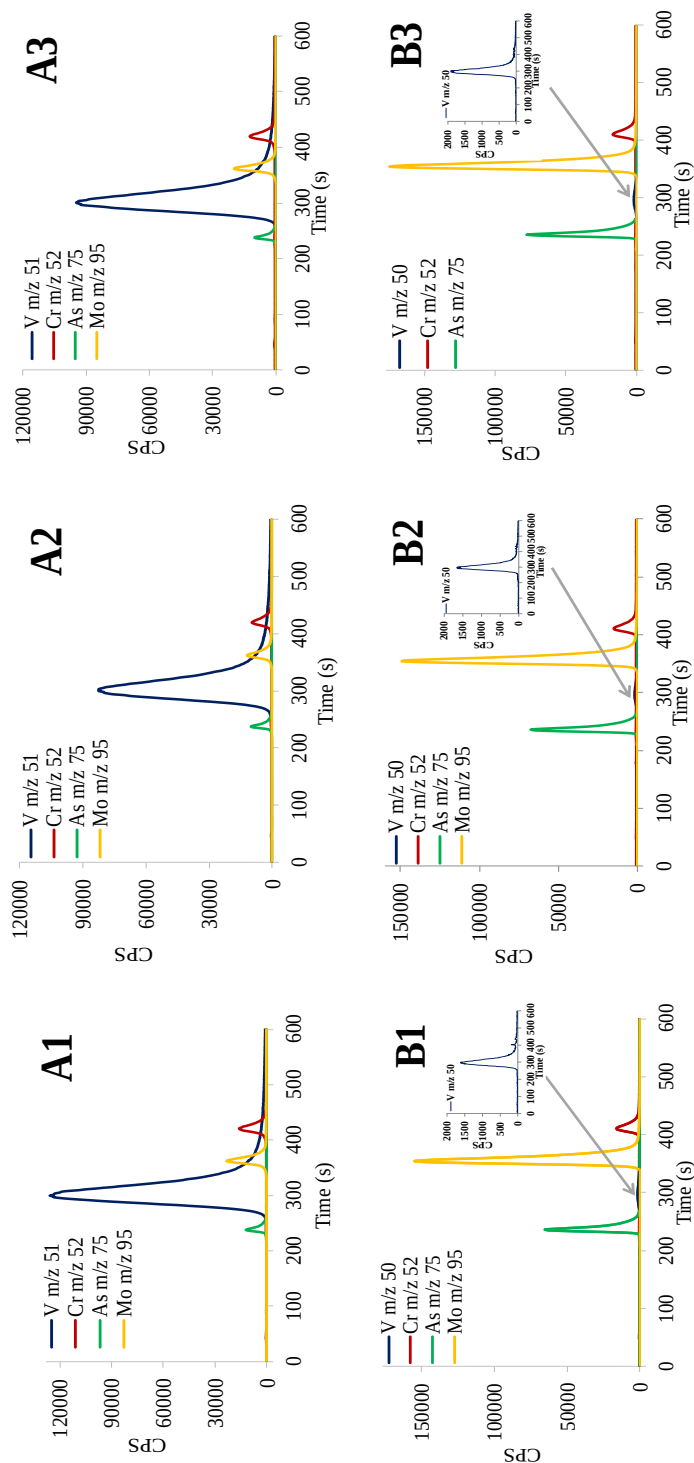


Figure 4.11: Simultaneous separation of chromate, arsenate, molybdate and vanadate in leachates from building composites determined by HPLC-ICP-MS. (A1-A3) leachate samples 1 day after immersion (samples diluted 1:2 with alkaline buffer) and (B1-B3) leachate samples 9 months after immersion into MilliQ water. Compositions of building composites are provided in Table 4.8.

As can be seen from the data in Table 4.8, sulphites and other reducing agents originating from building composites triggered the reduction of chromate, arsenate,

molybdate and vanadate. The Cr(VI), As(V), Mo(VI) and V(V) concentrations represented about 40–70% of their total elemental content. Data from Figure 4.11 demonstrate that the developed HPLC-ICP-MS analytical procedure is applicable for the simultaneous speciation analysis of chromate, arsenate, molybdate and vanadate in highly alkaline leachate samples. Selective separation of chromate from vanadate (Figure 4.10) and the possibility to detect the eluted V species by ICP-MS at the low abundance ^{50}V isotope extend its applicability for simultaneous speciation analysis to real world samples with significantly higher vanadate concentrations than chromate, arsenate and molybdate (Figure 4.11 B1-B3). The developed simultaneous speciation HPLC-ICP-MS procedure also appreciably reduces the time and the cost of analysis.

The results presented in Chapter 4.2 are based on the data of the published article by Drinčić et al. [145].

4.3 Determination of Hexavalent Cr in River Sediments from Industrially Exposed Sites by Speciated Isotope Dilution Inductively Coupled Plasma Mass Spectrometry

Within the EU-funded 7th framework project GLOBAQUA (Navarro-Ortega et al., 2015), pollution with potentially toxic elements was investigated in water and sediments of the Sava River under extreme flow events [64]. The results revealed that at the industrially exposed sites from stainless steel production and other metallurgic activities, total Cr concentrations in sediment samples collected in 2015 were up to 200 mg kg⁻¹. Although in the last decade, Cr concentrations in the Sava sediments tended to decrease and Cr exhibited low environmental mobility [146], [125], [63], [64], it was necessary to verify if they contained hazardous hexavalent Cr. The accurate determination of trace amounts of Cr(VI) in sediment samples is still very challenging.

Therefore, in this part of the Doctoral Dissertation a reliable and sensitive analytical procedure for the determination of Cr(VI) in sediments, which is based on speciated ID-ICP-MS, was developed.

4.3.1 Optimisation of the extraction procedure

First, the procedure for quantitative extraction of total Cr(VI) from sediment was optimized. The experiments were performed on a sediment from the reference location Mojstrana. To follow the potential species interconversion during the extraction procedure, the sediment was doubly spiked with $^{50}\text{Cr(VI)}$ and $^{53}\text{Cr(III)}$, so that the spiked Cr concentration in the 10-times diluted extract was 10 µg L⁻¹. Speciation of Cr in 10-times diluted sediment extracts was performed as described in paragraph 3.3.2.4, recording Cr isotopes at m/z 50, 52 and 53. Preliminary experiments did not provide significantly different results when the extraction time was 0.5, 1 or 2 h. Therefore, 1 h was applied for the extraction of Cr(VI) from sediment. The solid-to-liquid ratio was optimised by the use of a certified reference material CRM 041 (Cr(VI) in soil) by analysing 0.25, 0.5, 1 or 2 g of sample, to which 10 mL of alkaline extract was added. The results are presented in Table 4.9. The data revealed that 1 or 2 g of sample gave the same result, which closely matched with the certified value. The use of 0.5 g and 0.25 g of sample also gave satisfactory agreement with the certified value, which was, however, slightly worse due to poorer homogeneity. Therefore, to assure adequate sample homogeneity and to achieve low

LODs, 2 g of sediment sample to which 10 mL of extracting solution was added, was chosen as the optimal solid-to-liquid ratio.

Table 4.9: Determination of Cr(VI) in certified reference material CRM 041, Chromium VI - Soil, applying different amounts of sample and 10 mL of alkaline extract. The certified value for Cr(VI) 130 ± 2.31 mg kg⁻¹.

Sample weight (g)	Cr(VI) determined (mg kg ⁻¹)
0.25	126 ± 6
0.5	138 ± 6
1	129 ± 6
2	129 ± 6

In Figure 4.12A, a typical chromatogram of the ⁵⁰Cr(VI) and ⁵³Cr (III) doubly spiked sediment extract obtained by the HPLC-ICP-MS procedure is presented. Separated Cr species were monitored at m/z 50, 52 and 53.

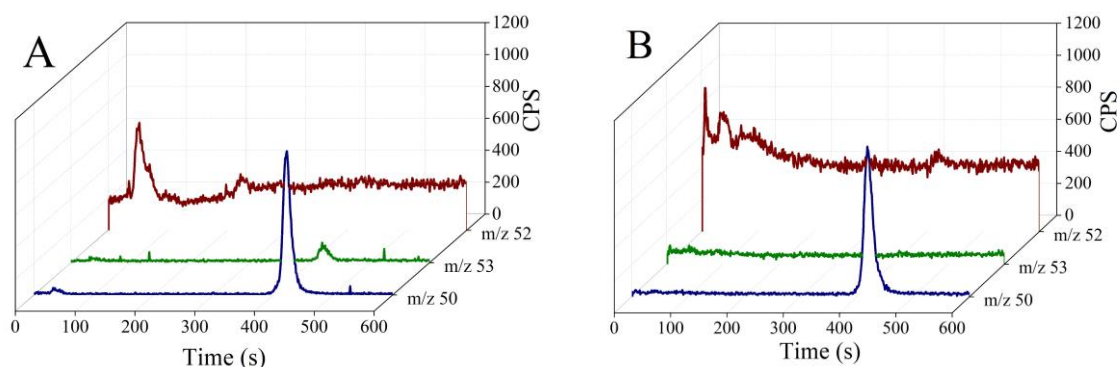


Figure 4.12: Chromatograms of Cr species from 10 times diluted sediment extracts (Mojstrana) doubly spiked with ⁵⁰Cr(VI) and ⁵³Cr(III), obtained by the HPLC-ICP-MS procedure. Cr was recorded at m/z 50, 52 and 53. The extraction solutions 2% NaOH + 3% Na₂CO₃ (A), 2% NaOH + 3% Na₂CO₃ + 0.4 mol L⁻¹ MgCl₂ (B) were used. Final concentrations of Cr spikes in diluted extracts were 10 µg L⁻¹ of ⁵⁰Cr(VI) and 10 µg L⁻¹ of ⁵³Cr(III).

Data from Figure 4.12A demonstrate that at m/z 52, indigenous Cr(VI) was not detected in the sediment extract analysed. The added ⁵⁰Cr(VI) recorded at m/z 50 was quantitatively separated on the column resin. The same peak areas of ⁵⁰Cr(VI) were obtained from spiking solutions prepared in the alkaline extract and in the alkaline sediment extract (the difference between the measured peak areas was <2%). This indicates that ⁵⁰Cr(VI) added was not reduced during the extraction procedure. From the elution profile of separated Cr species at m/z 53, it can be seen that, as a consequence of the high pH of the sediment extract (pH 12) and elevated temperature (80 °C), about 20% of added ⁵³Cr (III) was oxidized to ⁵³Cr(VI) during the extraction procedure. To prevent Cr(III)

oxidation, 0.4 mol L⁻¹ MgCl₂ was added along with the doubly isotopically enriched spiking solution containing ⁵⁰Cr(VI) and ⁵³Cr(III), and the extraction procedure was applied (Figure 4.12B). It is evident that the added ⁵³Cr(III) was not oxidised (⁵³Cr(VI) was not detected). At highly alkaline conditions Mg(OH)₂ was formed, which co-precipitated Cr(III) and thus prevented its oxidation to Cr(VI) [147],[102]. From comparison of peak areas for ⁵⁰Cr(VI) in the alkaline extract and ⁵⁰Cr(VI) added to the sediment extract, it was also demonstrated that Cr(VI) was not reduced. The latter experiments confirmed that under the optimised extraction procedure, no species interconversion occurred during the extraction step.

4.3.2 Quantification of Cr(VI) in sediments by speciated ID-ICP-MS and accuracy check

The optimised extraction procedure as described in paragraph 3.3.2.4 was then applied for the determination of Cr(VI) in sediments of the Sava River. The use of enriched stable isotopes allowed accurate determination of Cr(VI) by speciated ID-ICP-MS and correction for possible species interconversion during the extraction procedure [129], [56]. After extraction, the speciation procedure was applied, and the isotopic ratio of ⁵⁰Cr(VI)/⁵²Cr(VI) (RVI50/52) was determined and corrected for mass bias. A typical chromatogram of a doubly spiked sample for determining the isotope ratio RVI50/52 is presented in Figure 4.13.

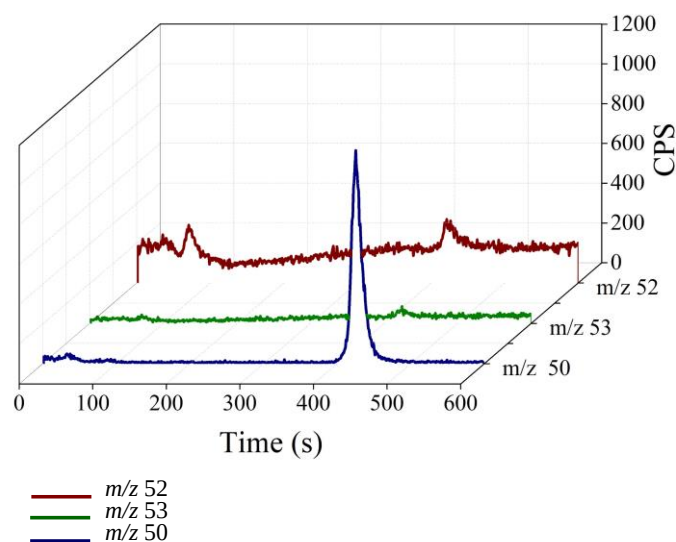


Fig. 4.13: A typical chromatogram of a doubly spiked sample (Jesenice 3) obtained from a 10 times diluted sediment extract by the HPLC-ICP-MS procedure, recorded at m/z 50, 52 and 53, used for determining the RVI50/52 ratio. The extraction solution 2% NaOH + 3% Na₂CO₃ + 0.4 mol L⁻¹ MgCl₂ was used. Final concentrations of Cr spikes in diluted extracts were 10 µg L⁻¹ of ⁵⁰Cr(VI) and 10 µg L⁻¹ of ⁵³Cr(III).

Since no species interconversion occurred under the optimised extraction procedure, it was possible to determine the concentration of Cr(VI) in sediment by speciated ID-ICP-MS based on a single (⁵⁰Cr(VI)) spike. Cr(VI) extracted from the sediment was calculated using equation (1), as proposed by Rodríguez-González et al. [130]:

$$c_S = c_{Sp} \frac{m_{Sp}}{m_S} \frac{M_S}{M_{Sp}} \frac{A_{Sp}^{50}}{A_S^{52}} \left(\frac{R_m - R_{Sp}}{1 - R_m R_S} \right) \quad (1)$$

CS and CSp are the concentrations of Cr(VI) in the sample and the spike, respectively, mS and mSp the mass taken from sample and spike in the mixture, respectively, and MS and MSp the elemental atomic weights of the element in the sample and the spike, respectively. AS52 and ASp50 are isotope abundances for isotopes in the sample and spike, respectively. Rm is the isotope ratio of isotopes (52/50) in the mixture. RS is defined as the isotope ratio of isotopes (50/52) in the sample ($RS = (AS50)/(AS52)$) and RSp, as the isotope ratio of isotopes (52/50) in the spike ($RSp = (ASp52)/(ASp50)$). Since no species interconversion occurred during the extraction, the correction factor for species interconversion was not considered in the above calculations.

4.3.3 Accuracy check

The accuracy of the determination of Cr(VI) by speciated ID-ICP-MS was verified by analysing the certified reference material CRM 041, Chromium VI - Soil. Good agreement between the Cr(VI) determined (129 ± 6 mg kg⁻¹) and the certified value (130 ± 2.31 mg kg⁻¹) was obtained, confirming the accuracy of the analytical procedure applied.

The accuracy of the developed analytical procedure was also evaluated by the spike recovery test. To 2 g of sediment sample (Mojstrana), 0.5 mg Cr(VI) kg⁻¹ was added, and the optimised extraction procedure was applied. The concentration of Cr(VI) in the spiked sediment was determined by speciated ID-ICP-MS. The recovery, calculated as a ratio between the determined and added Cr(VI) concentration was found to be 97%, confirming the accuracy of the developed analytical procedure.

4.3.4 Analytical figures of merit for the determination of Cr(VI) in sediment extracts by HPLC-ICP-MS

4.3.4.1 Linearity of measurement

The linearity of measurement for Cr(VI) was confirmed over the concentration range from LOQ to 100 µg L⁻¹, with a correlation coefficient (R^2) of 0.998.

4.3.4.2 Limits of detection and quantification

The instrumental LOD and LOQ for the determination of Cr(VI) were calculated as the concentrations that provided a signal (peak area) equal to 3s and 10s of the blank sample in the chromatogram, respectively. To calculate the LOD and LOQ, eight blank samples (0.2% NaOH + 0.3% Na₂CO₃) were injected, and the HPLC-ICP-MS procedure was applied. The LOD for the determination of Cr(VI) in the extract was found to be 0.025 µg Cr(VI) mL⁻¹, and the LOQ was 0.08 µg Cr(VI) L⁻¹. When Cr(VI) was extracted from 2 g of sediment sample into 10 mL of alkaline extraction solution, which was before measurements 10 times diluted, the LOD of the analytical procedure applied for Cr(VI) was found to be 1.25 µg kg⁻¹, and the LOQ was 4.0 µg kg⁻¹. Mälder et al. (2016), who used alkaline digestion and IC-MS/MS for quantification of trace concentration levels of Cr(VI) in lake sediments, reported LOD of 14 µg Cr(VI) kg⁻¹ (wet weight), while Graham et al. (2009), who also applied alkaline digestion and ion-pairing RP-HPLC-ICP-MS for quantification of Cr(VI) in harbour sediments, reported LOQ of 40 µg Cr(VI) kg⁻¹. These LOD and LOQ are 10 times higher than found in our work. In other available literature on the determination of total Cr(VI) in sediments, LOD or LOQ for Cr(VI) were not reported.

4.3.4.3 Repeatability of measurement

The repeatability of measurement was tested for six consecutive speciation analyses of Cr(VI) of alkaline extract (pH 12) from a sediment sample (Jesenice 1) doubly spiked with $^{50}\text{Cr}(\text{VI})$ and $^{53}\text{Cr}(\text{III})$ ($10 \mu\text{g Cr L}^{-1}$). Good repeatability of measurement was obtained. The relative standard deviation (RSD) for $^{50}\text{Cr}(\text{VI})$ was found to be $\pm 4.8\%$.

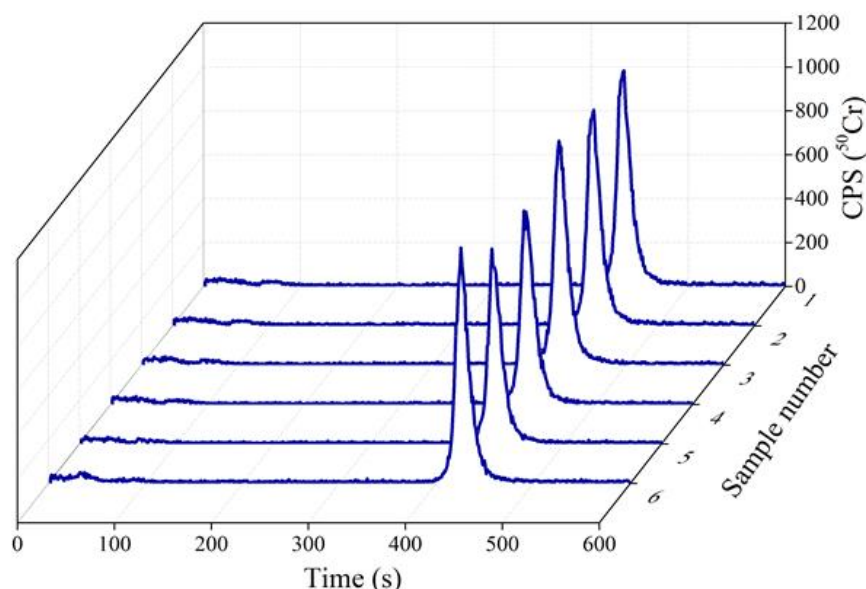


Figure 4.14: Six consecutive speciation analyses of 10 times diluted sediment extract (Jesenice 1) prepared in 2% NaOH + 3% Na_2CO_3 + $0.4 \text{ mol L}^{-1} \text{MgCl}_2$, doubly spiked with $^{50}\text{Cr}(\text{VI})$ and $^{53}\text{Cr}(\text{III})$. Chromatograms were obtained by the HPLC-ICP-MS procedure. Cr was recorded at m/z 50. Final concentrations of Cr spikes in diluted extracts were 10 ng mL^{-1} of $^{50}\text{Cr}(\text{VI})$ and 10 ng mL^{-1} of $^{53}\text{Cr}(\text{III})$.

4.3.5 Analysis of total Cr and Cr(VI) in sediments of the Sava River

The concentration of total Cr in sediments of the Sava River was determined by ICP-MS after microwave-assisted digestion of sediment samples (paragraph 3.2.2.2). The concentration of Cr(VI) was determined by applying the optimised extraction procedure and speciated ID-ICP-MS. The uncertainty of the analytical procedure was estimated based on the protocol described by Konieczka and Namiński [148]. The results presented in Table 4.10 represent the average value of three independent determinations of total Cr and Cr(VI) $\pm$ expanded uncertainty ($k=2$).

Table 4.10: Determination of total Cr and Cr(VI) in the Sava River sediments by ICP-MS and HPLC-ID-ICP-MS, respectively. Results represent the average value of three independent determinations of total Cr and Cr(VI) $\pm$ expanded uncertainty ($k=2$).

Sampling site	Total Cr (mg kg^{-1})	Cr(VI) ($\mu\text{g kg}^{-1}$)
Mojstrana	23.8 ± 1.2	<1.25
Jesenice 1	52 ± 2	<1.25

Sampling site	Total Cr (mg kg ⁻¹)	Cr(VI) (µg kg ⁻¹)
Jesenice 2	61 ± 2	<1.25
Jesenice 3	62 ± 2	4.2 ± 0.6
Jesenice 4	39.1 ± 1.4	<1.25
Jesenice 5	41 ± 1.6	<1.25
Jesenice 6	50 ± 2	<1.25
Radovljica 1	191 ± 8	<1.25
Radovljica 2	57 ± 2	<1.25
Gobovce	32.0 ± 1.2	<1.25
Slavonski Brod	90 ± 4	5.1 ± 0.8
Županja	138 ± 6	<1.25
Sremska Mitrovica	136 ± 6	<1.25
Šabac	105 ± 4	3.3 ± 0.63
Beograd	88 ± 4	<1.25

A low total Cr concentration (25 mg kg⁻¹) was determined in the sediment from the reference location Mojstrana. Elevated Cr concentrations were observed at the downstream locations influenced by the metal works Acroni Jesenice, which produces high quality steel. Huge amounts of steel slag deposited at the riverbank contaminated the Sava sediments with Cr. At sampling sites Jesenice 1–6, total Cr concentrations ranged from 40 to 60 mg kg⁻¹. Due to sediment transport during flash floods and as a consequence of hydropeaking from the large hydropower plant system Moste, sediment accumulated behind the dam is transported with the river flow and deposited at downstream locations Radovljica 1 and 2 (total Cr content 190 and 60 mg kg⁻¹, respectively). At the sampling site Gobovce, a location not influenced by the upstream industrial steel making activities, the total Cr concentration (30 mg kg⁻¹) was found to be similar to that at the reference point. At the lower Sava stretches, total Cr concentrations at industrially exposed sites ranged from 90 to 140 mg kg⁻¹. At Slavonski Brod, the elevated Cr concentrations in sediments are related to the activities of the smelting-plant Saint Jean Industries Free Zone, Đuro Đaković, while at Županja, they are related to the operation of the agricultural machinery factory and well developed heavy metal industry. At Sremska Mitrovica, contamination with Cr arises mainly from the Metalfer steel mill, producing construction steel. At the Šabac sampling site, the elevated Cr concentration is connected to the activities of Hesteel Serbia Iron and Steel Tinplate. At Belgrade, there is no specific heavy metal industry. Contamination with Cr is most probably a consequence of sediment transport from the upstream contaminated sites.

Data from Table 4.10 further indicate that among the 15 samples analysed, Cr(VI) was detected in only three samples, at sampling sites Jesenice 3, Slavonski Brod and Šabac. Its concentrations were close to LOQ and ranged from 3 to 5 µg kg⁻¹, representing only 0.003 to 0.007% of total Cr content in the sediments analysed. These data indicate that the presence of reducing agents (e.g. Fe(II) ions) in waste materials from the metallurgical and steel-making industries inhibit Cr oxidation in the sediments. Due to this and the extremely low Cr(VI) concentration, hexavalent Cr in the Sava sediments does not represent a considerable environmental hazard.

The results presented in Chapter 4.3 are based on the data of the published articles Vidmar et al. [63] and Drinčić et al. [149].

Chapter 5

Conclusions

In this Doctoral Dissertation, the leachability of selected elements was investigated from a building composite by applying NEN 7475 test and modified leaching protocols. As a model specimen, building composite prepared from a 98% mixture of fly ash (80%) and cement (20%), and 2% of EAF dust was used. Due to the release of Ca(OH)_2 and CaCO_3 from composites, the pH of leachates was high (pH 9–12), resulting in precipitation of Ba, Fe, Mn, Co, Ni, Cu, Zn, Cd, Sb, Hg and Pb. On the contrary, As, Cr, Mo and V that are present at alkaline pHs in a form of oxoanions were leached in substantial concentrations. To compare the NEN 7375 test against the modified procedure (without replenishing of leaching solution), compact building composites were immersed into MilliQ water and samples taken at points in time, as specified by the NEN test. It was demonstrated that the range of leaching of As, Cr, Mo and V was lower when the leaching was based on diffusion (NEN 7375 test, replenishing of solution), while three to ten times higher extent was observed when leaching was based on diffusion and dissolution of contaminants (leaching solution was not replenished). The data demonstrated that the use of modified leaching protocols, applying synthetic surface and sea water as leaching solutions, which is not replenished during the course of the experiment (simulation of the diffusion and dissolution of the contaminants), is appropriate for the estimation of the extent of leaching of toxic elements from building composites when a monolithic material is immersed into stagnant environmental waters. The use of ground composites made it possible to simulate the conditions when the material is disintegrated over time in the environment. Speciation analyses provide complementary information on the release and immobilization of toxic elements and their chemical species from building composites under simulated environmental conditions. The proposed leaching protocols provide novel alternatives for the evaluation of long-term environmental impacts of building composites, with approaches that closely imitate the environmental conditions.

A novel analytical procedure was also developed for the simultaneous speciation analysis of chromate, arsenate, molybdate and vanadate by anion-exchange HPLC-ICP-MS. In multiple standard solutions prepared at pH 12, the separated Cr, As, Mo and V species were quantitatively eluted from the column resin and detected on-line by ICP-MS, recording m/z 52, 75, 95 and 51, respectively. Under the applied chromatographic conditions, selective separation of Cr and V species was achieved. This enabled us to measure the eluted V species at the low abundance (0.25%) ^{50}V isotope, which is also the mass of ^{50}Cr isotope (abundance 4.345%). Using ^{50}V isotope in ICP-MS detection, simultaneous speciation analysis was possible in highly alkaline leachates of building composites containing significantly higher concentrations of vanadate than chromate, arsenate and molybdate. The developed analytical method is reliable, accurate (spike recoveries between 98 and 102%), repeatable ($\text{RSD} < \pm 3.0\%$) and fast (chromatographic

separation in 10min). To the best of our knowledge, this is the first report on simultaneous HPLC-ICP-MS speciation analysis of chromate, arsenate, molybdate and vanadate in highly alkaline samples. The possibility of the use of ^{51}V and ^{50}V isotopes in ICP-MS detection extends the applicability of the method to simultaneous speciation analysis in samples with wide concentration ranges of vanadate.

For the analysis of Cr(VI) in environmental samples with complex matrices, it is essential to apply appropriate analytical methodologies, which would ensure maximal species integrity during the analytical procedure. A sensitive and reliable analytical method for the determination of Cr(VI) in sediments was developed. To extract total Cr(VI) from sediments, hot ultrasound-assisted alkaline extraction (2% NaOH + 3% Na₂CO₃) was applied. Addition of 0.4 mol L⁻¹ MgCl₂ prevented Cr(III) oxidation during the analytical procedure. To control for species interconversion during the extraction procedure and for the calculation of Cr(VI) concentration by speciated ID-ICP-MS, the sample extract was doubly spiked with enriched $^{53}\text{Cr(III)}$ and $^{50}\text{Cr(VI)}$ stable isotopes. The accuracy of the analytical procedure was confirmed by the analysis of standard reference material and the spike recovery test. LOD obtained (1.25 $\mu\text{g Cr(VI) kg}^{-1}$) was appreciably lower than LODs reported by other researchers for the analysis of total Cr(VI) in sediments. The main advantages of the developed method are: (i) Cr speciation is not compromised during the analytical procedure, (ii) the analytical procedure enables selective determination of Cr(VI), (iii) the use of isotopically enriched Cr tracers importantly contributes to the validity of the obtained results, and (iv) high sensitivity of method, which enables determination of trace amounts of Cr(VI) in sediments. The analysis of sediment samples of the Sava River revealed that despite relatively high total Cr concentrations at industrially exposed sites (50–190 mg kg⁻¹), their Cr(VI) concentrations were very low, mostly below the LOD. In sediments where Cr(VI) was detected, its concentrations were lower than 5 $\mu\text{g kg}^{-1}$, representing less than 0.007% of the total Cr content. Thus, Cr(VI) in the Sava River sediments does not represent a considerable environmental burden. The developed analytical procedure with the use of isotopically enriched Cr tracers will be further applied in studies of oxidation-reduction processes of Cr in the Sava sediments under different environmental conditions (oxic, anoxic) and the presence of different oxidising and/or reducing agents. To the best of our knowledge, this is the first report on the occurrence of hexavalent Cr in the sediments of the Sava River. The reported analytical methodology could also be used to evaluate the environmental hazard posed by Cr(VI) contamination of sediments in the case of other rivers impacted by the industrial activities.

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Publications Related to the Thesis

Journal Articles

- A. Drinčič, I. Nikolić, T. Zuliani, R. Milačič, and J. Ščančar, “Long-term environmental impacts of building composites containing waste materials: Evaluation of the leaching protocols,” *Waste Manag.*, vol. 59, 2017.
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Conference Paper

- A. Drinčič, I. Nikolić, T. Zuliani, R. Milačič, and J. Ščančar, Building composites from fly ash, cement and electric arc furnace dust : environmental impacts, in Proceedings : part 1. Ljubljana: Mednarodna podiplomska šola Jožefa Stefana, 2016.
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Other Publications (optional)

Journal Articles

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Biography

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