

INNOVATIVE APPROACHES FOR SUSTAINABLE REMEDIATION OF CONTAMINATED WATERS AND SOILS

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Doctoral Dissertation
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SOILS

Doctoral Dissertation

NAPREDNI PRISTOPI ZA TRAJNOSTNO
REMEDIACIJO ONESNAŽENE VODE IN ZEMLJIN

Doktorska disertacija

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Abstract

The reuse of municipal wastewater for secondary people's needs is a sustainable approach to managing water scarcity. For this reason, we examined the processes that simultaneously occur in the additional treatment of water from the outflow of a small biological treatment plant (SBWTP), with different zero-valent iron nanoparticles (nZVI) and complementary methods of water remediation. We studied three different nZVIs: synthesized in the laboratory, Nanofer STAR and Nanofer25 slurry. The first ones proved unsuitable for water purification due to the release of boron, Nanofer STAR had too low reactivity. The most appropriate ones, Nanofer25 slurry, were used to research the optimization of the amount of nZVI and the operating parameters (mixing and settling time) to remove the selected pollutants from the water. In order to achieve the desired, more than 90% disinfection efficiency, 0.25 g/L nZVI was required. For a mixing time longer than 400 min, bacterial re-growth and desorption of the elements occurred. When concentrations of nZVI were lower than 0.25 g/L, the settling of iron particles after nanoremediation was less effective due to their stabilization with the organic matter. With the optimized nanoremediation process, most bacteria and most organic pollutants were removed from the water. The remaining bacteria were removed with sodium dichloroisocyanurate and organic contaminants by adsorption onto activated carbon. After the nanoremediation, the content of ammonia was slightly increased; however, it was removed in the subsequent process by ion exchange on zeolites. Thus, a multi-step remediation procedure for the re-use of municipal wastewater was established.

Immobilization is one of the most effective methods for remediation of contaminated soil. The soil is mixed with the additives, which leads to the formation of an inert composite. For the study of remediation, the most contaminated part of the soil from the area of Old Zinc-works site in Celje was used, which was classified as hazardous waste on the basis of exceeded limit concentrations of water-soluble Zn. We investigated the efficiency of various industrial wastes (paper ash, coal fly ash, ladle slag from steelmaking and red sludge from bauxite processing) as additives for immobilization of the soil. Paper ash, coal fly ash and ladle slag have the potential to form hydration products for the chemical immobilization of contaminants. Red mud was not hydraulically active and was partially neutralized. Experiments with using low amounts of additives have shown that the immobilization of PTE is in accordance with known pH curves for cationic metals (Cd, Pb, Zn) and Mo as the oxyanion. Increase of the effectiveness of immobilization in composites with time is associated with the formation of new minerals in hydration and pozzolanic reactions. Adsorption of pollutants is the main mechanism of immobilization using red mud. Composites using paper ash, coal fly ash and red mud are environmentally acceptable, considering the inertness limit values, while composites with ladle slag have exceeded the limit for Mo in the aqueous eluate. The combination of paper ash with other additives, in comparison with binary systems, increased the efficiency of immobilization and improved the geotechnical properties of the composite. All composites, except those with ladle slag, are potentially useful as building materials for remediation in contaminated sites in the form of geotechnical embankments or fills.

Povzetek

Ponovna uporaba komunalne odpadne vode za sekundarne potrebe ljudi je trajnostni pristop za obvladovanje pomanjkanja vode. Zato smo v obravnavanem delu preučevali procese, ki se simultano pojavijo pri obdelavi vode, zajete na iztoku male biološke čistilne naprave (SBWTP), z različnimi nanodelci nič-valentnega železa (nZVI) in komplementarnimi metodami remediacije vode. Preučili smo tri različne nZVI: sintetizirane v laboratoriju, Nanofer STAR in Nanofer25 slurry. Prvi so se zaradi sproščanja bora izkazali kot neprimerni za čiščenje vode. Nanofer STAR je imel prenizko reaktivnost. Najbolj primerni, Nanofer25 slurry, so bili uporabljeni za raziskave optimizacije količine nZVI in obratovalnih parametrov (čas mešanja in usedanja) za odstranitev izbranih onesnaževal iz vode. Za doseganje želene, več kot 90-odstotne učinkovitosti dezinfekcije je bilo potrebno uporabiti 0,25 g/L nZVI. Pri mešalnem času, daljšem od 400 min, je prišlo do ponovnega razraščanja bakterij in desorpcije elementov. Ko so bile uporabljene koncentracije nZVI, nižje od 0,25 g/L, je bilo usedanje železovih delcev po nanoremediaciji manj učinkovito, in sicer zaradi njihove stabilizacije z organsko snovjo. Z optimiziranim procesom nanoremediacije je bila večina bakterij in večji del organskih onesnažil odstranjen iz vode. Preostale bakterije smo odstranili z natrijevim dikloroizocianuratom, organske kontaminante pa z adsorpcijo na aktivno oglje. Po nanoremediaciji je bila nekoliko povišana tudi vsebnost amonijaka, ki smo ga v nadaljnjem procesu odstranili z ionsko izmenjavo na zeolitih. Tako je bil vzpostavljen večstopenjski postopek čiščenja za ponovno uporabo komunalne odpadne vode.

Za sanacijo onesnaženih tal je ena od najbolj učinkovitih metod imobilizacija. Pri tem se zemljina zmeša z aditivi, kar vodi k nastanku inertnega kompozita. Za študij remediacije je bil uporabljen najbolj onesnažen del zemljine z območja Stare Cinkarne v Celju, ki je bila na podlagi preseženih mejnih koncentracij vodotopnega Zn klasificirana kot nevaren odpad. Raziskali smo učinkovitost različnih industrijskih odpadkov (papirniški pepel, premogov leteči pepel, ponovčna jeklarska žlindra in rdeče blato iz predelave boksita) kot aditivov za imobilizacijo. Papirniški pepel, premogov leteči pepel in ponovčna žlindra imajo potencial za tvorbo produktov hidratacije za kemično imobilizacijo kontaminantov. Rdeče blato ni bilo hidravlično aktivno in je bilo že delno nevtralizirano. Poskusi imobilizacije z uporabo nizkih deležev aditivov so pokazali, da je izluževanje PTE v skladu z znanimi krivuljami odvisnosti pH za kationske kovine (Cd, Pb, Zn) in Mo kot oksanionski element. Povečanje učinkovitosti imobilizacije v kompozitih s časom je povezano z nastajanjem novih mineralov v hidratacijskih in pucolanskih reakcijah. Adsorpcija onesnažil je glavni mehanizem imobilizacije z uporabo rdečega blata. Kompoziti z uporabo papirniškega pepela, premogovega letečega pepela in rdečega blata so glede na mejne vrednosti za inertnost okoljsko sprejemljivi, medtem ko so kompoziti s ponovčno žlindro presegli mejo za Mo v vodnem izlužku. Kombinacija papirniškega pepela z drugimi aditivi je v primerjavi z binarnimi sistemi povečala učinkovitost imobilizacije in izboljšala geotehnične lastnosti kompozita. Vsi kompoziti, razen tistih s ponovčno žlindro, so potencialno uporabni kot gradbeni material za sanacijo onesnaženih območij v obliki geotehničnih nasipov ali zasipov.

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Abbreviations

7thEAP	... Seventh Environmental Action Programme
AOP	... Advanced Oxydation Processes
AQE	... Aqua regia extraction
BET	... Brunauer, Emmett and Teller isotherm for specific sorption surface area
CAH	... Calcium aluminate hydrate
CASH	... Calcium aluminium silicate hydrate
CSH	... Calcium silicate hydrate
CAT	... Coal ash TE-TOL
CAV	... Coal ash VIPAP
CFU	... Colony forming units
CS	... Contaminated soil
d.m.	... Dry matter
EC	... European Commission
EDS	... Energy-dispersive X-ray spectroscopy
EEA	... European Environmental Agency
EU	... European Union
FESEM	... Field emission scanning electron microscope
GC-MS	... Gas chromatography – mass spectrometry
ICP-MS	... Inductively coupled plasma –mass spectrometry
IPS	... International Postgraduate School
JSI	... Jožef Stefan Institute
LSA	... Ladle slag ABS
LSH	... Ladle slag Harsco
MPN	... Most probable number
NaDCC	... Sodium dichloroisocyanurate
nZVI	... Zero-valent iron nanoparticles
OS	... Oxidative stress
PA	... Paper ash VIPAP
PTE	... Potentially toxic elements
RIR	... Reference intensity ratio
RM	... Red mud
RS	... Republic of Slovenia
ROS	... Reactive oxygen species
SAED	... Selected area electron diffraction
SBWTP	... Small biological wastewater treatment plant
SEM	... Scanning electron microscope
SFD	... Soil framework directive
TEM	... Transmission electron microscope
UCS	... Unconfined compressive strength
UN	... United Nations
US EPA	... United States Environment Protection Agency

UV	. . .	Ultra Violet light
UWWTD	. . .	Urban wastewater treatment directive
XRD	. . .	X-ray powder diffraction
XRF	. . .	X-ray flourescence
WEI	. . .	Water Exploitation Index
WFD	. . .	Water Framework Directive
WHO	. . .	World Health Organization
ZAG	. . .	Slovenian National Building and Civil Engineering Institute

Symbols

$2\theta^\circ$	... Diffraction angle
AsO_4^{2-}	... Arsenate
BOD_5	... Biochemical oxygen demand
BO_4^{4-}	... Borate
C_i	... Initial concentration
C_x	... Concentration after treatment
Cl^-	... Chloride
COD	... Chemical oxygen demand
CrO_4^{2-}	... Chromate oxyanion
d_{10}	... 10% of passing of grains
d_{50}	... 50% of passing of grains
d_{90}	... 90% of passing of grains
E^0	... Standard redox potential
Fe^0	... Elemental iron
FeCl_3	... Iron(III) chloride
H_2	... Hydrogen gas
H_2O_2	... Hydrogen peroxide
KA_{ow}	... Octanol-water partitioning coefficient
LD_{50}	... Lethal dose (median)
NaBH_4	... Sodium borohydride
N	... Nitrogen
N_2	... Nitrogen gas
NH_4^+	... Ammonia cation
NO_2^-	... Nitrite
NO_3^-	... Nitrate
O_2	... Oxygen
$\text{OH}^\cdot$	... Hydroxyl radical
$\text{O}_2^{\cdot-}$	... Superoxide radical
O_3	... Ozone
PO_4^{3-}	... Phosphate
SO_4^{2-}	... Sulphate
SeO_4^{2-}	... Selenate
TN_b	... Total bound nitrogen

Chapter 1

Introduction

1.1 General Introduction

Health and well-being of all living beings is highly dependent of clean environment. However, with industrial development, climate changes and exponential increase of human population, the pressure on nature and its resources is increasing. We are all part of the same planet, and negative consequences of environmental degradation are inevitably reflecting in hazards for the health of humans, animals and the environment, shortage of resources, food and water, loss of biodiversity. As Hardin stated in its "Tragedy of a Commons" (1968) [1]: "We live in a finite world, with finite resources, that cannot support infinite growth...", and with pollution "we are fouling our own nest." Circular economy and sustainable development currently represent the best socio-economic systems that could help us embrace the philosophy of synergetic coexistence of industry and nature by decoupling the economic growth from environmental degradation [2]. As an imperative for the future development, the European Commission (EC) has already chosen to do everything possible to sustain and preserve this world as a healthy place with clean environment worth living in. The European Union (EU) wants to set new global standards in sustainable development by presenting itself as the best example. By adopting a sustainable way of development, EU has obliged to manage natural resources responsibly by protecting habitats and biodiversity, and by adapting the economic growth to the rational use of resources by developing a circular system of materials transfer. The development will not be achieved on cost environmental pollution [3]. Sustainable development should also be an ideal for socio-economic development and environmental protection on a global scale. At the United Nations (UN) conference Rio +20, Sustainable Development Goals with 169 targets were set to achieve sustainable development by 2030. The global Agenda 2030, which was adopted by EU in its 7th Environment Action Programme (7thEAP) [4], has also set the following two goals: ensuring clean water and its sustainable management; protection, restoration, and sustainable management of land.

It is estimated that the industry, which provides ecological solutions, is worth more than a billion EUR and is going to double in the next 10 years. Employment in the EU environmental management and technology sector is growing by 3% per year and it is estimated that 400,000 new jobs will be available only in the renewable energy sources sector by 2020. Paying for implementation of environmental protection is therefore not only an investment in human health and well-being but also creates new economic benefits for ecologically developed countries [4].

However, despite all possible economic benefits, the ultimate goal of sustainable development and environmental protection is to protect the health of humans and all other living beings. Interactions between organisms and surrounding environment are highly complex. It is very difficult to correlate environmental risks, due to a contamination, directly with health issues [5]. Nowadays, it is therefore necessary to undoubtedly confirm the environmental

acceptance of chemicals or industrial activities before their use, which is in line with the implementation of the Precautionary principle in EU [4].

Low environmental standards during 200 years of industrialization caused severe environmental degradation. Numerous “old burdens”, contaminated historical industrial sites lay in Europe, causing environmental and health problems of millions of Europeans [6]. On the other hand, additionally, a lot of effort is needed to restore again a good ecological and chemical status of Europe’s water bodies, after years of degradation [7].

Nowadays, protection of health of humans, animals and the environment is a very challenging task. Contamination can be present in a form of diffuse and/or localized sources, which are subtle rather than obvious, and involving different media at once (soil, water, air and biota). Therefore, the contamination issues raise questions that transcend disciplinary boundaries and demand involvement of different scientific approaches to bring the problem from initial characterization to the final solution [8]. The fast development of analytical methods has allowed us to detect more hazardous substances in different media, at low concentrations and in different forms species. This information has brought us to the knowledge that primary risks do not originate from total concentrations of these substances but are dependent of chemical speciation and complex interaction between different media [9]. Transport or transfer of harmful substance from one phase to another, especially to/through cell membranes of living organisms, is the basic condition, which can result in toxic effects. This is referred to as “bioavailability processes”, which are defined as the physical, chemical, and biological interaction that determine the exposure of living beings to hazardous substances associated with soil, water, air or food. Understanding of the bioavailability processes is crucial for environmental risk assessment and management. According to the US Environment protection agency [10], environmental risk is dependent of toxicity and exposure. Toxicity is dose dependent and specific for every chemical or potentially toxic element (PTE) [8]. The exposure is dependent on time (duration) and how much has the harmful substance spread in the environment or what is the exposed surface area of organisms it can reach. Generally, the most important factor of exposure is concentration of the contaminant in the environment [11].

The basic purpose of any remediation, soil or water, is to eliminate risks by reducing the bioavailability or exposure. This can be done by either taking the contaminants out of the system (by extraction, adsorption or degradation, if possible) or by cutting the transfer routes (by immobilization).

1.2 Nanoremediation of Wastewater for Reuse

1.2.1 Global water balance

Water is a finite resource and indispensable for the existence of life on Earth. Globally, about 97% of water is saline, found mainly in oceans and seas and only 3% is fresh water. Nearly 69% of the total freshwater is held in continental and mountain glaciers, about 30% in groundwater reservoirs and the remaining portion is stored in surface water bodies (lakes, rivers and swamps). Only approximately 1% of fresh water is available for human needs [12].

Water scarcity is, by UN [13] definition, the point at which the aggregate impact of all users impinges on the supply or quality of water, under prevailing institutional arrangements, to the extent that the demand by all sectors, including the environment, cannot be satisfied fully. Hydrological water scarcity levels are calculated from the ration between the number of population and quantity of available water. Water stress occurs if water supply per person drops below 1700 m³ per year, while water supply below 1000 m³ represents water scarcity, and absolute water scarcity is when the supply is lower than 500 m³ per person annually. On the other hand, World Health Organization (WHO) estimates that for a country to sustain its own agricultural production, the available water supply must be at least 750 m³ per capita per year

[14]. According to UN, approximately 1.2 billion people already live in areas of water scarcity. Almost 500 million more people will suffer this situation in a near future and additional 1.6 billion people will face the economic consequences of water scarcity [13]. Water scarcity is caused by multiple different factors, which are sometimes hard to distinguish one from another [15]. First, water consumption is growing. It has increased almost twice the rate of population increase in the last century. According to FAO - AQUASTAT [16] human consumption of water is regarded as withdrawal, as water cannot be completely taken from the natural system. It only depends on how long the humanity retains it for its use, and in what condition it is discharged into the natural system. Agriculture, which consumes more than 70% of entire water withdrawn by the humanity, is the main user, followed by the industry and other common human needs. The global demands have reached more than 4000 km³ of water in 2010. The over-exploitation of water resources has created huge problems, which is expected to grow worse in the future, with water scarcity occurring globally even in regions now considered water-rich [17], [18].

Second manmade cause for water scarcity is contamination of water sources and unsustainable management. The world's water is polluted by agriculture, industry and municipal discharges that can be divided on point and diffuse sources [19]. Agriculture is a diffuse contamination source that contributes to contamination with nutrients (phosphates, nitrogen based, organic animal excreta), pesticides (herbicides, insecticides, fungicides), salts (sodium, potassium, sulphate, magnesium, calcium, bicarbonate, chloride), pathogens (especially faecal coliforms), PTE (Cu, Se, Cd, Pb, As, Mn), organic matter, and emerging contaminants (hormones, feed additives, animal drug residuals) [20]. Municipal wastewater emissions are usually generated at point sources as discharges from sewerage or wastewater treatment plants. Every day new contaminants are emerging in the form of personal care products, pesticides, pharmaceuticals, endocrine disrupting compounds, flame retardants, plasticizers, and many more, which can threaten water sources due to their persistence and toxicity even at low concentrations [21], [22]. Currently, most of the conventional wastewater treatment technologies and wastewater treatment plants are inefficient for complete removal of these contaminants and are rather point sources for their release [21], [23], [24]. Due to inefficient water management 1.1 billion people do not have access to improved and safe drinking water supply, which would include basic safety measures such as disinfection or filtration of water [25]. Water contaminated with pathogenic organisms is used by millions of people, with fatal consequences, even in developed countries [26].

The third major cause for water scarcity is global climate changes. Trends in warming of the climate could cause that by 2025, 1.8 billion people will be living in countries or regions with water scarcity, and almost half the world's population will be living in areas of high water stress by 2030 [7]. Water scarcity in some arid and semi-arid areas could cause displacement of between 24 million and 700 million people [13]. According to EC over the last 30 years at least 11% of EU citizens were affected by water scarcity. European Environment Agency (EEA) estimates that 16 to 44 million people will suffer from water scarcity in Southern Europe by 2070 [27]. Especially the Mediterranean region is very susceptible for climate changes that lead to warmer climate, transforming it to semi-arid to arid region [15]. Europe has faced one of the worst cases of drought in 2003, when over 100 million EU citizens or one third of the EU territory was affected, causing 8.7 billion EUR of damage. In the same event, in Slovenia, 47,400 inhabitants suffered water scarcity and 119,180 m³ of water was delivered to them to mitigate the consequences of drought [28].

Therefore, several countries are already turning towards alternative sources for production of drinking water or water for crop irrigation, industry, and public needs. The latter are not necessarily environmentally friendly and sustainable; for example, desalination by reverse osmosis [29]. Nowadays, 15,000 desalination plants (at least 50% is based on reverse osmosis technology) around the World produces 77.4 million m³ of water daily, which is approximately

1% of the world's total water consumption. This already affects environments, especially due to discharges of brines and spent pretreatment chemicals in natural water bodies [30].

UN and EU have recognized the potential of municipal wastewater, which can be considered as a secondary source of water in areas affected by scarcity [31]. Over 90, 80 and 60% of municipal wastewater is already reused in Cyprus, Israel and Malta, respectively, mainly for irrigation in agriculture [32]. EC states that approximately 1 billion m³ of treated municipal wastewater is reused annually in EU, which is only 2.5% of the total volume of effluent water from wastewater treatment plants and less than 0.5% of freshwater taken from natural sources. According to EC, water reuse is part of the action plan for circular economy, which should enhance regulatory and financial incentive, to help reach the goal of reuse of 6 billion m³ annually, by the year 2025. However, quality requirements have to be set and a technology has to be developed for safe water reuse within the scope of Water Framework Directive (WFD) [33] and to ensure the availability of water in adequate quantity. Methods for remediation must be robust, available at low cost, with low energy consumption and minimal impact on the environment [17]. One of the most promising tools for wastewater remediation for its reuse is nanotechnology, which can offer new possibilities for degradation of persistent organic contaminants, disinfection, removal of PTE, and desalination [34].

1.2.2 Basic treatment of municipal wastewater

Municipal wastewater has variable composition, which depends on climate, community size, living standards, quality of water supply, degree of industrialization etc. [35], [36]. It can be roughly estimated that it contains 99% of water and 1% of suspended and dissolved substances. It is brown to brow-grey coloured, turbid, with odour of decaying organic matter or sulphide. It can contain from 250 – 850 mg/L total dissolved solids, 100 – 350 mg/L suspended particulate matter, 100 – 300 mg/L of total organic carbon. Total concentration of N ranges from 20 – 80 mg/L, NH₄⁺ can range from 12 – 50 mg/L and organic nitrogen from 8 – 35 mg/L, while concentrations of nitrites (NO₂⁻) and nitrates (NO₃⁻) are even more variable. Total phosphorus in a form of orthophosphate ranges from 6 – 10 mg/L. General measure for content of organic substance in wastewater are biochemical oxygen demand (BOD₅) and chemical oxygen demand (COD), which range from 100 – 300 and 250 – 1000 mg of O₂ per litre, respectively. Proteins, hydrocarbons, fatty acids and oils represent the main part of organic substances. Other organic substances in micro- or even nano-gram per litre concentrations generate from personal care products, persistent organic contaminants, plasticizers, pharmaceuticals, petrol derivatives, and many others. PTE that can be most commonly found in most municipal wastewaters are Cd, Cr, Cu, Fe, Pb, Mn, Hg, Ni, and Zn [21], [24] [36]. Microorganisms, especially bacteria, are present in municipal wastewater in great numbers and represent a persistent problem that could substantially hinder the potential for its reuse. Bacteria that are indicating for fecal contamination of water are coliform bacteria (including *Escherichia coli*) fecal Enterococci, *Clostridium perfringens*, and *Salmonella* sp. [37]. Probable number of coliforms can reach more than 10 million in 100 mL of wastewater. There are also other pathogenic microorganisms, which include algae, archaea, viruses, fungi and yeasts, protozoa and helminths [38].

Municipal wastewater is collected in a central sewerage system in a form of so-called agglomerations. From there it is directed into the wastewater treatment plants. Wastewater treatment plants are designed to receive a predetermined amount of municipal wastewater or pollution load that is accounted in units regarded as Population Equivalents (PE). It is predicted that one PE is an organic biodegradable load that has BOD₅ of 54 g of O₂, which is equivalent to a load that an average person creates in 24 hours [38]. Large municipal wastewater treatment plants are design to receive wastewater from large sewerage systems with more than 10,000 PE and up to 150,000 PE. Small biological wastewater treatment plants (SBWTP) are designed for less than 2000 PE, usually for 100 PE. They are suitable to be used in areas with dispersed settlement, where it is feasible to build small sewerage systems.

Treatment methods for purification of municipal wastewater are broadly divided into physical, chemical and biological. Physical treatment units include screening, comminution, flow equalization, sedimentation, flotation, and granular-medium filtration. Chemical precipitation, adsorption, disinfection, chlorination, etc. are regarded as chemical treatment methods. Biological systems are the following: activated sludge processes, aerated lagoon, trickling filter, rotating biological contactors, pond stabilization, anaerobic digestion, and biological nutrient removal. Wastewater treatment systems with the use of active organic sludge are the most commonly used in the developed world. This is especially due to relatively simple management and cost effectiveness [39]. Treatment of wastewater in SBWTP is performed on a basis of the use of activated biological sludge in multiple stages [17]. In the first stage the removal of suspended particulate matter by sedimentation in primary settling tank is performed. Wastewater then flows into the aeration tank for secondary biological treatment. It is based on multiple processes that include removal of nitrogen species, phosphorus and nutrients. First, by different means (compressors, blenders, rotating contractors etc.) air is introduced into wastewater to induce aerobic microbiological processes. Biologically active material is sustained in suspension by mixing or stabilization on porous floating carriers (for example moving bed bio-reactor, trickling filter). Microorganisms are concentrated in mud chips – floccules, which can have up to 10,000 m² of active specific surface area available for wastewater purification in 1 m³ large basin. In the presence of oxygen microorganisms rapidly consume nutrients, divide and thus increase the amount of organic matter that settles as sludge with bounded contaminants. Hydraulic retention time of wastewater in SBWTP is from a few hours to a few days. Efficiency for removal of organic contaminants, especially persistent ones, from wastewater is increasing with longer hydraulic retention times [23]. Therefore, this parameter has to be optimized from case to case, based on content and composition of organic contaminants and BOD₅ in wastewater which is flowing in the SBWTP [40].

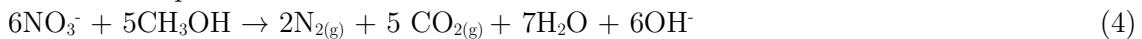
Removal of nitrogen species is complicated and includes different chemical reactions and microorganisms [41]. First, organic bound nitrogen, for example from urea (NH₂COHN₂), is transformed into inorganic form of NH₄⁺ (Eq. 1).



Bacteria from genus *Nitrosomonas* transform NH₄⁺ into nitrite NO₂⁻. The latter is transformed into NO₃⁻ by bacteria from genus *Nitrobacter*. The whole aerobic process of nitrification is taking place at neutral pH and at a temperature between 10 and 35 °C, according to reaction mechanisms in Equations 2 and 3.



This is followed by denitrification processes, which take place in compartments of SBWTP where anaerobic conditions are established. Concentration of O₂ in water must be less than 0.5 mg/L and redox potential < -100 mV. The process is performed by different facultative anaerobe microorganisms (*Achromobacter*, *Acetobacter*, *Acinetobacter*, *Agrobacterium*, *Bacillus*, *Chromobacter*, *Flavobacterium*, *Halobacterium*, *Hypomicrobium*, *Neisseria*, *Paracoccus*, *Propionibacterium*, *Pseudomonas*) that consume NO₃⁻ and simple hydrocarbons (for example CH₃OH) as an energy source, thus transforming it into N₂ and CO₂ gas according to the mechanism in Equation 4.



A group of microorganisms regarded as a phosphate accumulating organisms concentrate phosphate in a form of biomass during aerobic processes.

PTE are mostly accumulated in a biomass and thus separated from water. By means of microbiological treatment different organic contaminants can be degraded [42]. However, due to their persistence and longer retention times needed for degradation, persistent organic contaminants are in many cases released from SBWTP untreated with effluent waters [24].

Bacteria and other pathogenic microorganisms also represent a problem in effluent water from SBWTP, as they are only partly removed from municipal wastewater [43].

Most of suspended biomass settles in the last part of the treatment at the SBWTP, where water clarifies before release.

As stated before, the SBWTP removal efficiency for micro-contaminants, PTE and reduction of number of pathogenic microorganisms in wastewater is limited [23], [43]. Despite the fact that effluent waters from SBWTP are not appropriate for reuse, they can be regarded as a potential source of water in front of our doorstep. Additional treatment system is needed to make it safe [39], [44]. However, it is very important that secondary treatment of municipal wastewater is performed as efficient as possible to achieve higher efficiency and economic acceptability of tertiary treatment for water reuse [45].

1.2.3 Conventional methods for water treatment and reuse

Different engineered and natural systems or methods are available for processing of effluent water from wastewater treatment plants for its reuse. The factors that limit the selection of the appropriate one is efficiency in removal of contaminants and pathogens, energy requirements, generation of waste, formation of disinfection by-products and costs [44]. According to the terminology and concepts of EC, water reclamation technologies can be classified into non-conventional (extensive) and conventional (intensive). Non-conventional are natural systems that include riverbank filtration, direct injection, wetlands, natural reservoirs for purification, etc., which require a large amount of space, low energy, and a substantial amount of time [45].

Conventionally engineered systems require minimal space and time for water purification; however, consumption of chemicals and energy can be high. The latter can be divided into physical (sand filtration, pulverized or granulated activated carbon, micro-, ultra-, and nano-filtration, reverse osmosis, heat treatment and distillation), chemical (precipitation and coagulation, adsorption, ion exchange, photocatalysis, UV, ozonating, chlorination), and biological water purification (for example biologically active carbon) [44], [46], [47].

Precipitation and coagulation is most commonly used for softening of the water, removal of PTE, fluoride, organic contaminants and phosphorus. The principle of this method is to precipitate dissolved contaminant into a form agglomerates or floccule due to a surface charge modification. These are then easily removed by filtration methods. Different inorganic chemicals are utilized, for example $\text{Ca}(\text{OH})_2$, $\text{Na}_2\text{Al}_2\text{O}_4$, FeSO_4 , FeCl_3 , $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, or synthetic and natural polymers, which are for example polyacrylamide, polyethylene oxide, poly diallyl dimethyl ammonium chloride, poly styrene sulfonic acid, and starch, guar gum, alginate, glycogen, dextran, respectively [46], [48].

Adsorption can be performed by different media, which usually have a high specific surface area with surface with high concentration of surface adsorption sites. We can distinguish between physisorption, which originates from van der Waals forces, and chemisorption, which originates from the formation of strong covalent bonds. There are numerous adsorption materials used for water purification. However, the most widely used are activated carbon, activated alumina, and silica gel, with average specific surface areas of 700-1400, 345-415, and 300-850 m^2/g , respectively. Activated carbon can be used in the form of granules or powder. It is very effective for removal of organic contaminants due to its hydrophobic surface that enables binding nonpolar organic solutions, including halogenated hydrocarbons and dyes. Meanwhile alumina and silica are mostly used for the removal of PTE, phosphates, Cl^- and F^- [46], [47].

Ion exchange is a reversal process, which is induced by coulombic attractive forces between ions in water and charged surface functional groups (S-). Ions attached (A^{n+}) to the immobile phase, which is most commonly zeolites or synthetic resins, exchange with the ions of contaminant in the water (B^{n+}) that have the same valence. After surface exchange sites are

saturated with ions of contaminant, they can be regenerated by concentrated salt solution of ions A^{n+} (simplified in Equation 5) [47].



Natural or synthetic zeolites are aluminosilicate minerals with cage-like crystalline lattice formed of SiO_4 tetrahedra and Al_2O_3 octahedra. Negative charge is balanced by alkali or earth alkali elements, which can be exchanged by different positively charged ions of contaminants from water (especially potentially toxic elements and ammonia). Ion exchange resins are made of polymers, which are chemically modified so different surface functional groups are formed for exchange of either negatively or positively charged ions. Sulfonic and carboxylic acid groups are able to exchange positive ions, while amino groups exchange anions [47].

Advanced oxidation processes (AOP) are becoming increasingly important methods of water purification as they offer solutions for degradation of persistent organic contaminants and pathogenic microorganisms. Generally, AOP are based on the formation of powerful oxidizing radicals, known as reactive oxygen species (ROS), of which the most commonly known are hydroxyl radical ($OH^\bullet$), superoxide radical ($O_2^{\bullet-}$), and hydrogen peroxide (H_2O_2) [49]. Chemical AOP are Fenton's reagent, which is going to be explained in the chapter regarding nZVI remediation mechanism, and peroxidation, which utilizes ozone (O_3) and H_2O_2 [50]. Photochemical AOP use UV irradiation for the photolysis of H_2O_2 or O_3 , Photo-Fenton reaction ($H_2O_2/Fe^{2+}/UV$), and heterogeneous photocatalysis (nano-oxides of transitional metals/UV). The latter is increasingly used with the development of nanotechnology, especially nanoscale TiO_2 and other semiconducting catalysts. This is due to their low energy band gap between the valence and conduction electron band. Therefore, they can be photo-excited for electron donating and accepting sites, which induce oxidation-reduction reactions for the formation of ROS [49]. Sonochemical AOPs are based on the use of ultrasound, which creates cavitation bubbles. The latter then collapse at supercritical conditions ($T = 2000 - 5000$ K, $P = 6 \cdot 10^4$ kPa) at micro-scale, and cause sonolysis of water molecule and consequent formation of ROS [51]. Electrochemical AOPs utilize the following mechanisms for the production of ROS: anodic oxidation process, electrocatalytically generated Fenton's reagent and the simultaneous anodic oxidation with boron-doped diamond anode [52].

Membrane filtration methods are divided into microfiltration, ultrafiltration, nanofiltration, and reverse osmosis, which are able to separate microparticles from 0.025 to 10 μm size, macromolecules from 5 to 100 nm, molecules from 0.5 to 5 nm, and solvated ions of salts <1 nm, respectively. Permeating water is forced through a membrane. Microfiltration uses pressure <0.2 MPa, ultrafiltration >1 MPa, nanofiltration between 4 and 20 MPa, and reverse osmosis between 20 and 80 MPa [53]. Electrodialysis membrane treatment does not need high pressure and is an exception as ions of salts are separated from water by electric potential-driven membrane. Cationic charged membranes attract negative ions while anionic membranes remove positively charged ions. Meanwhile, permeate is purified and depleted of salts, which diffuse through semipermeable membrane towards charged membranes [30].

However, conventional remediation methods have certain drawbacks. Distillation is for example very energy consuming and usually applicable only in regions with high solar irradiation. Filtration in granular materials is facing problems with clogging of filtering pores, scaling, microbiological contamination, and possible formation of hazardous particulate matter (activated carbon, alumina). Also, large amounts of toxic liquids and sludge from pretreatment and filter regeneration are a substantial environmental problem. Coagulation/flocculation consumes high quantities of chemicals, which are not easy to handle and can leave hazardous by-products in water, and create high volumes of toxic waste sludge [47].

1.2.4 Nanoremediation

The accepted definition of nanomaterial by the EC [54] states that this is a natural, manufactured or incidentally made material. It can be in the form of unbound particles or as

agglomerates, where at least 50% or more particles reach one or more external dimensions between 1 and 100 nm. The development of advanced characterization techniques (for example scanning tunneling microscope) and advanced synthesis procedures, in the 1980s, boosted the development of nanotechnology. In the 21st century, nanotechnologies are industry and science worth multibillion Euros, which are shaping a development of medicine, electronics, constructions and engineering, energy management and obtaining, ecological solutions etc. [55].

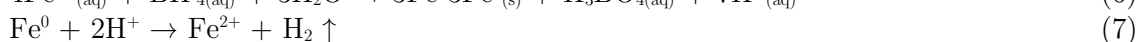
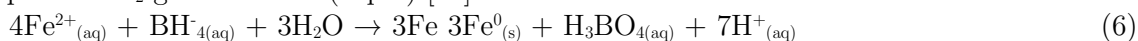
Nanoparticles have a high proportion of surface exposed atoms due to their small size and a high specific surface area. For example, particle of 1 nm has approximately 50% of its atoms on its surface. This is the main reason for enhanced reactivity, special physical and optical properties, which are different from their large particulate forms. Chemical composition, surface micro-characteristics and shape of nanoparticle also determine their properties [56].

The use of nanoparticles for water remediation and wastewater treatment can enhance efficiency of conventional methods both as sorbents or catalysts for chemical degradation of contaminants [57]. Some nanomaterials such as titanium dioxide, silver, carbon nanotubes and iron are already commonly used for water purification [34]. For example, nanoscale metals, and polymeric nanofibers foster high concentration of surface sorption sites for removal of contaminants. Nano-zeolitic crystalline structures, certain nanoscale noble metals or oxides can form enhanced filtration media with abilities of disinfection or degradation of contaminants. Photocatalytic nanomaterials, such as titanium nanoparticles or fullerenes can serve for solar driven disinfection or organic contaminants degradation systems [58].

Among different nanoparticles, those made of iron are considered to be the environmentally acceptable material with multiple possibilities for environmental management [59]. The amorphous metal iron nano-chains, which are in this work regarded as nanoscale zero-valent iron particles (nZVI), have been known in material sciences since the late 1950s [60]. Intensive research work for use of nZVI in environmental applications has been initiated worldwide in 1997 [61]. In that time, Wang and Zhang [60] proved that effectiveness of nZVI for degradation of halogenated organic compounds is much higher than of larger particles of elemental iron. Granular iron of micro and millimeter size was used for construction of permeable reactive barriers as an effective remediation method for contaminated groundwater since 1990s [62]. Since 1997 numerous scientific findings have further confirmed much higher efficiency of nZVI compared to larger particles for the removal of PTE, nitrogen species, organic contaminants, and microorganisms from water [63]. There were already some cases in Europe, USA, and China where nZVI have been used for groundwater and industrial wastewater remediation [64], [65]. The technology of nZVI production has reached commercial status in many countries worldwide. However, it has not yet gained general acceptance for its use in water treatment facilities. This may be due to concerns regarding their long-term stability, transformation and eco-toxicity, lack of comparable studies for different nZVI materials and deployment strategies [66]. There is also not much knowledge about their environmental behaviour, efficiency, and the limiting parameters for water remediation [59].

1.2.4.1 Nanoparticles of zero-valent iron

nZVI are produced relatively simply using various chemical and physical processes, which can be divided on *top down* and *bottom up* approaches. For the purposes of basic scientific studies nZVI synthesized via borohydride (NaBH_4) reduction of ferrous salts in water solution has been the most frequently used *bottom up* approach for laboratory synthesis [61]. Synthesis is performed via reductive precipitation according to the reaction mechanism (Eq. 6) and as a by-product H_2 gas is formed (Eq. 7) [67].



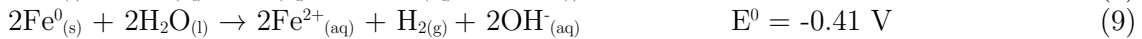
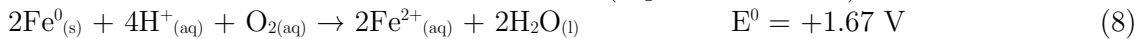
Carbothermal methods for the preparation of nZVI were developed on a principle of reduction of oxide iron nanoparticles at temperatures $>500^\circ\text{C}$ in a presence of carbon as a

reducing agent [68]. Nanofer nZVI, which are manufactured by Nanoiron s.r.o., and Reactive Nano Iron Particles, manufactured by Toda Kogyo Ltd., are most extensively used commercial nZVI products, which are both produced by reduction of iron oxide nanoparticles at high temperatures (350 – 600 °C) in the presence of H₂ as the reducing agent [66]. This can also be regarded as a top down approach. Electrochemical methods are based on the reduction of iron from solution by cathode, where nZVI are precipitated and resuspended by ultrasonic waves [69]. As environmentally friendly methods of synthesis the plant extracts of green and black tea, coffee, lemon, etc. were tested as reducing agents for the reduction of iron salts and precipitation of nZVI. Lithography grinding and precision milling of bulk iron materials are considered to be *top down* methods [67].

Despite their experimentally proved effectiveness for the removal of contaminants, nZVI have weaknesses, including a lack of stability, difficult separation from the medium being purified, rapid passivation of the material, and limited mobility of the particles due to the formation of agglomerates. Therefore, different modifications were tested, which included doping with other metals (Pd, Pt, Ag, Cu, Ni, etc.) [70], surface coating (carboxyl methylcellulose, starch, holing, etc.), emulsification in oil, and deposition or support on a stable matrix (activated carbon, montmorillonite, silica, alginate, graphene, chitosan, etc.) [66].

Although different procedures for synthesis of nZVI can be used, the composition is generally the same. The particles size is being less than 100 nm, on average 80 nm. They are spherical and comprise of a core and a shell. The core is formed by a well crystalline α -body centered crystalline or microcrystalline (semi-amorphous) Fe⁰. The shell is composed of iron oxide or hydroxide minerals [71], [70].

Differences between differently synthesized nZVI are reflected in their crystalline structure, the size of the Fe⁰ core, and the iron (hydr)oxide shell [70]. The influence of these differences on the water remediation is however unknown. It is generally accepted that the main driving forces of water remediation processes with nZVI are corrosion processes of the Fe⁰ core. Elemental iron has a strong tendency in an aqueous environment to return to a low-energy state in the form of iron (hydr)oxide. Fe⁰ dissolution is an anodic reaction that favors the formation of soluble ionic products (ferric or ferrous iron ions). The anodic reaction is coupled with the reduction of redox amenable species at the cathode. The primary components that enable corrosion of Fe⁰ are dissolved O₂ and water (Equations 8 and 9).



The reaction with dissolved oxygen (Eq. 8) is thermodynamically favoured. The ferrous iron (Fe²⁺) that is primarily formed in these reactions can then undergo further oxidative transformation to the Fe³⁺ and precipitates in the form of mixed Fe(hydr)oxides [66], [70].

Experimental proofs for successful use of nZVI for remediation of water have been reported. Some examples for remediation of PTE are listed here: alkaline earth metals, including Cr [72], [73], Co [74], Cu [75], [72], Pb [76], [77], Zn [78], Mo [72], Ni [75], Ag [76], V [75], Cd [76], As [75], [65], Se [79]. The scavenging mechanisms (schematically on Fig. 1.1) for the removal of metal contaminants from wastewater rely on the redox chemistry of iron and metal ions.

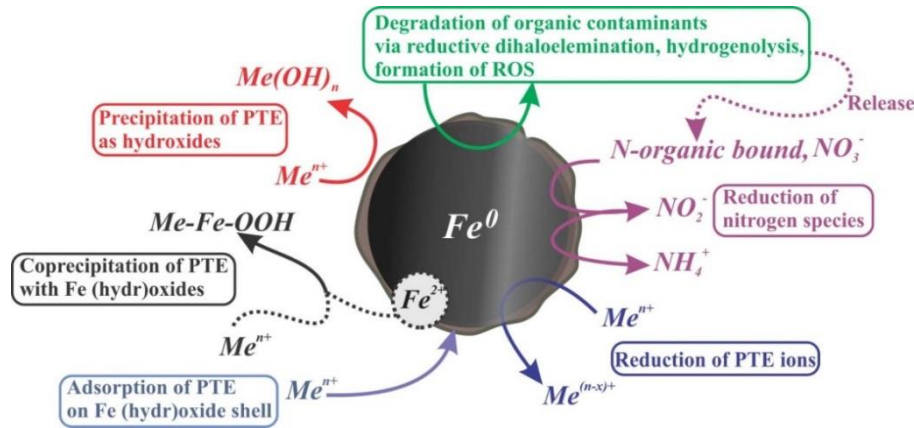


Figure 1.1: Schematic presentation of contaminants removal mechanisms from water by nZVI (redrawn according to [70]).

Some mechanisms for removal of PTE, organic contaminants and nitrogen species are described in Table 1.1 (according to the above-mentioned sources and [65], [70], [80], [81]).

Table 1.1: Mechanism for remediation of selected inorganic species by nZVI.

Parameter	Reaction for remediation	Mechanisms
Nitrate and nitrite	$\text{NO}_3^- + 4\text{Fe}^0 + 10\text{H}^+ \rightarrow 4\text{Fe}^{2+} + \text{NH}_4^+ + 3\text{H}_2\text{O}$ $\text{NO}_2^- + 4\text{Fe}^0 + 8\text{H}^+ \rightarrow 4\text{Fe}^{2+} + \text{NH}_4^+ + 2\text{H}_2\text{O}$	Formation of NH_4^+ , which can be removed by ion exchange
Antimony (Sb)	$\text{Sb} + \text{H}_2\text{O} \rightleftharpoons \text{SbO}^+ + 2\text{H}^+ + 3\text{e}^- \quad E^0 = 0,21 \text{ V}$ $2\text{Sb}_2\text{O}_3 + \text{H}_2\text{O} \rightleftharpoons 2\text{Sb}_2\text{O}_5 + 4\text{H}^+ + 4\text{e}^- \quad E^0 = 0,69 \text{ V}$ $\equiv\text{FeOH}^0 + \text{Sb}(\text{OH})_3 \rightarrow \equiv\text{FeOSb}(\text{OH})_2^0 + \text{H}_2\text{O}$ $\equiv\text{FeOH}^0 + \text{Sb}(\text{OH})_6^- \rightarrow \equiv\text{FeOSb}(\text{OH})_5^- + \text{H}_2\text{O}$	Reduction of Sb(V) species to Sb(III), followed by a surface chemisorption to or coprecipitation with Fe-hydroxides
Arsenic (As)	$\text{H}_3\text{AsO}_4 + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{HAsO}_2 + \text{H}_2\text{O} \quad E^0 = 0,56 \text{ V}$ $\text{As}^{3+} + (1-x)\text{Fe}^{3+} + \text{H}_2\text{O} \leftrightarrow \text{As}_x\text{Fe}_{(1-x)}\text{OOH} + 3\text{H}^+$	Reduction of As(V) species to As(III), followed by a surface chemisorption to or coprecipitation with Fe-hydroxides
Copper (Cu)	$\text{Cu}^{2+} + 2\text{e}^- \rightleftharpoons \text{Cu}_{(s)} \quad E^0 = 0,34 \text{ V}$ $\equiv\text{FeOH} + \text{Cu}^{2+} \rightarrow \equiv\text{FeOCu}^+ + \text{H}^+$	Possible is reduction of Cu(II) species to Cu(0) or chemisorption to or coprecipitation with Fe-hydroxides
Cadmium (Cd)	$\text{Cd}^{2+} + 2\text{e}^- \rightleftharpoons \text{Cd}_{(s)} \quad E^0 = -0,40 \text{ V}$ $\text{Cd}^{2+} + \equiv\text{FeOH} \rightarrow \equiv\text{FeOCd}^+ + \text{H}^+$ $\text{Cd}^{2+} + 2(\equiv\text{FeOH}) \rightarrow \equiv(\text{FeO})_2\text{Cd} + 2\text{H}^+$	Chemisorption to or coprecipitation with Fe-hydroxides
Chromium (Cr)	$\text{CrO}_4^{2-} + 8\text{H}^+ + 3\text{e}^- \rightleftharpoons \text{Cr}^{3+} + 4\text{H}_2\text{O} \quad E^0 = 1,51 \text{ V}$ $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightleftharpoons 2\text{Cr}^{3+} + 7\text{H}_2\text{O} \quad E^0 = 1,36 \text{ V}$ $x\text{Cr}^{3+} + (1-x)\text{Fe}^{3+} + 3\text{H}_2\text{O} \rightarrow \text{Cr}_x\text{Fe}_{1-x}(\text{OH})_3 + 3\text{H}^+$ $\equiv\text{FeOH} + \text{Cr}_2\text{O}_7^{2-} \rightarrow \equiv\text{Fe-Cr}_2\text{O}_7^- + \text{OH}^-$	Reduction of Cr(VI) species to Cr(III), followed by a surface chemisorption to or coprecipitation with Fe-hydroxides
Nickel (Ni)	$\text{Ni}^{2+} + 2\text{e}^- \rightleftharpoons \text{Ni} \quad E^0 = -0,25 \text{ V}$ $\equiv\text{FeOH} + \text{Ni}^{2+} \rightarrow \equiv\text{FeO-Ni}^+ + \text{H}^+$	Possible is reduction of Ni(II) species to Ni(0) or chemisorption to or coprecipitation with Fe-hydroxides
Selenium (Se)	$\text{HSeO}_4^- + 3\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2\text{SeO}_3 + \text{H}_2\text{O} \quad E^0 = 1,15 \text{ V}$ $\text{H}_2\text{SeO}_3 + 4\text{H}^+ + 4\text{e}^- \rightleftharpoons \text{Se} + 3\text{H}_2\text{O} \quad E^0 = 0,74 \text{ V}$ $\equiv\text{FeOH} + \text{SeO}_3^{2-} \rightarrow \equiv\text{FeSeO}_3^- + \text{OH}^-$	Reduction of Se(VI) species to Se(IV), followed by a surface chemisorption to or coprecipitation

Parameter	Reaction for remediation	Mechanisms
Lead (Pb)	$\text{Pb}^{2+} + 2\text{e}^- \rightleftharpoons \text{Pb} \quad E^0 = -0,13 \text{ V}$	Possible is reduction of Pb(II) species to Ni(0), precipitation of Pb(OH) ₂ , or chemisorption to or coprecipitation with Fe-hydroxides
	$\equiv\text{FeOH} + \text{Pb}^{2+} \rightarrow \equiv\text{FeOPb}^+ + \text{H}^+$	
	$\equiv\text{FeOH} + \text{Pb}^{2+} \rightarrow \equiv\text{Fe}(\text{OH})_3 + \text{Pb}(\text{OH})_2 + \text{H}^+$	
Zinc (Zn)	$\text{Zn}^{2+} + 2\text{e}^- \rightleftharpoons \text{Zn} \quad E^0 = -0,76 \text{ V}$	Precipitation of Zn(OH) ₂ or chemisorption to or coprecipitation with Fe-hydroxides
	$\equiv\text{FeOH} + \text{Zn}^{2+} \rightarrow \equiv\text{FeOZn}^+ + \text{H}^+$	
	$\equiv\text{FeOH} + \text{Zn}^{2+} \rightarrow \equiv\text{Fe}(\text{OH})_3 + \text{Zn}(\text{OH})_2 + \text{H}^+$	

The mechanisms for degradation of organic contaminants and disinfection by nZVI are based on the formation of ROS [82], [83]. ROS can be formed via multiple mechanisms. The most commonly described is the Fenton reaction, which is known for more than 110 years, and it was first described by H. J. H. Fenton [84].

Reaction pathway for the formation of ROS with the use of nZVI is described according to Equations from 10 to 13 and it is initiated by introduction of nZVI in water in the presence of O₂. With oxidation of Fe⁰ and release of Fe²⁺, H₂O₂ is formed. Part of H₂O₂ is then neutralised for oxidation of remaining Fe⁰. The rest can react with Fe²⁺ and forms OH• radical in acidic environment (Eq. 12). In neutral environment (pH near 7) the mechanism in Equation 13 is preferred, where O₂•⁻ radical is formed [85].



In a photo-induced Fenton system, the most optimal is the use of UV-C light with a wavelength of 180 to 290 nm, where the reaction mechanism for the formation of OH• is as written in reaction (14) [86].



It has also been described in scientific literature that the presence of certain organic ligands (L) or chelates (formate, citrate, oxalate, EDTA) can also contribute to enhanced formation of ROS [87]. The mechanism is described in Equations 15 to 19. The formation of a complex between Fe²⁺ and L is crucial for the formation of O₂•⁻ and OH• in acidic environment in the presence of O₂ [88].



The bactericidal effects of nZVI, which are schematically presented in Fig. 1.2 for bacterial cell, were investigated from the viewpoint of eco-toxicity and for possible use as a wastewater disinfectant. The toxicity of nZVI differs within the same genus or even the same species of bacteria, and also depends on the growth phase of the bacterial cell [89], [90]. On the contrary, iron oxide and hydroxide nanomaterials have no pronounced bactericidal effects [91], [92]. nZVI particles have been proved to effectively inactivate *Escherichia coli* [93], [94], [95]. They are able to inactivate different types of gram positive and gram-negative bacteria. In comparison to bacteria, fungal species are much more resilient to the action of nZVI [90]. nZVI particles act against microorganisms directly by nanoparticle-cell interactions or indirectly by changes in water chemistry. It is suggested that the majority of the cytotoxic effects are a consequence of microbial cell membrane disruption and oxidative stress (OS) [90]. Adsorption onto the outer cell membranes could lead to increased permeability or disruption of the membrane lipid bilayer. In this way, cell mobility and access to nutrients become compromised, allowing Fe²⁺ to enter the cell [83], [91], [93], [94]. Once Fe²⁺ enters the cell it can react with H₂O₂ produced

in mitochondria and, via Fenton reaction, releases ROS that puts microbial cells under severe OS. [96]. OS is caused by high intracellular concentrations of ROS that cells are unable to neutralize [97]. Proposed are different mechanisms that can, via chemical reactions of ROS with cellular constituents, cause destruction of bacteria or living cells [83]. Lipid peroxidation causes the removal of hydrogen from unsaturated fatty acid chain that can cause the loss of integrity of cell membranes [98]. Protein oxidation is caused by the site-specific processes, which occur on the iron binding sites of proteins that react with hydrogen peroxide thus generating ROS. The consequence is cross-linking of the proteins and formation of hydrophobic bonds that disrupt the enzymatic activity in the cell [83], [99]. Probably the most fatal mechanism causing bacteria inactivation with ROS is DNA and RNA oxidation or mutation. ROS attack base and saccharide moiety of DNA that leads to saccharide fragmentation and strand breaks [83], [97].

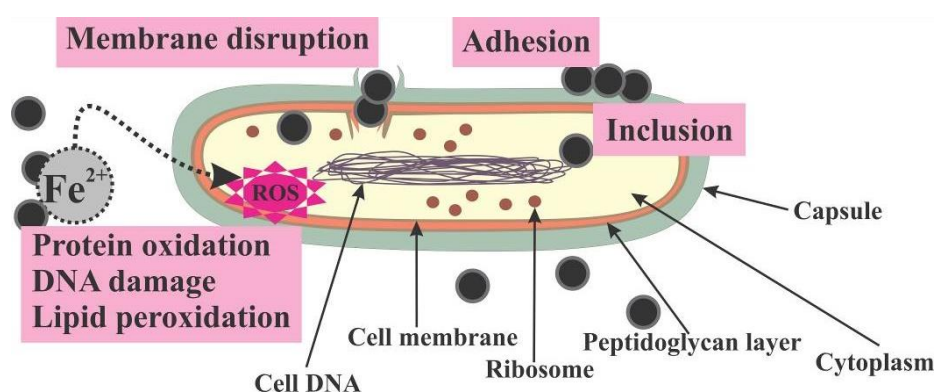


Figure 1.2: Schematically presented mechanisms for disinfection by nZVI (Redrawn according to [83]).

Potential of nZVI for remediation of water contaminated with organic contaminants was also extensively investigated. Here some examples of removal of organic contaminants are listed: β -lactam and nitroimidazole-based antibiotics [100], [101], azo dyes [102] [103], chlorinated solvents [104], [105], chlorinated pesticides [106], [107] [108], organophosphates [108], [109]p-chlorophenol [109], polybrominated diphenyl ethers [110], polychlorinated biphenyls [111] and perchlorate [112]. The mechanisms of degradation of chlorinated organic compounds by reductive dehalogenation are also well known [70].

1.2.5 EU water legislation

The need to improve and safeguard EU water was initially highlighted in 1988. New contaminants and threats to the surface and ground water quantity and quality have emerged in the late 1990s. Nowadays, the EU legislation on water policy is based on Directive 2000/60/EC, e.g. Water framework directive (WFD) [113]. EU countries are obliged to follow EU policy and the requirements of the WFD and its related documents: Directive on environmental quality standards in the field of water policy, EU objectives on surface waters 272/2009, Directive regards priority substances in the field of water policy [114], [115], [116]. The main purpose of the WFD is to maintain the good quality of water bodies and to preserve natural ecosystems and biodiversity. EC has stated that water should be regarded as a heritage that we need to protect, defend and treat. According to environmental objectives of the WFD, EU Member States are obliged to prevent deterioration of all water bodies, protect, restore, and enhance good ecological and chemical status of water bodies, reduce pollution from priority substances, limit the input of contaminants into the groundwater, balance abstraction and recharge of aquifers, reverse upward trend in the concentration of any contaminant in groundwater. Indicative list of the priority contaminants was set, which include organohalogen compounds, organophosphorus compounds, organotin compounds, substances proved to possess

carcinogenic or mutagenic properties or properties which may affect endocrine-related functions, persistent hydrocarbons and persistent and organic toxic substances that bioaccumulate, cyanides, metals, arsenic, biocides and plant protection products, materials in suspension, substances which contribute to eutrophication, and substances which have an unfavourable influence on the oxygen balance (can be measured as BOD₅, COD₅). These parameters have to be taken into considerations in the evaluation of efficiency of remediation technologies for water reuse.

EU has addressed the water pollution problem by the Municipal Waste Water Treatment Directive (UWWTD) [117], the Nitrates Directive [118], the Plant Protection Products Directive [119], and the Industrial Emissions Directive [120]. These Directives protect water resources from pollution by nutrients and/or other chemicals from agriculture, households and industry. The UWWTD was adopted by EU in 1991, with a purpose to protect the environment from adverse effects of municipal wastewater discharges. The UWWTD lays down four principles regarding wastewater treatment: planning, regulation, monitoring, and reporting. In the first part it sets a demand that municipal wastewater must be collected in agglomerations, which is a centralised sewage system of one settlement. At least secondary treatment of discharges with the use of wastewater treatment plants is required for agglomerations >2000 PE. Meanwhile, tertiary or more advanced treatment is required in areas, which are sensitive for ecological degradation or chemical pollution. The important part of the UWWTD also states that controlled disposal or reuse of sewage sludge must be ensured. If possible or whenever appropriate, reuse of effluent water must be assured. According to data from 2017, 95% of the EU's municipal waste water is collected and over 85% is treated according to the Directive's requirements. However, big differences exist between regions. Northern and Central Europe already treat more than 70% of wastewater by minimally tertiary treatment, and leave it less than 20% untreated. Meanwhile in Eastern Europe, region that according to EEA distribution also includes Slovenia, less than 50% of municipal wastewater receives tertiary treatment [121]. However, EU commission recognizes that implementation UWWTD could contribute more to the challenges of circular economy and efficient resource management (reuse of water and extraction of valuable raw materials from wastewater treatment cycles), more effective treatment of wastewaters (emerging contaminants), and to establish more efficient economic models of financing of water services. It is estimated that EU countries will invest more than 25 billion EUR in wastewater collection, treatment and management infrastructure yearly in a period from 2015 to 2018, to meet the legislation criteria.

Beneficial effects of WFD and UWWTD were summarized in a document "Blueprint to Safeguard Europe's Water Resources" [7]. EU's water policy has been successful in helping to protect and restore water bodies of Europe. Most of it has achieved good status. However, it is estimated that 40% of them is still at ecological risks or under a hazard of chemical contamination. However, water scarcity problems, caused by global climate changes, imbalances in water demand and poor water management have forced EU to take further action. The goal is to prevent realization of models, which predict that water scarcity lasting through a whole year is going to occur in 50% more river basins of Europe by 2030. Options, proposed by EC, are to develop infrastructure for more efficient water supply, modernize irrigation technologies, or develop alternative sources for water supply. However, adverse environmental effects, for example due to discharges by the use of reverse osmosis or due to over-extraction, should be avoided. All measures should be in consensus with the WFD. This means that development of sustainable, environmentally friendly and efficient methods for municipal wastewater reuse is urgent for successful adaptation to future problems with water scarcity [7], [15]. Establishing of special regulation and encouraging mechanisms for reuse of water, especially in agriculture or for industrial purposes, is proposed. This can also serve as

the opportunity for EU economy as water management and treatment technology market is growing rapidly, and will reach 1000 billion EUR by 2020 on a global scale [45].

In response, EC has established a European Innovation Partnership on Water to unlock the full potential of water sector, where reuse and recycling of water are one of the top priorities. According to EC, water reuse can provide the following economic, social and environmental benefits: increased water availability, sustainable use of water, drinking water substitution (keep drinking water for drinking and reclaimed water for other secondary purposes), reduced hazard of over-abstraction of groundwater, more energy efficient compared to other methods (desalination, deep water pumping), reduction of nutrient losses and loads into receiving natural waters, reduced manufacturing costs due to a higher quality of reclaimed water, increased agricultural production and reduced application of fertilizers, enhanced protection of surface water bodies, and increased employment. Some possibilities for reuse of water are listed in Table 1.2 (summarized according to [45], [122] [123]).

Table 1.2: The main uses of reclaimed water in the world.

Category of use	Uses
Municipal uses	Irrigation of public parks, sporting facilities, private gardens, roadsides; Street cleaning; Fire protection systems; Vehicle washing; Toilet flushing; Air conditioners; Dust control
Agricultural uses	Food crops not commercially processed; Food crops commercially processed; Pasture for milking animals; Fodder; Fibre; Seed crops; Ornamental flowers; Orchards; Hydroponic culture; Aquaculture; Greenhouses; Viticulture
Industrial uses	Processing water; Cooling water; Recirculating cooling towers; Washdown water; Washing aggregate; Making concrete; Soil compaction; Dust control
Recreational uses	Golf course irrigation; Recreational impoundments with/without public access (e.g. fishing, boating, bathing); Aesthetic impoundments without public access; Snowmaking
Environmental uses	Aquifer recharge; Wetlands; Marshes; Stream augmentation; Wildlife habitat; Silviculture
Potable uses	Aquifer recharge for drinking water use; Augmentation of surface drinking water supplies; Treatment until drinking water quality

There is a lack of water reuse criteria on EU level. EC [124] has released a guidance document, in which microbiological risks for reuse of water in agriculture have been addressed. The document sets only one indicative parameter, which is for *Escherichia coli*. The strictest criteria, which are for irrigation of fields with vegetables that can be eaten raw, are ≤ 100 MPN/100 mL of *Escherichia coli*. The strict quality control and disinfection measures are advised in a case of wastewater reuse [124]. Only several Member States have formed a legislative framework and regulations for water reuse. The most developed are Cyprus, France, Greece, Italy, Portugal, and Spain. In their regulations for reuse of water the following criteria are included: intended use, analytical parameters, limit values, monitoring protocols, and preventive measures for health and environment protection. The reuse of water in these countries is limited to secondary human purposes and agricultural use. They have also set different restrictions. In Cyprus it is forbidden to irrigate leafy vegetables, bulbs or tubers that are eaten raw. In France 4 quality classes for reuse of water are set and it is forbidden to use untreated wastewater. Seven reuse categories and quality classes are set in Greece. In Italy reuse of municipal wastewater is possible for agriculture, non-potable municipal needs, in the industry, according to different quality requirements. Portugal has set 4 categories for reuse in

irrigation (raw vegetables, public areas, cooked vegetables and orchards, fodder and industrial plants). Spain has set quality requirements for 24 categories of municipal wastewater reuse. However, it is forbidden to reuse water for human consumption, hospitals, bathing, fountains, or where it can represent any risk for human health [45]. Selected limit values set by these countries are given in Table 1.3.

The water policy in Slovenia is based on Waters Act (Official Gazette of RS, No. 56/15) [125]. Water policy is also regulated by the Environmental Protection Act (Official Gazette of RS, No. 61/17) [126] and The Nature Conservation Act (Official Gazette of RS, No. 46/14) [127]. The total amount of water, available in Slovenia is estimated to be 32.1 km³, which is 16,000 m³ per inhabitant annually. Groundwater aquifers in Slovenia are of two types, fissure and intergranular. In 2015, 897.2 million m³ of water was withdrawn, 79% from surface and 21% from groundwater sources. Most of groundwater, 162.2 million m³ was used as drinking water, while 709.9 million m³ of surface water was used for agriculture and industry. Water Exploitation Index (WEI), which is calculated as mean total water consumption divided by relative yearly amount of available water from natural sources, is relatively low for Slovenia, approximately 3%. Despite relatively low WEI, a negative trend in lowering groundwater levels at some intergranular aquifers was already observed, due to an overexploitation and climate changes that cause negative water balance during droughts. Also, rising number of rights for private, commercial, industrial or agricultural water abstraction is worrying as for example approximately 40,000 rights were granted up to the mid-2016 [128]. This could lead to worsening of the state of aquifers both from the view of quality and quantity as external control over privatised water sources is usually less efficient. This is also not in line with the SDG from Rio +20, which states that by 2030, universal and equitable access to safe and affordable drinking water for all will be achieved.

In Slovenia, policy regarding municipal wastewater and their purification is regulated by multiple laws. Decree on the emission of heat in the discharge of wastewater into public sewers and water (Official Gazette of RS, No. 98/15) [129] sets the limit values for discharging of treated wastewaters from wastewater treatment plants into the sewerage. Approximately 58% of inhabitants in Slovenia were connected to wastewater treatment plants, and 50% of wastewater treatment was performed on tertiary level, in 2014. According to the ambitious plan, regarded as Operational program for collection and treatment of municipal waste water (Updated for the period from 2005 to 2017), Slovenia planned to establish at least secondary treatment for 95% of municipal wastewater in the whole country up to the end of 2017. Due to technical problems and difficulties with financing this goal was not achieved. New plan was set in the Decree on the discharge and treatment of municipal wastewater [129]. Deadlines were moved to the year 2021, if agglomeration is located on a sensitive area, or to a year 2023 in other areas. Sensitive areas are those susceptible to eutrophication and worsening of ecological conditions. They include water bodies with a status of bathing waters, or water bodies which are part of the protected area with drinking water sources.

In this study, SBWTP for <2000 PE will be taken into consideration due to multiple reasons. Slovenia has a dispersed settlement, where construction of agglomerations > 2000 PE is not economically feasible. Therefore, it is more appropriate to use SBWTP for agglomerations <2000 PE, which can be constructed according to standards SIST EN 12255-5:2000 [130], SIST EN 12255-6:2002 [131], and/or in a form of artificial aerated wetlands. If the construction of <2000 PE agglomerations is not possible, <50 PE can be constructed with SBWTP according to SIST-TP CEN/TR 12566-5:2009 [132] or internationally accepted equivalent systems. Decree on separation and treatment of municipal wastewater also regulates the limit values of BOD₅ and COD for effluent waters from wastewater treatment plants of different sizes. Limit values for SBWTP of <2000 PE are 30 and 150 mg O₂ per L of BOD₅ and COD, respectively.

Table 1.3: Limit values from legislation of 7 EU countries for water reuse (summarised from sources cited by [45]).

Parameters	Cyprus	France	Greece	Italy	Portugal	Spain	Slovenia
BOD ₅	10		<10	20			
COD	70	60		100			
TDS (mg/L)	10	15	<2	10	60	5 - 35	100
Dissolved solids (mg/L)			<450		640		2000
Turbidity (NTU)			<2			1 - 15	
Conductivity (µS/cm)	2500		<700	3000	1000	3000	2000
pH	6.5 - 8.5		6.5 - 8.5		6.5-8.4		
NH ₄ ⁺ (mg/L)				2			
NO ₃ ⁻ (mg/L)			<5				10
SO ₄ ²⁻ (mg/L)				500			
Cl ⁻ (mg/L)	300		<140	250	70		100
F ⁻ (mg/L)				1.5			
Fats and oils (mg/L)	5			10			
Mineral oils (mg/L)				0.05			
Na (mg/L)			<3				70
<i>E. coli</i> (MPN/100 mL)	5	<100000	<20	100		0	
Enterococci (MPN/100 mL)		2 to 4					
Coliforms (CFU/100 mL)					100		1000
<i>Salmonella</i>				0		0	
Intestinal worms eggs	0				<1		
Nematodes eggs						0.10	

Due to efficient wastewater treatment, it is estimated that in Slovenia 96% of surface water bodies have a good chemical status, while from an ecological point of view 59% of water bodies achieve at least a good status. There is also a pronounced trend in the improvement of chemical conditions of groundwater aquifers, where concentrations of nitrates and pesticides are lowering. However, bad chemical status was detected for some intergranular aquifers in the areas of intensive farming, which still represents the highest threat to groundwater quality. Regarding the reuse of water in Slovenia, a Decree on the limit input concentration values of dangerous substances and fertilizers in soil (Official Gazette of RS, No. 19/17), was in force until April 2017 [133]. This document included limit values for reclaimed water intended for reuse in agriculture (Table 1.3).

1.3 Remediation of Soils

1.3.1 Global and Slovenian soil issues

Soil is a top layer of earth's crust that is formed by mechanical or (bio)chemical weathering of geological base ground – bedrock. In geotechnical literature soils can also be divided regarding the origin of their formation on residual (formed on site) and those which were formed by redistribution and sedimentation processes as alluvial, lacustrine, marine, glacial or eolian deposits [134]. Beside natural soils, nowadays, the term municipal soils (also man-made or anthropic soils) has established to define soils, which are extensively influenced or

transformed by human activities, with contamination/remediation, agricultural activities, geotechnical stabilisation, etc. [135]. From an engineering point of view, by one of the definitions, soil can be regarded as unbound aggregate of mineral grains, organic matter, where pore spaces between grains are filled with gas or liquid [136]. Meanwhile, standardized definition states that soil is an assemblage of mineral particles and/or organic matter in the form of deposit (sometimes of organic origin), which can be separated by gentle mechanical means and which includes variable amounts of water and air (SIST EN ISO 14688-1:2004 [137]). Soil is a complex and dynamic system, which can be regarded as practically non-renewable, as soil formation processes are very slow. Basic soil functions are food and biomass production, storage, filtration and transformation of carbon, nitrogen, phosphorus, and other elements. However, due to degradation socio-economic as well as environmental functions of soil are under pressure. Currently the most important soil degradation processes in EU are erosion, loss of organic matter, compaction, landslides, sealing, and contamination [138], [139].

Approximately 33% of global agricultural soils, or more than 2 billion hectares of land, is moderately to heavily degraded by contamination, erosion, salinization, compaction, acidification and nutrient depletion. Contamination is the most important and most detrimental process of soil degradation. This is because basic soil functions are in most cases of contamination irreversibly damaged and cannot be restored even with the most advanced remediation technology [140], [141]. European Soil Data Centre conducted a survey on contaminated sites in Europe using the European Environment Information and Observation Network for soil (EIONET-SOIL), within the scope of Thematic Strategy for Soil Protection in 2011-2012. There are roughly 342,000 identified contaminated sites in EU, while 1.47 million are potentially and not yet confirmed to be contaminated. According to EEA, at least 250,000 sites require urgent remediation [142]. According to the definition of the European Commission, contaminated site is a location, where the presence of hazardous substances, due to an anthropogenic contamination, poses a significant risk to human health or environment, taking into account land use [139]. Most of contaminated sites are a legacy of inappropriate disposal and treatment of waste, followed by industrial activities, which include mining and metallurgy. The most commonly occurring contaminants are potentially toxic elements (PTE), which are present in 34.8% of all cases of soil contamination. Mineral oils are found in soil from 23.8% of all contaminated sites. Polycyclic aromatic hydrocarbons, benzene-toluene-ethylene-xylene, chlorinated hydrocarbons, phenols and cyanides, which occur in 10.2%, 8.3%, 1.3% and 1.1% of all cases, respectively. Other types of contaminants are present in 20.5% of contaminated sites [143]. For comparison, in the USA, PTE are present in 69% of all cases [144]. Contaminated sites in the Central and Eastern Europe were most commonly the consequence of past industrial activities, poor management, inefficient pollution prevention technologies (air pollution control, wastewater treatment, waste processing) and uncontrolled emissions [145].

In Slovenia 194 degraded sites were evidenced, together measuring approximately 900 ha, which include locations with past or present industrial, military, transport, infrastructural, and mining activities. Approximately 110 degraded sites have the origin in industrial and mining activities [146]. Based on the results of different investigations, it is estimated that pseudo-total concentrations of PTE, determined by *aqua regia* extraction (AQE), exceed critical limit values according to the Slovenian Decree on limit values, alert thresholds and critical levels of dangerous substances into the soil (Official Gazette of RS, No. 68/96 [147]) on about 80 km² [148]. Four Slovenian mines are considered large: Idrija, Mežica – Topla, Litija and Žirovski vrh. At least 25 ore processing plants and smelters, and 33 iron works are known, and among them those located in Jesenice, Ravne na Koroškem and Štore are still operating. This industrialization caused some severe environmental problems, causing soil contamination with PTE. The case of Celje is one of the most representative examples of soil contamination in Slovenia. Therefore, it is described here and is used as a case study for soil remediation experiments.

1.3.1.1 The case of the Old Zinc-works (Celje)

Celje basin is one of the oldest, most industrialized and also one of the most heavily contaminated areas in Slovenia. This is due to multiple strategic factors: vicinity of metal ore rich hinterland, nearby coal-mining basin in Posavje and railway logistic connections with major markets (Austria, Germany, and Italy). At the end of the 19th century metallurgical and smelting industry was centralised in Celje. Already in 1873, the first Zn ore smelter and coke production factory were established in the area, which is nowadays known as the Old Zinc-works site ("*področje stare Cinkarne*"). The rolling mill for Zn plate production had started in 1888. The Zn sulphide ore smelter and production of sulphuric acid were started in 1911. Production of Zn pigments, copper vitriol ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), ultramarine ($\text{Na}_{8-10}\text{Al}_6\text{Si}_6\text{O}_{24}\text{S}_{2-4}$), rongalite ($\text{CH}_3\text{NaO}_3\text{S}$), Pb massicot and litharge (orthorhombic and tetragonal PbO), minium (Pb_3O_4), and Cr compounds for leather tanning were started after major technical and engineering upgrades in 1922. Metallurgical activities for Zn production and processing were closed down in 1970, when the industrial activities in the Old Zinc-works site were directed in the production of chemicals and manures. All industrial activities were abandoned on the Old Zinc-works site by the end of 1985. The most severe pollution activities were dated back to the period from 1873 to 1990. Zinc ore tailings, ashes, slags from smelting and refining of Zn were disposed into the wetland, between the factory and Hudinja River in a few meters thick layers or mixed with soil to stabilize ground. Tars were disposed in pits and poured over slag deposits (Fig. 1.3).



Figure 1.3: The Old Zinc-works site (1), pile of metallurgical slag (2), municipal wastes illegal dump site (3), leaching in a trench at the site (4 – marked by an arrow), layer of contaminated soil mixed with slag (5 - dotted lines), tar stained soil (6).

Ore particles and chemicals were accidentally scattered to the ground [149]. Due to low standards in air pollution control, fumes and contaminated particles spread toxins over the Old Zinc-works site and a wider area of the Celje basin [150]. After the 1990s, additional contamination was induced due to a non-selective and explosive demolition of the old industrial infrastructure in 2002. The site has also become a location for illegal deposition of various wastes.

In 2005, chemical analyses were made on core samples from eight boreholes, 9 to 10 m deep, located in the area of the Old Zinc-works site. Soil samples from cores were analysed for pseudo-total (AQE) concentrations of PTE. The values of Zn ranged from 787 to 75,790

mg/kg, for Cd from 4.8 to 593 mg/kg, for Pb from 91 to 94.66 mg/kg and for As up to 881 mg/kg. The standard leaching procedure for waste (SIST EN 12457-4:2004 [151]) was also carried out. The results showed a small degree of mobility of PTE. According to the Slovenian legislation on landfilling of wastes (Official Gazette of RS, No. 36/16 [152]), the readings for Pb (from 0.8 to 5.7 mg/kg), Cd (from 0.1 to 4 mg/kg), Zn (from 9 to 240 mg/kg), and the content of sulphate (up to 14,890 mg/kg d. m.) were above the values for inert materials [153], [154].

During construction works at the Old Zinc-works site in 2009 approximately 13,600 m³ of soil was excavated. Chemical analyses of soil have shown that Cd, Pb, Zn, As, and sulphate in the leachates exceed the limit values for non-hazardous waste in accordance with the Slovenian waste and landfilling legislation. Thus, excavated soil was regarded as hazardous waste, to which code 17 05 05* was assigned [155]. Due to an inefficient management with this hazardous waste, EU commission started a lawsuit against Slovenia in front of the Court of Justice of the European Union. The verdict stated that the state has to manage the excavated contaminated soil properly within the next three years [156].

Numerous deposits of slag and metallurgical wastes, originating from the industrial activities at the Old Zinc-works site, nowadays represent point sources of pollution that pose risks for exposure to PTE for inhabitants of Celje. Some known locations are the area of the so-called “new Zincworks” (Cinkarna, Metalurško-kemična Industrija Celje, d.d.), city park, railway station Celje – Štore, and illegal depot at village Teharje (Bukovžlak). At least 8 larger point sources of slag and metallurgical waste deposits exist within the city of Celje (Municipality of Celje, pers. com. 2017).

The Environmental assessment report [157] made on the 45.8 ha wide industrial area of Cinkarna d.d. has confirmed the existence of layers of slags and industrial wastes, mixed with soil, which are covering a major part of the area. Thickness of layers is up to 4 m, and approximately 2 m on average. Concentrations of PTE (AQE) reached up to 180,000 mg/kg of Zn, 530 mg/kg of Sb, 10,000 mg/kg of As, 3200 mg/kg of Ba, 660 mg/kg of Cd, 160,000 mg/kg of Cu, and up to 45,000 mg/kg of Pb. Up to 120 mg/L of Zn were also detected in groundwater samples.

The problem in Celje also represents diffused distribution of contaminants. Metals Zn, Cd, Pb are dispersed in the densely populated Celje basin. Contamination with PTE can be detected on more than a 70 km² wide area [158]. In the internal zone, which involves the whole Celje city centre of 18 km², the pseudo-total concentrations (AQE) in soil are ranging from 598 – 8573 mg/kg for Zn and 1.5 -59 mg/kg for Cd. In a smaller area the critical content of Pb (Official Gazette of RS, No. 68/96) is the dispersed, ranging from 128 to 1508 mg/kg. The contaminants are distributed in the direction from NW to SE, which also correlates with the prevailing direction of the wind in the Celje basin [148], [159], [160].

Only a few studies of PTE transfer to vegetables that were grown in Celje have been made so far. They have shown that Cd, and Zn, are accumulating in different plant parts. However, the risk of transfer of PTE to humans was thus not fully evaluated. It was proved that the uptake of PTE by vegetable is highly dependent of plant species accumulation ability and concentration of PTE in soil [158].

Air emissions of Zn and Cd in a form of dust particles were confirmed by scientific studies, as a cause of historic soil contamination in Celje [161]. However, there are no studies that would confirm that air emissions are connected to any adverse health effects of citizens of Celje.

1.3.2 Behavior of PTE in soil

Anthropogenic inputs of PTE in soils are atmospheric deposition (from combustion of fossil fuels and waste, smelting, cement production etc.), land application of sewage sludge, land disposal of industrial waste, application of fertilizers and agrochemicals [162], [163].

On the field of characterization of PTE contamination, the major change in perception happened in the 1980's. It was recognized that the determination of total concentrations of elements in soil does not indicate their plant uptake potential or toxicity. To assess bioavailability, mobility and toxicity of PTE it is crucial to make a speciation study [164].

Generally, PTE can be present in soil in two phases:

- Pore solution phase species: free hydrated ions, inorganic complexes, organic complexes, bound to colloids (e.g. clay, organic matter);
- Soil solid phase species: exchangeable bound, complexed or occluded within organic matter, adsorbed or occluded in (hydr)oxides of iron and manganese, adsorbed or occluded in carbonates, as precipitates (carbonates, phosphates, sulfides, sulphates), as structural components in aluminosilicate minerals [165].

PTE in their most simple dissolved form exist as solvated ions surrounded by water molecules (for example $\text{Zn}(\text{H}_2\text{O})_6^{2+}$). Elements occur as cations (Cd^{2+} , Zn^{2+} , Pb^{2+} , etc.) or as oxyanions (MoO_4^{2-} , CrO_4^{2-} , $\text{H}_2\text{AsO}_4^-/\text{HAsO}_3^{2-}$, $\text{SeO}_4^{2-}/\text{SeO}_3^{2-}$, etc.) in their most simple state [164]. Metals in the form of cations are generally mobile under acidic conditions and less mobile in the alkaline environment. On the other hand, metals forming anions or oxyanions are less mobile under low pH values [166]. PTE can form soluble or volatile organometallic compounds in soil, for example: monomethyl arsenate $\text{CH}_3\text{AsO}_3^{2-}$, dimethyl arsenate $(\text{CH}_3)_2\text{AsO}_2^-$, monomethyl selenide $(\text{CH}_3)_2\text{Se}$, methyl selenone $(\text{CH}_3)_2\text{SeOO}$, monomethyl mercury CH_3Hg^+ , dimethyl mercury $(\text{CH}_3)_2\text{Hg}$, tetraethyl lead $(\text{CH}_3\text{CH}_2)_4\text{Pb}$. Organometallic forms of PTE are introduced to the environment by human pollution, or they can originate from natural biomethylation processes [167].

Metal cations behave as Lewis acids, capable of accepting an electron pair, while ligands are Lewis bases and can provide a free electron pair to form a chemical bond. The presence of ligands (HCO_3^- , SO_4^{2-} , PO_4^{3-} , Cl^- , F^- , OH^- , etc.) in soil solution enables the formation of complexes and precipitates. Ligands form strong covalent bonds when difference between electronegativity of ligand and metal cation is less than 1.7. Electrostatic (ion) bonding is formed otherwise. Transitional elements hydrolyse in water thus forming hydroxide-complexes (for example ZnOH^+), which can have a low solubility (for example $\text{Cr}(\text{OH})_3$, $\text{Pb}(\text{OH})_2$, $\text{Cu}(\text{OH})_2$) or form soluble complexes (for example $\text{Cr}(\text{OH})_2^+$, $\text{Cu}(\text{OH})_3^-$, $\text{Pb}(\text{OH})_4^{2-}$) at high pH values. It is known that OH^- anion is the most important inorganic ligand [164], [168].

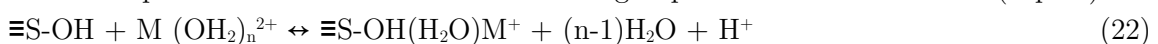
Sorption is a general term that defines retention mechanisms of PTE at solid surfaces. It is divided between three processes: adsorption, surface precipitation, and absorption. Solid phases that enable sorption are most commonly inorganic colloids such as clays, metal oxides and hydroxides, carbonated and phosphates and organic matter of detritus origin (Bradl, 2004). Adsorption can be described by two general terms: a) specific adsorption (including more selective, less reversible reactions of chemisorbed inner-sphere complexes) and b) non-specific adsorption (or simply ion exchange which involves rather weak, less selective outer-sphere complexes, reversible in nature). Specific adsorption is a formation of Lewis salt-type compounds on the solid surface. Metals in soil solution act as Lewis acids while surface functional groups (such as $-\text{OH}$, $-\text{SH}$, or $-\text{COOH}$) as Lewis bases. For example, $\equiv\text{Fe}-\text{OH}$ surface hydroxyl groups and cationic metal ion (M^{2+}) forming a surface complex (Eq. 20).



These types of complexes can also be formed with metal oxyanions, for example HAsO_4^{2-} , where $\equiv\text{S}-\text{OH}$ represents a random surface functional group (Eq. 21).

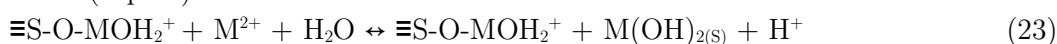


Another type of adsorption electrostatic interactions is called outer-sphere complex or cation exchange. Here weak coulombic attraction between metals and charged soil surface is formed. This type of complex is positioned at a certain distance from the surface with water molecule interposed between the surface functional group and bounded metal ion (Eq. 22).



Functional group is a chemically reactive molecular unit on a surface of soil solid phase structure, which is in contact with the solution [166], [168], [169]. The density of functional groups defines adsorption capacity of the soil solid phase. The soil constituents with the largest capacity are (hydr)oxide minerals, aluminosilicates and organic matter. Inner sphere complexes can also be divided into monodentate (metal species forming one bond with one surface functional group) or bidentate (metal species forming two bonds; one with each of two surface functional groups). On the surface of alumina hydroxides aluminol surface groups ($\equiv\text{Al-OH}$) are defined. Surface of aluminosilicates includes aluminol and silanol ($\equiv\text{Si-OH}$) functional groups. Iron (hydr)oxides can possess at least four different types of hydroxyl functional groups generally described as $\equiv\text{Fe-OH}$. The density of inorganic functional groups can vary in the range of 2 - 12 sites/nm². The most significant functional groups found in soil organic matter are carboxyl (-COOH), carbonyl (-CO) and phenolic groups [169].

The surface precipitation model is defined as a three-dimensional growth of a new solid phase on solid surface (in contrast to two-dimensional surface adsorption). This is mainly the function of pH and redox potential at which metals can precipitate as oxides, hydroxides, carbonates, sulphides, phosphates etc. Surface precipitation processes represent two reactions: formation of surface complex of metal ion (M) and surface (S) and precipitation of M at the surface S (Eq. 23).



Absorption represents two different chemical mechanisms. First is diffusion of metal from soil solution into the soil solid phase where it is incorporated into the crystal lattice or in pore spaces of soil minerals [168].

Sorption processes of metal ions on soil constituents are influenced by a redox potential, pH, speciation of metals involved, metal competition, soil composition and aging. At acidic pH values functional groups are protonated and adsorption of metal cations is inhibited. With increasing the pH towards alkaline values, sorption sites are deprotonated, and adsorption of metal cations is possible, while metals in the form of oxyanions cannot be adsorbed. Sorption of metals can also be influenced by selectivity that depends on factors such as chemical nature of the reactive surface group, adsorbate/adsorbent ratio, the ionic strength of the soil solution, and the presence of ligands [166], [164], [169].

Soil organic matter plays a key role in metal behaviour in soils mainly by significantly contributing to the soil cation exchange capacity. It can form inner and outer sphere complexes with metals even at low pH values. By that, it can contribute to the mobility of metals by the formation of complexes with soluble organic matter or formation of low soluble organometallic compounds [168], [164].

A major part of total content of metallic and metalloid elements in soil is associated with the soil solid fraction in various forms and associations. The most stable and immobile fraction of metals is the one included in a crystal lattice of stable minerals (for example silicates, aluminosilicates, manganese or iron oxides) from which it can be released only upon very slow weathering processes [164].

Release of PTE from contaminated soil creates risk for environment and human health. Possible are multiple different release mechanisms and subsequent transfer pathways for exposure of humans and other living beings to PTE. Some of these are schematically presented in Fig. 1.4 (redrawn after the synthesis of data from different sources; mainly according to [8]).

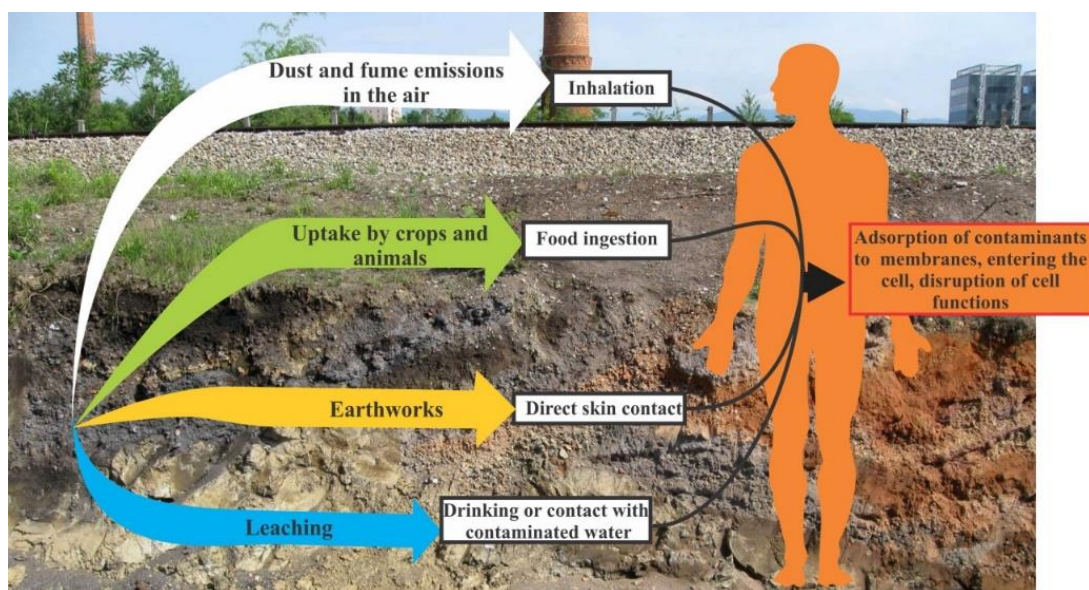


Figure 1.4: Transfer pathways of PTE from soil to human organism, and bioavailability processes in squares (soil profile from the Old Zinc-works site in the background).

At contaminated sites, which are the legacy of smelting and metallurgical activities, the release of PTE is controlled by physical chemical stability and mineralogical composition of deposited residues, slags, ashes, tailings, etc. [170]. There are multiple possible mechanisms of release (dissolution, volatilization, dust emissions, transfer through trophic levels – food). Change in pH is the most common mechanism for release of PTE, which generally become mobile in acidic and highly alkaline environment. Acidity and alkalinity cause desorption of PTE and dissolution of slag matrix, oxides, or silicate minerals, which releases PTE [171], [172]. However, slags can contain high temperature minerals, which are very resistant to a chemical attack (for example spinels, mullite) and minerals with high acid neutralization capacity, like olivine or pyroxene [173], [174]. Carbonic acid, from dissolution of CO_2 in rainwater, and sulphuric acid, from oxidation of sulphide minerals (for example pyrite), are most commonly present at contaminated sites due chemical weathering of primary minerals. Although water solubility of sulphides is considered to be low at standard conditions, they can become a source of soluble PTE upon oxidation [175]. Precipitation of secondary minerals is induced from released PTE and available ligands. They are less stable and are usually the source of water soluble species of PTE in soil [170]. However, precipitation of secondary minerals can also lead to the formation of more stable secondary mineral phases, like in the case of lead phosphate, pyromorphite [176].

Leaching is one of the most common mechanisms for the transfer of PTE that is causing the indirect exposure of humans and living beings through skin contact and ingestion, by drinking contaminated water [8]. Leaching from contaminated soils is basically controlled by the solubility of PTE bearing minerals, which are found on contaminated sites. In Table 1.4 solubility data are given for minerals containing Cd, Pb and Zn, which are commonly found at contaminated sites, such as the Old Zinc-works [170], [177], [178].

Table 1.4: Solubility of selected minerals at standard conditions (20 °C, 101.325 kPa).

Name	Formula	Dissolved g/100 mL	Solubility (log K _{sp})
Cd-chloride	CdCl ₂	135	/
Otavite	CdCO ₃	3.932 · 10 ⁻⁵	-11.3
Cd-hydroxide	Cd(OH) ₂	2.697 · 10 ⁻⁴	-14.7
Monteponite	CdO	0.48	15.103
Greenockite	CdS	1.292 · 10 ⁻¹²	-31.66
Cd-phosphate	Cd ₃ (PO ₄) ₂	6.235 · 10 ⁻⁶	-38.1
Cd-sulphate	CdSO ₄	76.6	-0.172
Cd-arsenate	Cd ₃ (AsO ₄) ₂	7.091 · 10 ⁻⁶	-13
Anglezite	PbSO ₄	0.00443	-7.79
Cerussite	PbCO ₃	7.269 · 10 ⁻⁵	-12.8
Crocoite	PbCrO ₄	1.71 · 10 ⁻⁵	-13
Mimetite	Pb ₅ (AsO ₄) ₃ Cl	/	-36
Wulfenite	PbMoO ₄	1.161 · 10 ⁻⁴	-15.8
Pb(II)-Chloride	PbCl ₂	1.08	-4.8
Pb(II)-Hydroxide	Pb(OH) ₂	1.615 · 10 ⁻⁴	-8.15
Massicot	PbO	/	12.894
Galena	PbS	6.767 · 10 ⁻¹³	-31.27
Pb-Hydroxypyromorphite	Pb ₅ (OH)(PO ₄) ₃	/	-62.79
Hydrocerussite	Pb ₂ CO ₃ (OH) ₂	/	-45.3
Smithsonite	ZnCO ₃	4.692 · 10 ⁻⁵	-9.9
Zn(II)-Chloride	ZnCl ₂	432	/
Zn(II)-Hydroxide	Zn(OH) ₂	/	-17
Zincite	ZnO	1.6 · 10 ⁻⁵	11.33
Zincosite	ZnSO ₄	53.8	3.93
Sphalerite	ZnS	/	-28.75
Zn-Hydroxylapatite	(Zn _x Ca _{1-x}) ₅ (PO ₄) ₃ (OH)	/	-57.7

The ratio between total concentration of contaminant in soil solid phase and its concentration in pore solution at chemical equilibrium can be given as a partitioning coefficient K_d (cm³/g), which is very dependent on the solubility of mineral phases and sorption/desorption mechanisms of PTE [179], [180]. Release of PTE, given as D_s or mass quantity (kg) of released contaminant from known volume of contaminated soil at contaminated site, can be calculated according to Equation (24), as reported by US EPA [181].

$$D_s = \left\{ \frac{1}{\left(\frac{1 + K_d \cdot \rho_b}{\theta_c} \right)} \right\} \cdot C_t \cdot V \quad (24)$$

θ_c is capacity of water available for leaching of contaminants in unsaturated soil zone. It is given as volumetric amount of water in volume of soil (m³/m³), calculated as a difference between wilting point and field capacity. Soil bulk density is given as ρ_b (Mg/m³), C_t (kg/m³) is total concentration of contaminant in a volume of soil, and V (m³) is a volume of contaminated soil, which is exposed for leaching.

Further on, mass quantity of released contaminant per event (PQ_i) can be modelled according to Equation (25) [181]:

$$PQ_i = \left(\frac{Q_r}{R_t} \right) \cdot D_s \quad (25)$$

where Q_r is a depth of rainwater runoff (m), R_t is a total infiltrated rainfall quantity (L/m²). The amount of released contaminant can be calculated by multiplying the PQ_i by a number of average rainfall events in determined time scale.

After the release of PTE, mass flow of the contaminants to the groundwater can be calculated as a contaminant loading rate L_c (mass/time) (Eq. 26).

$$Lc = q \cdot A \cdot C_0 \quad (26)$$

where q is hydraulic conductivity (m/s), A is an area of contaminated site (m^2), and C_0 concentration of contaminant in eluate (mg/L). The transport of contaminants by water at contaminated sites is intrinsically dependent on water balance that determines the amount of water available for leaching processes [181]. Infiltration rate (I) of rainwater is controlled by a surface runoff, which is rising with rainfall intensity. Infiltration is also determined by a specific coefficient of infiltration, which is changing in relation to ground composition (clay, silt, sand etc.), land use (farmland, field, road, etc.), general vegetation type (grassland, woods, crops, etc.), and slope of the terrain. Further on, the amount of water, which is percolating (PERC) through the contaminated landmass, is reduced due to evapotranspiration (ET) and groundwater that flows out of the system (ΔWS) [182] (Eq. 27).

$$PERC = I - ET - \Delta WS \quad (27)$$

However, eluate from contaminated soil is partially depleted of PTE during its flow through soil. This is because of the sorption to soil minerals (soil retention capacity), when contaminants are become partitioned between solid and liquid phase [180]. Therefore, when the plume of contaminated eluate reaches the aquifer it is already partly diluted. The degree of dilution or recharge of aquifer with contaminated water (eluate) can be given by Dilution Attenuation Factor (DAF) according to Equation 28 [8]:

$$DAF = 1 + \left(\frac{Q_{gw}}{Q_l} \right) = 1 + \left(\frac{q \cdot i \cdot d}{A \cdot I} \right) \quad (28)$$

where Q_{gw} is groundwater discharge, given as hydraulic conductivity (q) times hydraulic gradient (i) times mixing depth of groundwater with eluate (d). Recharge by contaminated eluate (Q_l) depends on the area of contaminated site (A) and infiltration rate (I) or the amount of PERC.

Transfer of PTE to the organism is followed by exposure, which can lead to the intake of a certain amount of PTE, for example by ingestion of contaminated soil or water (Fig. 1.3). However, not all PTE, which are taken into the organism, are bioavailable. The calculations of bioavailability are basically a ratio between the concentration of PTE adsorbed by the body, divided by total concentration of PTE in ingested media (soil, water) [5].

Modelling of bioavailability of PTE after dermal exposure must take into account the following parameters: chemical concentration of PTE on skin (C_d), exposed skin surface area (SA), PTE adherence factor – mg of soil per cm^2 skin (AF), PTE absorption factor (ABS), body weight (BW), exposure frequency (EF), exposure duration (ED), period of averaged exposure. The equation for PTE intake from dermal exposure is as follows (29) [8]:

$$Intake = \left(\frac{C_d \cdot SA \cdot AF \cdot ABS}{BW} \right) \cdot \left(\frac{EF \cdot ED}{AT} \right) \quad (29)$$

Calculation for intake due to ingestion of PTE is similar (Eq. 30) and is dependent of the following parameters: Concentration of contaminant (C_c) in water, or soil, ingestion rate (IR), and relative absorption factor (RAF) are included.

$$Intake = \left(\frac{C_c \cdot IR \cdot RAF}{BW} \right) \left(\frac{EF \cdot ED}{AT} \right) \quad (30)$$

where RAF can also be regarded as a relative bioavailability [8].

Each metallic element also possesses its own distinctive chemical characteristics that determine in which form it is going to be present in soil under specific physicochemical conditions. Distribution and mobility of PTE in soil is very complex because they can exist in a variety of chemical species. In this work the specific behaviour of elements As, Cd, Cr, Cu, Pb and Zn in soil is summarised. These PTE are commonly present in cases of soil contamination and represent the highest health risks [5], [183].

1.3.2.1 Arsenic

Arsenic (As) is a chalcophilic metalloid element. Estimated average As content in non-enriched soils is 5 mg/Kg, in volcanic soils it can reach up to 20 mg/Kg and in some agricultural soils approximately 165 mg/Kg [163], [184]. Arsenic occurs in the environment in about 245 mineral species that include arsenides, sulfides, sulfosalts, arsenites or arsenates. Most common natural minerals are arsenopyrite (FeAsS), enargite (Cu_3AsS_4), orpiment (As_2S_3) and realgar (AsS).

In soil As is mainly present in three oxidation states -3, +3 and +5. Arsenite (As(III)) exists as a weak arsenous acid (As(OH)_3). This species is thermodynamically most stable in reducing conditions (E_h from -200 mV to <300 mV) and in a range of pH values from 4 to 8. It can be present in soil in a various protonated form: HAsO_3^{2-} , H_2AsO_3^- , or H_3AsO_3 (Prohaska, and Stinger, 2005, Arai, 2010). Generally, As(III) exhibits high mobility in soils due to weak sorption on soil constituents (clays, Mn, Fe and Al (hydro)oxides). The sorption of As(III) is also very pH dependent which means that it gradually increases at pH values from 4 to 6 and decreases at pH >6. Trivalent As also has a high affinity for adsorption or co-precipitation with sulphur compounds [184], [185].

Under oxidizing conditions arsenate (As(V)), present as arsenic acid (H_3AsO_4), is the most common form of arsenic in soil with its deprotonated forms H_2AsO_4^- and HAsO_4^{2-} . It behaves as oxyanion, forming metal arsenate complexes and readily precipitates in the presence of metal cations ($\text{Ca(AsO}_4)_2$, Na_2AsO_4 , Mn_3AsO_4 , AlAsO_4 , $\text{Fe(AsO}_4)_2$). Co-precipitation and adsorption with alumina and iron oxides is very pH dependent which means that it is enhanced at acidic pH values. Arsenate can precipitate as low soluble mineral scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$) under acidic oxidizing conditions [185].

The behaviour of As is also influenced by the presence of competing anions (Cl^- , NO_3^- , SO_4^{2-} , PO_4^{3-}) that can substantially suppress arsenate sorption. This phenomenon is particularly pronounced by desorption of As in the presence of phosphates (Ciu et al., 2010).

Arsenic compounds are used in agriculture (insecticides, herbicides, fungicides, algacides, cattle and sheep medicine, poultry feed additive), in production of ceramics and glass, and as wood preservatives [162]. The sources of soil contamination with As are in most cases industrial processes like smelting, fossil fuel or waste combustion and especially its excessive use in agriculture [162]. The possible exposure routes are through inhalation of volatile As species and contaminated dust particles or by ingestion of contaminated food and drinking of As contaminated water. It is known that As has many toxic effects on the human organism. It can cause cancer, negatively interfere to metabolic processes, cause damage in lungs and cytotoxic effects on other organs including skin [177].

1.3.2.2 Cadmium

Cadmium is a soft, ductile, silver-white, electropositive metal with two principle valence states: +2, and 0. Cadmium was discovered in 1817. Naturally Cd is mostly present in zinc or phosphate deposits, mainly in the form of minerals greenockite (CdS) and otavite (CdCO_3). Its average abundance in earth's crust is 0.15 mg/kg [177].

Cadmium is obtained as a byproduct of Zn recovery processes or by recycling of Ni-Cd batteries. It is collected as dust or a fume on bag house or electrostatic precipitators during roasting of Zn concentrates. Approximately 23,000 tons of Cd was produced in the world in 2016. The production is declining slightly, because Cd is replaced by other elements (especially Zn) in the production of batteries, pigments and composite materials [186].

Metallic Cd is resistant to corrosion by water due to a formation of protective coating of CdO . It is however attacked by dilute acids (HCl , HNO_3 , H_2SO_4) and it is also prone to combine with halogens and thus forming soluble salts (for example CdCl_2). On the other hand, alkalis do not attack elemental Cd. Cadmium has a standard electrode potential of -0.4025 V

and can thus displace a number of less electropositive elements in the activity series from their salt solutions (for example Cu, Pb, Ag, Hg, Sn, Sb) [177].

However, despite its high toxicity, Cd compounds are used in a number of applications. Cadmium is mostly used for Ni/Cd batteries production, anti-corrosion coatings, pigments, stabilizers for polymers, different alloys, electronic and photovoltaic compounds [183], [163].

From a geochemical and environmental point of view Cd is known as an element that is part of the »Big three« group – Hg, Pb, Cd, of the most problematic metal contaminants [183]. Its natural occurrence in soil is largely dependent of the concentrations of Cd in parental rock which can vary from < 0.10 to 0.3 mg/kg in igneous rock and from 0.3 to 11 mg/kg for sedimentary rock [166]. In nature the occurrence of Cd in association with Zn minerals is very significant, where it is usually present in the form of greenockite (CdS) and otawite (CdCO₃). Both, Zn and Cd are in the same group of the periodic system and have similar geochemical characteristics. Usually the concentrations of Cd are approximately 200 times lower than Zn in soils or rocks (Chaney, R.L., 2010). Cd contamination is related mainly to the smelting, application of Cd rich Zn and phosphate fertilizers, disposal and application of sewage sludge, disposal of batteries and pigment and plastic waste, corrosion of galvanized steel [183].

The most common form of Cd in soils is Cd(II). At pH values higher than 8 main Cd species present in soil are Cd(OH)₂ or CdCO₃. Under reducing conditions and in the presence of sulphate Cd is precipitated as a very low soluble CdS [163], [184].

The behaviour of Cd in soils is highly pH dependent and generally, the mobility of Cd is lowering with the increase of pH. This is related to the competition for adsorption sites at lower pH values and to precipitation of low soluble Cd(OH)₂, CdCO₃ and Cd₃(PO₄)₂ at higher pH values. Important factors determining Cd mobility are also redox potential (precipitation of poorly soluble species in reducing conditions), and the presence of organic matter (Cd is prone to form stable complexes with organic matter) [162], [187]. Another important factor determining mobility of Cd in soils is the presence of chloride. Chloride can cause the formation of highly soluble complexes (CdCl⁺, CdCl₃⁻, CdCl₄²⁻), especially at neutral and even at alkaline pH values [163].

At low concentrations of Cd in soils, the main reaction mechanism with soil constituents is adsorption. Nevertheless, this process is highly influenced by the presence of competing divalent cations, Zn and Ca. This effect is especially pronounced when Cd is adsorbing on the surface of the clays, while when adsorbing to the amorphous iron hydroxides this effect is negligible [188]. Strong specific adsorption of Cd on carbonates also predominates in calcareous soils. Generally, differences between soil types (especially texture, redox potential and pH) have a great influence on Cd retention. Typically, adsorption of Cd is less efficient at lower pH values [166].

There are many known toxic effects of Cd on the human organism. Cadmium can cause nausea, vomiting, diarrhea, headache and other symptoms of acute poisoning. The LD₅₀ for rats is in a range of 250 mg/kg. While at chronic exposure liver, kidneys and bones can be permanently damaged. These effects are caused mainly because Cd can substitute Zn or Ca (essential for organisms). The main source of Cd toxicity is ingestion of contaminated food (some vegetable can accumulate Cd), through inhalation of contaminated dust particles, or by drinking contaminated water [189].

1.3.2.3 Chromium

Chromium (Cr) is a transitional element with six known valence states: +6, +5, +4, +3, +2, 0. Chromium is one of the less common elements in nature. In the environment it is usually occurring in the form of compounds. Chromium is obtained from chromite ore (named by ore mineral chromite FeCr₂O₄). It is also associated with mafic and ultramafic rocks containing Fe deposits. This is the consequence of possible isomorphic substitution of Cr³⁺ ion with Fe²⁺ (both have almost the same ionic radius). The average concentrations of Cr in soils are

estimated to be 54 mg/kg, and they vary significantly in rock: from 1800 mg/kg in ultramafic igneous to 10 mg/kg in limestone sedimentary rocks [163].

Depending on pH and redox potential of the soil Cr can exhibit a wide range of oxidation states. In soil it is commonly present in Cr(III) and Cr(VI) as the most stable state, in the form of four basic species. Two trivalent forms Cr^{3+} and CrO_2^- and two hexavalent forms $\text{Cr}_2\text{O}_7^{2-}$ (dichromate) or CrO_4^{2-} (chromate) [162], [163].

The behaviour of Cr in soil is controlled by a variety of factors, like redox potential, oxidation state of Cr, pH, mineral composition, presence of competing ions or complexing agents. One of the most important processes in soil regarding Cr are the reactions between soil solution and soil solid phase, where hydrolysis, redox reactions, adsorption and precipitation of Cr(III) and Cr(VI) takes place [166].

Generally, Cr(III) is the most stable at E_h values < 0.4 V and at pH values between 4 and 8. It is present as a cationic species as hydrolysis products ($\text{Cr}(\text{OH})^{2+}$, $\text{Cr}(\text{OH})_2^+$). At pH values of >5 it precipitates as $\text{Cr}(\text{OH})_{2(s)}$ low soluble hydroxide complex. At pH values <5 its adsorption on soil particles limits Cr(III) mobility. In the range of pH values between 4 and 8 and E_h between 0.3 and 0.7 V, Cr(VI) exists mainly as HCrO_4^- (at pH values <6.5) or as CrO_4^{2-} (at pH values >6.5). This form is highly mobile and thermodynamically most stable under oxidizing conditions. Chromate is soluble in water and is a strong oxidizing agent [163]. Under aerobic conditions Cr(III) can be oxidized to Cr(VI) but generally this process is very slow at pH values <5 . However, the presence of Mn oxides can enhance the oxidation process [190]. In the presence of reducing agents (redox reactions with different inorganic species – Fe^{2+} , S^{2-} , electron transfer at mineral surface and reactions with humic or non-humic organic substances – carbohydrates, proteins) Cr(VI) can be reduced to Cr(III).

Large proportion of Cr in soil can be associated with organic matter, which can also decrease its sorption to other inorganic ligands or sorption sites [163]. Hexavalent chromium can be absorbed by a variety of solid phases in soil that poses surface hydroxyl groups: Fe, Mn, Al oxides, clays. The amount of adsorbed Cr(VI) is increasing with decreasing pH. It also precipitates readily in the presence of metal cations (for example Ba^{2+} , Pb^{2+} , Ag^{2+}). On the other hand, Cr(III) is rapidly adsorbed by Fe and Mn oxides and clays at the increasing of pH values. It can also form complexes with inorganic (NH_3 , OH^- , Cl^- , F^- , SO_4^{2-}) and soluble organic ligands [166].

Chromium is used worldwide for manufacturing of stainless steel and alloys, paint and pigments and for leather tanning and as a wood preservative. The major sources of Cr contamination are most commonly related to the emissions from the smelting, steel and electroplating industry, misuse in agriculture, sewage sludge disposal, cement production, leather tanning [162]. While Cr(III) is an essential element for living organisms, Cr(VI) is one of the most toxic metals. It can be introduced into an organism through inhalation of contaminated dust, or by drinking contaminated water. Due to Cr(VI) strong oxidizing character it is associated with allergic dermatitis, to increased incidence of cancer, namely it is mutagenic and teratogenic [163], [183].

1.3.2.4 Copper

Copper (Cu) is a transitional metal element with three common valence states: +2, +1, 0, but the divalent form is the most common in nature. Copper is the third most abundant metal element in the human body and the 26th in the earth's lithosphere. The average concentrations in the soils range from 13 to 24 mg/Kg. Copper cannot accommodate in the crystal lattice of silicate minerals but it can form covalent bonds with sulphide anions (S^{2-}) thus forming a number of sulphide and sulphate minerals. The main natural sources of Cu are the hydrothermal deposits of mineral chalcopyrite (CuFeS_2) in igneous rock and also sedimentary rock where copper is associated mainly with malachite ($\text{Cu}_2\text{CO}_3(\text{OH})_2$) [163]. Copper can be present in the soil mainly as Cu(II), which can form many different species. Among them

cationic (Cu^{2+}) and $\text{Cu}(\text{OH})^+$ are the most mobile in soils. At pH values below 7 $\text{Cu}(\text{OH})^+$ and $\text{Cu}_2(\text{OH})_2^{2+}$ are the most abundant hydrolysis products. Anionic hydroxyl complexes $\text{Cu}(\text{OH})_3^-$ and $\text{Cu}(\text{OH})_4^{2-}$ are formed at pH values above 8. The cupric form ($\text{Cu}(\text{II})$) is the least soluble at the pH values ranging from 7 to 8 [162], [163].

Copper is one of the least mobile metals in soils due to its strong affinity to adsorb to soil constituents. Although its mobility can be enhanced in highly alkaline or acidic soils the effect of pH on the behaviour of Cu in soils is to be relatively less pronounced than for other divalent metal cations [162]. Copper exhibits strong affinity for soil organic matter, which influences the mobility of Cu. It forms complexes with humic and fulvic acids, low molecular weight soluble organic complexes and complexes with chelates [166]. Clays and oxides of iron and manganese are also very important sorbents for Cu in soil over a wide range of pH values. Here the main mechanism is specific adsorption [166], [191]. In the neutral and alkaline environment or in calcareous soils $\text{Cu}(\text{II})$ can precipitate as sparingly soluble copper carbonate (CuCO_3). In reducing environment at the presence of sulphur, Cu can precipitate as $\text{CuS}_{(s)}$ [184].

Copper is generally in use for the production of wires and pipes, brass and bronze alloys, in agriculture (for fertilizers, bactericides, fungicides, feed additive), wood preservatives (chromate copper arsenate). The contamination of soil with copper is related to industrial activities (smelting, mining), excessive use of Cu enriched fertilizers, manure, feed additives and Cu based agrochemicals in agriculture [162]. Copper does not bio-accumulate and cannot be biomagnified. In high doses it can have harmful effects on the human organism which are expressed by anaemia, liver and kidney damage, stomach and intestinal irritation [183].

1.3.2.5 Lead

Lead is a soft, ductile, silver-grey, electropositive metal, which has three common valence states: +4, +2, 0. In nature, it can be very rarely found in its elemental form. Most commonly, it occurs in the form of minerals galena (PbS), anglesite (PbSO_4), minium (Pb_3O_4) and cerussite (PbCO_3). Its average concentration in the earth's crust is 12.5 mg/kg [177]. Lead is produced from its principal ore mineral, galena, which is usually associated with sulphide minerals of several metals (Ag, Fe, Cu, Zn, Bi, Sn, Sb). The ore concentrate is prepared by crushing and froth flotation processes. Lead concentrate is then roasted, which is followed by smelting in a blast furnace. Most of sulphate is removed during roasting. Then the roasted concentrate – sinter is mixed with coke, silica, lime, iron oxide, zinc oxide and alumina. The mixture is smelted at 1000 °C in a lead blast furnace. Slags, dusts, gases (CO and CO_2) and lead bullion are thus produced. In order to obtain high purity grade metal Pb electrolytic refining of lead bullion is commonly employed. World production of refined lead was 10.9 Mt in 2014 [192].

Metallic Pb is very resistant to water corrosion, due to a rapid formation of protective oxide layer (or silicate and carbonate in "hard" water). However, Pb has amphoteric characteristics and can thus react with bases and acids. In the presence of nitric or hydrochloric acid it forms soluble salts, lead(II) nitrate ($\text{Pb}(\text{NO}_3)_2$) and lead(II) chloride (PbCl_2). Lead is less aggressively attacked by sulphuric and hydrofluoric acid due to the formation of protective layer of less soluble lead(II) sulphate (PbSO_4) and sparingly soluble lead(II) fluoride (PbF_2). On the other hand, organic acids (for example acetic) form soluble salts with Pb (lead(II) acetate – $\text{Pb}(\text{CH}_3\text{COO})_2$). Lead has a standard electrode potential of -0.13 V (half-reaction $\text{Pb}^{2+} + 2e^- \leftrightarrow \text{Pb}$) and can be for example reduced by Fe [177].

Despite its toxicity, lead is extensively used for the manufacture of batteries. Its use also includes solders, bearings, cable covers, ammunition, plumbing, pigments, glassware, ceramics, and caulking [162]. In the past the main source of lead pollution was fuel combustion, because tetraethyl lead and tetraalkyl lead were added to the fuel as an anti-knock additive (banned in 1985 but was still used by some countries even by the end of year 2000). Other sources are smelting, sewage sludge and other effluents, coal combustion and misuse of Pb in agriculture. A

number of lead compounds is produced and used worldwide. Lead is considered to be one of the most widely spread toxic elements in nature [163]. In worldwide surface soils typical mean concentrations of Pb are ranging from 10 to 67 mg/kg (average 32 mg/kg) [162]. The general forms of lead released into the environment are ionic lead (Pb^{2+}), lead oxides or hydroxides and lead oxyanion complexes. Ionic lead is the most common and reactive form of Pb that usually forms mononuclear or polynuclear complexes, while most stable forms of Pb are its hydroxyl complexes [184].

The behaviour of Pb in soil is affected by three main factors: 1) specific adsorption to various solid phases, 2) precipitation of sparingly soluble or highly stable compounds, 3) formation of stable complexes or chelates by interaction with organic matter. Lead (II) compounds in soil are predominately ionic, while lead (IV) (which is rarely present in soils) forms mainly covalent bonds. The solubility and sorption of Pb on soil mineral phases are highly pH dependent and low at neutral pH values while with increased acidity the solubility of Pb is also enhanced. The effect is related to the competition for adsorption sites at low pH values [163]. Lead undergoes hydrolysis at pH values >4 , and $\text{Pb}(\text{OH})^+$ is dominant in the range from pH 6 to 10, above pH 9 the formation of stable low soluble $\text{Pb}(\text{OH})_2$ form is important. Above pH values of 11 soluble negative species $\text{Pb}(\text{OH})_3^-$ and $\text{Pb}(\text{OH})_4^{2-}$ predominate. Hydroxylated species above pH values of 12 are soluble and Pb mobility under highly alkaline conditions is enhanced [162], [166]. Lead can be adsorbed to clays over a wide range of Pb concentrations. Especially important is strong specific adsorption of lead on Mn and Fe oxides and solid organic matter.

Under reducing conditions in the presence of sulphate, Pb can precipitate as a PbS , a very low soluble species. While in the presence of microorganisms under anaerobic conditions, volatile organo-lead (tetramethyl lead) can be formed via microbial methylation [183], [184]. In calcareous soil the mobility of Pb is controlled by precipitation of sparingly or low soluble cerussite (PbCO_3) and hydrocerussite ($\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$). When pH values are above 6, Pb can precipitate in the presence of phosphate as hydroxypyromorphite ($\text{Pb}_5(\text{PO}_4)_3\text{OH}$), Pb orthophosphate ($\text{Pb}_3(\text{PO}_4)_2$), tetraplumbite phosphate ($\text{Pb}_4\text{O}(\text{PO}_4)_2$), which are very low soluble compounds [176].

Lead is a nonessential element for humans. Exposure and accumulations in the organism can cause the damage of the gastrointestinal tract, kidneys, and the central nervous system. Permanent brain damage has been noticed among children. It accumulates in bones and teeth. Lead poisoning can even cause death. Sources of lead poisoning were in the past related to the use of lead white pigments, inhalation of volatile organo-lead compounds and dust particles [177], [183].

1.3.2.6 Zinc

Zinc is a bluish white lustrous electropositive metal, which has two principle valence states +2 and 0. Zinc is widely distributed in nature, where it occurs mostly in the form of minerals sphalerite (ZnS), gahnite (ZnAl_2O_4), calamine, willemite (Zn_2SiO_4), hemimorphite ($\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$), smithsonite (ZnCO_3), franklinite (ZnFe_2O_4) and zincite (ZnO). The average abundance of Zn in the earth's crust is 70 mg/kg. Zinc is principally produced from sulfide ores of sphalerite. The ore concentrate is first roasted to produce zinc sinter of ZnO and ZnSO_4 [177].

Zinc sinter is used to produce refined metal Zn. Most commonly the Imperial Smelting Furnace is employed for that purpose. There the sinter is mixed with a reducing agent (usually coke) and heated to 1300 °C. Elemental Zn thus evaporates and is precipitated upon collection. Another way of obtaining Zn is by electrolysis of zinc sulfate solution, where Al cathodes and Pb anodes are used. Global production of metal Zn was 13.2 Mt in year 2014 [193].

Zinc is a highly electropositive metal that can replace many less electropositive metals from their aqueous solutions. Namely it has a redox potential E^0 of -0.7618 V (for half reaction Zn^{2+}

+ 2e⁻ ↔ Zn), which is lower than Cu²⁺, Pb²⁺ or Fe²⁺. It has amphoteric characteristics and thus it can react with both acids and bases. Zn evolves H_{2(g)} when it reacts with HCl and H₂SO₄. However, it does not evolve H_{2(g)}, when it reacts with H₂CO₃ or HNO₃. Zinc also dissolves in a concentrated solution of caustic alkalis, where it forms soluble zincate salts (Na₂ZnO₂, K₂ZnO₂). Zinc is one of the most widely used metals. Most common applications of Zn are the production of galvanized steel and die castings, chemical additive for rubber and paints, for electrodes, as a reducing agent. Steel is galvanized with a thin layer of Zn that acts as a sacrificial anode, which prevents corrosion. Well known are also uses of high purity Zn for the preparation of alloys with Al, Cu and Mg, also brass and bronze [177].

The behaviour of Zn in soil is influenced by several factors such as pH, cation exchange capacity, the presence organic matter and clay and iron oxide content. Zinc is one of the most mobile metals because it forms a soluble compound at acidic and neutral pH values. Its solubility decreases with the increase of pH values above the neutral area [184]. In soils, Zn usually occurs in +2 oxidation state and forms a number of complexes with different organic and inorganic ligands.

Zinc hydrolyses at pH values around 6 (first hydrolysis product is ZnOH⁺) and forms solid precipitate ZnOH_{2(s)} at pH values from 7 to 10. At the pH values higher than 10 it forms negatively charged species Zn(OH)₃⁻ and Zn(OH)₄²⁻ [162]. At higher pH values and in calcareous soils the adsorption of Zn is enhanced due to the sorption on surface of carbonates. It can also precipitate as sparingly soluble minerals calcium hydro zincite (CaZn₂(OH)₆ · 2H₂O) or smithsonite (ZnCO₃) and as Zn(OH)_{2(s)} [194]. Among clay minerals, those with basic structural make up of 2:1 (for example illite or montmorillonite) exhibit greater fixing capacity for Zn than 1:1 clays (like kaolinite). Mobility of Zn is also controlled by the formation of complexes with Cl⁻, PO₄⁻, NO₃⁻, SO₄²⁻ and with different organic ligands. Under reducing conditions and in the presence of sulphate, Zn precipitates as very low soluble ZnS [166], [184]. A major fraction of Zn in soil is also associated with Fe and Mn oxides, by adsorbing or coprecipitating on their surface [195].

The sources of Zn soil pollution are most commonly zinc smelters and mines, where in the vicinity of them a surface layer of soil can contain up to 4% of Zn. Other sources are misuse of Zn rich fertilizers and application of manures from farms where a Zn-enriched diet is practiced, coal and waste combustion [162], [163], [183].

Although in small concentrations Zn is essential for the normal biological activity, in excessive amounts it can be toxic. It can accumulate in the animals' body and biomagnifies up the food chain, causing adverse effect in humans and other higher organisms. It can also negatively influence the biological activity in the soil. Reported are adverse effects due to the inhalation of metal fumes [163].

1.3.3 Soil remediation

Worldwide, management of contaminated land poses a great challenge in the scope of human and ecosystem health on one hand and from economic and social development on the other [196]. Remediation of soil contaminated with PTE is very complicated due to multiple reasons. PTE are usually associated with organic contaminants; their spatial distribution is heterogenic within soil matrix. PTE cannot be destroyed or degraded like organic contaminants. Their physical and chemical form very much determines the environmental risks and feasibility of remediation methods [197].

The most basic division of remediation methods is according to the location of implementation, either *in situ* or *ex situ*. This approach demands a very detailed knowledge about geochemical, hydrogeological and geological characteristics of contaminated sites as well as information about the extent, spatial distribution, concentrations and other characteristics of contamination [144]. *Ex situ* remediation is performed on excavated soil. The latter can be transported off the site to the treatment facility or equipment can be brought to the site to

perform remediation on site. *Ex situ* remediation is usually applied in municipal areas or with point sources, where rapid action is needed for elimination of contamination. Advantage of *ex situ* is that it can be easily controlled, verified and implemented regardless of the local geological conditions. On the other hand, need for off site remediation area, requirement for heavy processing and transporting equipment, and risks for exposure due to contaminants spreading are the main disadvantages of the *ex situ* approach. The *in situ* approach is more appropriate for diffuse contamination of large areas [144], [183], [197]. Due to lower risks for exposure and lower labour intensity, the use of *in situ* methods is preferred. However, in cases of complex soil contamination, *ex situ* treatments are needed [184]. Remediation methods can also be divided into three categories according to hazard-alleviating measures. 1. Gentle *in situ* remediation is performed to restore the functionality of soil (for example as agricultural land). 2. *In situ* harsh soil restrictive measures are used in cases of heavy contamination, when the only option is to isolate/encapsulate the soil because any other remediation activity would represent too high risks. 3. *In situ* or *ex situ* harsh soil destructive methods completely change the structure of contaminated soil in order to eliminate hazards related to contamination [198].

Rehabilitation of environmental burdens related to soil contamination is performed very differently from case to case. Before any remediation actions are taken, it is very important to gather information about the contamination and to select the appropriate remediation method. According to the US EPA guidance [199] the initial stages of soil remediation project should be implemented in the successive steps as presented in Table 1.5.

Detailed characterization of the contaminated site is the prerequisite for successful remediation. Nowadays, a number of field laboratories and analyses are available (portable GC, XRF, colorimetric test for photometry, multi-measuring probes for physical/chemical parameters, etc.). This enabled us to perform a large number of fast and economically acceptable chemical analyses on site to get as much information as possible, without accidentally missing any of the scattered contamination source points. Geophysical methods, like electromagnetic conductivity, resistivity, ground-penetrating radar, etc. offer a non-destructive and fast prospection of large areas, with possibilities of detecting underground hidden sources of contamination. Excavation of sampling pits and prospecting trenches, drilling of boreholes with continuous cores can be performed in the last stage for in depth analyses of point sources of contamination [200].

The global practical and theoretical knowledge of different soil remediation methods is very large. Especially in the United States of America, the development of different alternative methods is very intensive. That results in the development of a number of options that were already tested in pilot or large-scale operations with different success rates. They are according to US EPA grouped into one of the four main categories for treatment of organic and inorganic contaminants: biological, chemical, physical or thermal treatment [201].

Remediation methods, which can be potentially used for PTE contaminated sites, can be generally divided between different approaches [183], [184], which are:

- immobilization,
- physical separation and chemical extraction,
- isolation,
- methods for the reduction of toxicity.

Table 1.5: Successive steps of the remediation project.

1. PRELIMINARY ACTIVITIES			
- preliminary assessment, - site inspection, - registration of contaminated site according to national legislation.			
2. SCOPING OF THE REMEDIAL INVESTIGATION/FEASIBILITY STUDY			
- collecting and analysing data, - identifying operational units (scale of the project), response scenarios, and remedial objectives, - set quality objectives, - project plans, - initiate stakeholders and beneficiaries.			
3.1. REMEDIAL INVESTIGATION		3.2. FEASIBILITY STUDY	
Site characterization:	Treatability investigation:	Development and alternatives:	Ananalysis of alternatives:
- field investigation, - define extent of contamination, - sources, types, and concentrations of contaminants, - baseline risk assessment.	bench and pilot remediation tests.	- identify potential remediation method, - screen alternative remediation methods, - reduce the number of possibilities by the use of detailed analyses, - set a range of multiple options.	Analyse alternatives against the quality objectives, environmental and legislative criteria.
4. PERFORM REMEDIATION:			
- selection of remediation method, - design of remediation activities, - implementation of remediation.			

The key factors influencing the selection of the best available remediation technology are economical acceptability, long-term effectiveness, commercial availability, general public acceptance, applicability to high contaminant concentrations, applicability to mixed contamination, toxicity reduction, mobility reduction and reduction of a contaminated soil volume [184], [202]. Each soil remediation method is designed to treat specific metal contaminants in soil under specific physicochemical conditions. However, a combination of multiple remediation methods is usually needed for large scale remediation projects (for example [203]). Therefore, it is crucial to know the basic characteristics, abilities and the end products of the soil remediation technologies to design an effective, feasible and economically acceptable remediation plan. In this work immobilization is described more in details. This is one of the most common and advanced remediation technologies, that are used over the world for the treatment of soil contaminated with PTE [144].

1.3.3.1 Immobilization

Immobilization is recommended by the European Commission as the Best Available Technology for treatment of large quantities of contaminated soil [204]. It can be performed at a relatively low cost (compared to other methods) *in situ* or *ex situ* with minimal disruption to the environment [205]. A variety of immobilization methods is available. Immobilization as *in situ* gentle remediation method is performed by mixing the additives, which chemically

transform PTE into sparingly soluble, low bioavailable and non-toxic species, with soil. Basic soil functions do not change so it can still serve as a substrate to support plant growth. Chemical immobilization mechanisms, which are induced during “gentle *in situ* immobilization”, include surface sorption processes (specific or chemisorption and non-specific adsorption, absorption), precipitation, and oxidation/reduction [206]. The adsorption mechanisms for Pb on iron hydroxide (goethite) are schematically presented in Fig. 1.5, based on Dzombak and Morel [191].

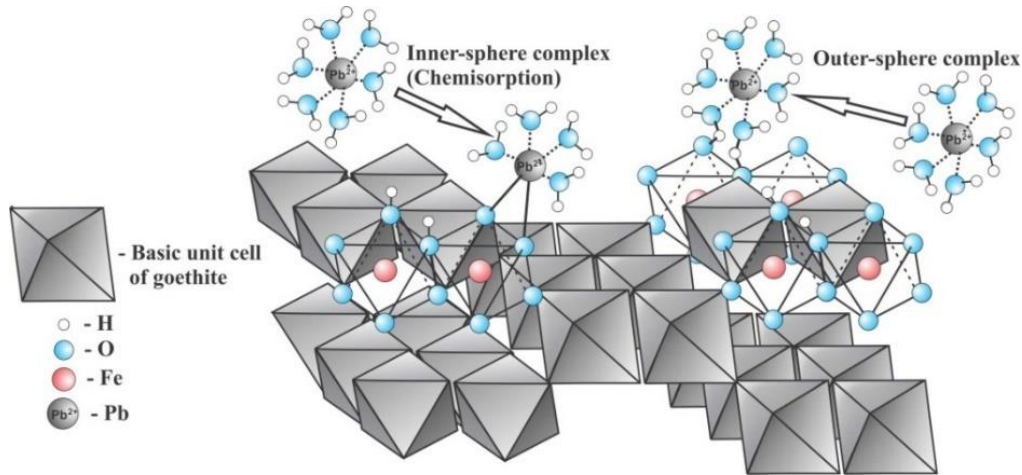
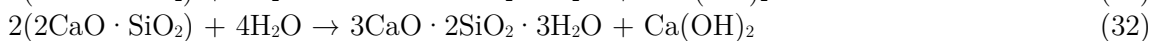
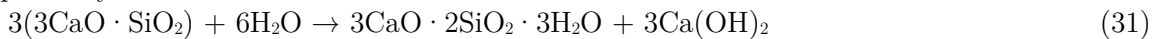


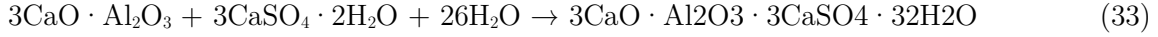
Figure 1.5: Schematic presentation of adsorption immobilization mechanisms.

Spreading of immobilization additives and subsequent mixing with soil is performed by simple agricultural equipment. Therefore, this immobilization method is usually used when contaminants are diffusely spread and present in relatively low concentrations. The most commonly used are phosphate compounds, zeolites, lime, ashes, compost or biosolids, and iron oxides [207]. For example, phosphate amendments have been extensively used for immobilization of Pb due to the formation of very low soluble pyromorphite mineral ($\text{Pb}_5(\text{PO}_4)_3\text{OH}$). However, care must be taken, as PO_4^{3-} can substitute AsO_4^{3-} on adsorption sites making it more mobile, bioavailable and toxic [205]. The drawback of this immobilization method is that it is not permanent and addition of additives has to be periodically repeated and immobilization effect regularly monitored [207], [208].

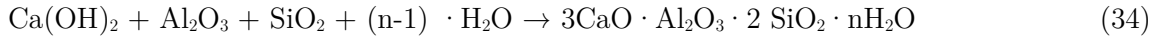
Second type of immobilization methods is solidification/stabilization, which is a harsh method that was developed (mainly) in the United States in the 1970s for two main purposes: stabilization of hazardous wastes (for example radioactive wastes) and for immobilization of contaminants *in situ* by injection of cement suspension with similar techniques as jet grouting [209]. Other reactive binders, such as lime, polymers or bitumen, and cements blended with supplementary materials were used to transform contaminated soil into monolithic, durable and low water permeable construction material. Cement supplementary additives (fly ashes, metallurgical slags, zeolites, lime, clays, industrial recycled materials etc.) were used to enhance immobilization properties [210]. Immobilization mechanisms in solidification/stabilization with the use of Portland cement were widely investigated and were attributed to the formation of products of hydration reactions and pozzolanic reactions (for example, [209], [211], [212], [213]). Calcium silicate phases alite ($3\text{CaO} \cdot \text{SiO}_2$) and belite ($2\text{CaO} \cdot \text{SiO}_2$) in contact with water form CSH gel ($\text{CaO} \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O}$) and portlandite ($\text{Ca}(\text{OH})_2$), as seen from Eqs. 31 and 32, respectively.



Hydration of calcium aluminates (for example $3\text{CaO} \cdot \text{Al}_2\text{O}_3$) in the presence of sufficient quantities of sulphate leads to the formation of ettringite ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$) according to Eq. 33.



Pozzolanic materials are also commonly used as supplementary materials in cement-based solidification/stabilization. Those are aluminium and/or silicon containing materials, which possess cementitious characteristics because in contact with water and alkaline activator for hydrolysis, such as portlandite, form for example calcium aluminate silicate hydrates (CASH) (Eq. 34) [209].



However, despite the beneficial results of remediation experiments for the immobilization of PTE in concretes from solidification/stabilization, described by previously mentioned studies, this use is not always justified. Namely, contaminants, for example organic pollutants, Cd, Pb and Zn, can interfere with hydration reactions and have detrimental consequences on setting and durability of concrete matrix [214].

It is accepted that immobilization mechanisms in solidification/stabilization can be divided on both physical (microencapsulation in durable low water permeable composites) [215] and chemical (adsorption, ion exchange, oxidation/reduction, pH stabilization, incorporation in new mineral phases) [216]. The chemical mechanisms are for example formation of double hydroxides ($\text{CaZn}_2(\text{OH})_6$), incorporation of Cd^{2+} or Pb^{2+} in CSH gel, and AsO_4^{3-} in Ettringite, formation of low soluble minerals (for example CaMoO_4), etc. [209], [212], [213]. Immobilization mechanism by incorporation in the CSH phase is commonly described as the combination of substitution of Ca^{2+} ions with cations of PTE or by incorporation of metal cations into interlayer structures of CSH [212], [217] as it is schematically presented in Fig. 1.6.

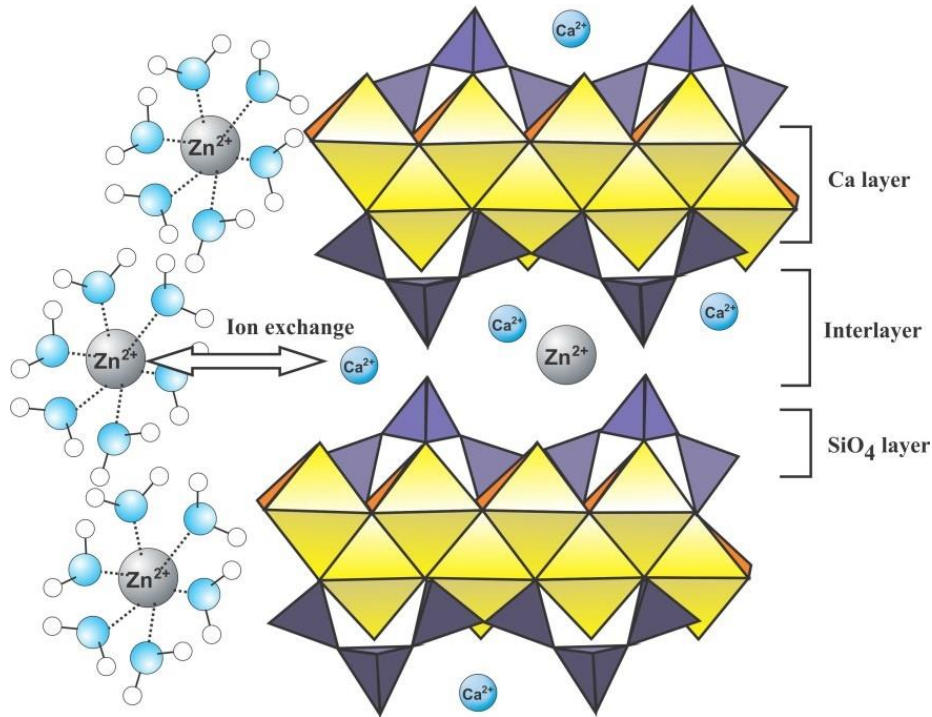


Figure 1.6: Schematically presented structure of CSH (redrawn according to [218]) and process of incorporation of Zn.

On the other hand, oxyanions AsO_4^{3-} , CrO_4^{2-} , or MoO_4^{2-} interexchange with SO_4^{2-} in crystalline structure of CAH phases, which was most commonly reported for ettringite [213] as it is schematically presented in Fig. 1.7.

Immobilization can also be performed by preparation of composites from contaminated soil and additives, which are later installed by basic geotechnical means for compaction. For successful immobilization, the composite has to be prepared in accordance with basic geotechnical procedures that include: preparation of mixture with appropriate amount of additive, addition of optimal amount of water, and compaction of material up to its maximal density. Only then low water permeability can be achieved, good compressive strength and durability of composite that enable physical immobilization. Also, optimal chemical immobilization, which is dependent on hydration reactions, pozzolanic activity, pH stabilization, and adsorption capacity of additives can be performed at these conditions [210], [215], [219], [220], [221].

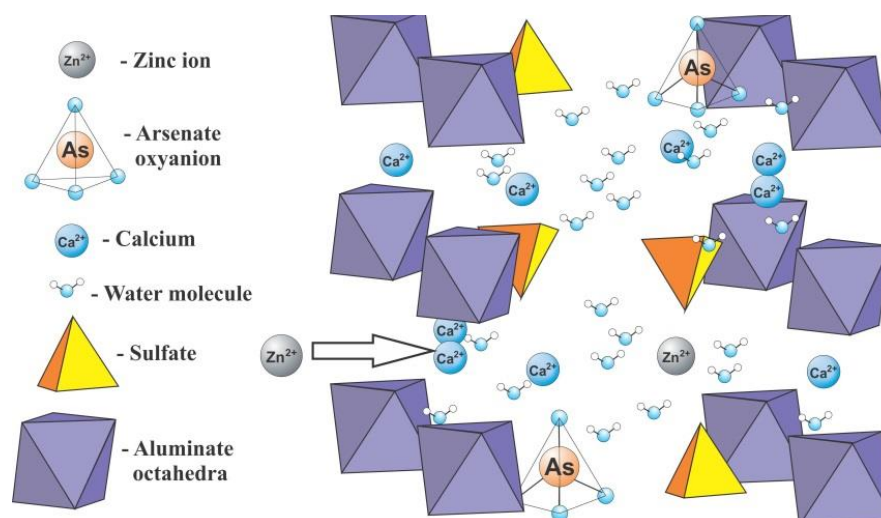


Figure 1.7: Schematically presented cross section of ettringite crystalline structure (redrawn according to different literature data) with a presentation of arsenate oxyanion and Zn ion incorporation.

Within the scope of this study for the purpose of immobilization fly ashes from coal combustion (CA) and ash from incineration of paper mill residues (PA), ladle slags from steelmaking (LS) and red mud (RM) from alumina production were investigated. There is a potential to use high volumes of these wastes as immobilization additives for remediation of contaminated soils.

1.3.3.2 Immobilization additives

1.3.3.2.1 Ashes

The use of coal fly ashes for improvement of soil is a well-known practice, with a purpose to enhance soil fertility, impact on biota and microbes, affect soil nitrogen cycle, for geotechnical stabilization, reduction of degradation, and finally for remediation [222]. It is estimated that globally about 750 million tons of different types of coal ashes are formed annually in coal combustion power plants [223]. Most of the coal ashes are disposed on landfills, and only 16% of it is recycled or reused. Therefore, beneficial use of these combustion residues was extensively investigated as the supplementary cementitious material, for gas cleaning (desulphurization, NO_x , Hg, and organics adsorption), wastewater treatment (adsorption of PTE, P, F, B, organic contaminants, dyes), for zeolite synthesis, and as recycled material in construction (lightweight aggregate, backfill, stabilizing agent) [224]. Division of coal fly ashes is based on their general chemical composition. According to ASTM 618 standard [225] division is on Class F and Class C, where the sum of the main oxides $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{FeO}_3$ is minimally 70 and 50%, respectively. For Class C more than 10% content of free CaO is indicative.

According to standard SIST EN 14227-4:2005 [226], coal fly ash division is based on total value of reactive CaO (determined according to SIST EN 197-1:2011 [227]), which should not be less than 5% for calcareous fly ash. It is considered that calcareous or Class C coal ash is formed during combustion of low-grade sub-bituminous coals and lignite. It has cementitious properties, when it reacts with water. On the other hand, siliceous or Class F ashes are formed during combustion of higher-rank bituminous coals and anthracites and are considered a pozzolanic material [224]. The most commonly occurring mineral phases in coal fly ash are aluminosilicate glass, mullite, quartz, anhydrite, magnetite, ettringite, hematite, lime, chlorite, feldspars and spinels. The ratios between phases change depending on the feed coal material and the process of combustion itself [222]. The potential of coal ash for the purpose of immobilization was already described in scientific literature, mainly in the context of solidification/stabilization, where it was used in combination with lime or as a supplementary cementitious material with Portland cement [210]. There were also attempts to use coal ash as the main immobilization additive [221], [228]. As the main PTE immobilization mechanisms are reported incorporation into newly formed mineral products of hydration reactions or due to the activation of pozzolanic phases, neutralization of acidity with alkaline pH, and adsorption onto particles of coal fly ash with high specific surface area [224], [220], [221], [219], [229]. The use of coal fly ashes for immobilization of PTE is relatively well and extensively investigated (for example [224], [228]).

Beside coal ashes, there are other ashes from energy production and from incineration of wastes, which have the potential for immobilization of PTE [230], [219]. Among them is paper ash, from incineration of paper mill sludge, a very perspective material. This is because its use for the preparation of geotechnical composites and for immobilization was recently successfully proved [231], [232]. The interest in beneficial valorisation of paper ash is originating from a growing trend in paper recycling, which has in Europe reached 71.7% of the paper and cardboard used in 2012. It is estimated that 11 million tons of residues from paper recycling were being generated in Europe annually by 2009. Approximately 70% of that represented deinking sludge [233]. The latter consists mainly of calcite, kaolinite and cellulose fibres, which are broken, after they are recycled 3 to 8 times, to a length too short to be reused [234]. The sludge is commonly incinerated at approximately 800 °C to gain heat for recycling processes at paper mill and to reduce volume for landfilling. The calorific value of sludge is around 8 – 9 GJ per tonne of dry solid matter, however due to a high content of water it is usually lower [235]. The combustion residue is paper ash, which can be used, for example, as supplementary cementitious material [236], [237], or binder for geotechnical composites [232], [238]. The scientific literature reports that PA is a highly alkaline material and can contain both pozzolanic phases, such as glass and metakaoline, and hydraulically active phases, such as lime, larnite, and mayenite. It can be used for the preparation of controlled low strength materials in civil engineering and it also has a great potential for immobilization of both PTE and organic contaminants [232], [239], [240].

1.3.3.2.2 Steelmaking slags

Ferrous slags are formed during iron and steel production. There are multiple types of ferrous slags, which are most commonly divided into blast furnace slag, electric arc furnace slag, and secondary slags. During the production of steel from scrap metal Electric Arc Furnace slag (EAF), Argon Oxygen Decarburization slag, and Ladle slag are formed [241], [242]. The roles of slag forming processes during steelmaking are stabilization of the thermodynamic conditions in the furnace, removal of elements that may harm properties of steel, and protection of molten metal from gas adsorption. Metallurgical steelmaking processes are divided into primary, where EAF C slag is formed, and secondary processes, which result in the formation of SMS slag and EAF S slag. According to Euroslag and Eurofer [242] there were 21.8 Mt of steelmaking slags produced in Europe in 2010. EAF C slag has a high potential for recycling in civil engineering

as a manufactured aggregate. Meanwhile, secondary slags are much less used due to the high content of soluble PTE, such as Cr, V, and Mo. It is also volumetrically unstable, which is a consequence of a mineralogical composition. Namely, the transformation of Ca_2SiO_4 from β to γ causes an increase in the crystal lattice size for 10 to 12%. Tensile forces cause disintegration of crystals leading to powdering of the slag. The same effect can be a result of hydration of MgO and CaO that might also be present in slag. Secondary slags are alkaline material, which contains several mineral phases that are hydraulically active, namely C2S (in β form), C12A7 and C3A. Thus, it can be used as a cementitious binder or a supplementary cementitious material and has the potential for immobilization of contaminants into newly formed hydration products or by adsorption [243]. Applicability of secondary slag was investigated for soil stabilisation [244] and construction of embankments [245]. However, there are only few studies, which deal with immobilization mechanisms of PTE by secondary slags [246], [243], [247], none of them describing the remediation of soil. A term ladle slag is used for secondary slags, which were used in this study, because the same slags, which were designated with this expression in published scientific studies [243], [247].

1.3.3.2.3 Red mud

Approximately 170 million tonnes of red mud were produced worldwide in 2015. For the production of 1 tonne of alumina 1.5 tonnes of red mud are formed in the Bayer process, which is the most frequently used technology for alumina production, used in roughly 95% cases [248]. The process is based on digestion the bauxite ore in hot NaOH solution. Afterwards alumina rich solution is separated from solid residual consisting of iron and aluminium (hydr)oxides, which is called red mud. The latter is currently regarded as a waste, and typically deposited in pits or lagoons in-land or discharged into deep sea. The environmental issues related with RM are connected to its high alkalinity (typically from pH 9 to 13) and possible presence of elevated total concentrations of PTE, for example As, Cu, Cr, and V [248], [249]. However, chemical and physical properties of the red muds vary considerably reflecting their different sources (differences in bauxite composition and the operation of the processing plant) [250]. This means that the potential recycling of each deposit of red mud has to be considered separately, in its own case study. The remediation of contaminated soil with red mud was mostly investigated for less contaminated soils, where immobilization efficiency was tested after mixing of a few mass % (maximally 10 wt.%) of red mud with soil [248]. Literature data reveal that high immobilization capacity of red mud is correlated with the large specific surface area of its particles, where high concentration of surface sorption sites is available for formation of inner sphere complexes with PTE. Different Fe and Al oxides or hydroxides minerals (for example goethite, boehmite), and/or aluminosilicates (for example cancrinite) poses high sorption capacity [251], [252], [253].

1.3.4 Soil legislation

Despite the importance for our society, there is still no specific soil legislation on the EU level. Currently, various policies contribute to soil protection, which are from the field of water, waste, chemicals, industrial pollution, nature protection, pesticides and agriculture. The Soil Data Centre (ESDAC), which is operating under EU Joint Research Centre (JRC) is the official organisation for soil data collection and processing. However, due to a lack of unified approach and cooperation of member states these data are still insufficient [5].

EU has prepared a strategy for the protection of soil, which was accepted by EC in September 2006. Its purpose was to establish a sustainable soil management, to set protective countermeasures for degradation, to sustain functionality of soil and to restore degraded sites. Part of the strategy was the proposal for the Soil framework directive [139]. The proposal included the information, which could serve as a basis for future preparation of soil protection laws in EU. Soil is regarded as a non-renewable resource and is vital to sustain human

activities and for the survival of ecosystems. Therefore, if possible, soil should be used in a sustainable manner, which preserves its basic functions to deliver ecological, economic and social services. Soil is a dynamic system that performs functions, of biomass production, storing, filtration and transformation of nutrients, supporting the water cycle, hosting a biodiversity pool, and acting as a platform for human activities, source of raw materials, carbon pool and sequestration catalysts. In the EU, soils are under increasing environmental pressure. The proposed SFD tackled the problem of soil contamination. It is needed to identify and establish data inventory of contaminated sites in EU, develop national remediation strategies, and remediation measures. Management of these sites is necessary to prevent and mitigate harmful effects on the human health and environment. It was proposed that remediation actions should aim at removal, control, containment or reduction of contaminants, all with a purpose to assure safe future use of the site so it no longer poses risk to human health or to the environment. The funding of these activities should be in line with the "polluter pays" principle. After the proposal of SFD has been pending for 8 years, it has been withdrawn by EC in 2014. Namely, certain member states blocked the adoption of the soil legislation in the European Council in 2010, referring to the subsidiarity principle, addition costs and administrative burdens.

EU Commission in its report from 2012 stated that the condition of soils in Europe is worsening. Although the Cohesion Policy has contributed 3.1 billion EUR for the rehabilitation of degraded sites in the period 2007-2013, there has been no apparent improvement in soil protection due to a lack of common policy. Protection of soil was integrated in 7thEAP [4]. The Programme has highlighted persistent unsustainable land use and soil degradation as one of the most problematic environmental issues. Contamination and sealing must be tackled by sustainable management to achieve land degradation and an exploitation-neutral world. This is even more important and in line with the commitment that the EU will cope with the problems of municipal areas, where approximately 70% of EU citizens are living and contamination can cause the most severe health problems. According to the 7thEAP progress in rehabilitation of contaminated sites in EU will be monitored, awareness about these problems will be raised, and development of BAT will be promoted [4].

Management of contaminated soil is usually affected by a waste or landfill directives [254], [255]. Excavated contaminated soil is regarded as non-hazardous or hazardous waste, which has to be managed according to the waste hierarchy, where landfilling is the least and reuse or recycling are the most desirable options. This is also in consensus with the principle that soil is a non-renewable natural resource, which should be preserved or re-used in a sustainable manner. In management of contaminated soils, the latter can meet end of waste criteria only through recovery operations regarded as R5: *Recycling/reclamation of other inorganic materials* (includes soil cleaning resulting in recovery of the soil), or R10: *Land treatment resulting in benefit to agriculture or ecological improvement* [254]. However, the lack of environmental end-of-waste criteria or criteria for the use of recycled materials in civil engineering creates problems in the utilization of remediated contaminated soil [196]. The highest imperative in the waste Directive, i.e. that the recycled material will not lead to overall adverse environmental or human-health impacts, has to be proved within the legal framework of the member states [256].

European Environmental Agency [257] has introduced the concept of land recycling development, which is within the scope of the 7thEAP. Soil is not regarded just as the non-renewable natural source but also as a base ground for human activities. Soil quality or status (contaminated/virgin/fertile etc.) can determine the use of space within the living environment. Therefore, with the use of Life Cycle Thinking, the selection of the remediation procedure that is going to have the lowest environmental impact is equally important as the prediction of the beneficial future use of the rehabilitated site. This is in line with sustainable land management,

which must prefer reuse of the rehabilitated brownfield site over construction on a greenfield site [257].

The policies on soil quality standards of Germany, Netherlands, and Canada are presented here as the cases of good practice. Their criteria and limit values are set based on predicted land use. German Federal Soil Protection and Contaminated Sites Ordinance [258] has set limit values for playgrounds, residential areas, parks and recreational sites, and industrial areas for parameters As, Pb, Cd, Cr, Ni and Hg. Pseudo total concentrations of PTE in soil with AQE are used. The same extraction procedure is used for testing of soil quality on grasslands for parameters As, Pb, Cd, Cu, Ni, Hg, and Tl. Meanwhile, for agricultural areas and gardens for food production limit values are set for As, Cu, Ni, Zn, Cd, Pb, Tl. Extraction with NH_4NO_3 (DIN ISO 19730:2009-07 [259]) is used, which elutes the fraction of PTE available for plant uptake. German soil quality standard also includes the evaluation of influence of contaminated soil on groundwater quality. For this purpose, extractions of pore solution or leaching procedure DIN 38414-4: 10.84 are used [260], with demineralised water.

Dutch Soil Quality regulations include more parameters for PTE (Sb, As, Ba, Be, Cd, Cr, Co, Cu, Hg, Pb, Mo, Ni, Tl, Sn, V, Zn) and organic contaminants than Germany or Canada. Soil classes for the residential function or industrial function have limit values set on pseudo total concentrations of PTE in soil, by aqua regia extraction. Based on the same extraction procedure interventional values are set for soil below surface water level and for emissions into soil. Meanwhile, the leaching procedure with demineralised water ($L/S=10$) is used for the application of materials in soil, NEN 7375 [261] (tank leaching of monolithic samples) and NEN 7373 [262] (column test for leaching of granular materials) are used for the determination of compliance of building materials in contact with soil or groundwater [263].

Canada has established comprehensive systems of soil quality standards, which include guideline values according to land use, agricultural, residential, commercial, and industrial use. Canadian system also includes a system for the evaluation of risks by identifying the transfer routes and exposure pathways, for determination of Soil Quality Guidelines for Human Health [264].

In the United States of America, the Environmental Protection Agency oversees national environmental management activities and monitors emissions of contaminants. Remediation activities and clean-up activities are funded by a “polluter pays” principle. Rehabilitation of degraded sites or the so-called Superfund clean-up is based on several acts. Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) were adopted in 1980, after Love Canal disaster. According to this act a National priority list of 1785 contaminated sites that require urgent remediation was set up. This was followed by adoption of the second act Resource Conservation and Recovery Act (RCRA) that allowed the public authorities to perform clean-up activities and recover funds by legal lawsuits from polluters. The Superfund Amendments and Reauthorization Act (SARA) was accepted in 1986 to enhance clean-up activities of contamination sites on the priority list by adding 8.5 billion USD new investments. US EPA is investing a lot of effort in research and development of new remediation technology and approaches [10]. The Superfund Innovative Technology Evaluation (SITE) program has supported remediation technology development within the scope of four related sub-programmes: Demonstration, Emerging Technologies, Monitoring and Measuring, Technology Transfer. The Contaminated Site Clean-Up Information (CLU-IN) is a US EPA forum for all soil remediation stakeholders, which provides information of all related topics [265].

On the other hand, United States, Environmental Protection Agency, has formed one of the most sophisticated and extensive soil and environmental quality standards, regarded as the tool for Regional Screening Levels for Chemical Contaminants at the Superfund Sites programme. The latter is part of the US EPA Risk Assessment tools and was made according to Guidance for Developing Ecological Soil Screening Levels [266]. Screening values can be used to identify those contaminants of potential concern in soils requiring further evaluation in a baseline

ecological risk assessment. The values are set as total concentrations for residential and industrial soils. However, limits are also set for air, groundwater, and tap water, as well as for daily intake and other risks related to exposure and toxicity of parameters.

In Slovenia soil policy is covered by an Environmental Protection Act (The Environmental Protection Act (Official Gazette of RS, No. 61/17 [267]), and a Decree on the limit, warning and critical levels of hazardous substances in the soil (Official Gazette of RS, No. 68/96 [147]). The latter sets criteria for soil quality on limit values, which are determined with AQE of pseudo-total concentrations of PTE in soil. Therefore, values are only informative and indicative for possible contamination or risk assessment. Mobility, bioavailability, or toxicity, which depends on the PTE speciation, is not determined. A new “Decree on status of soil” is in preparation, which is still based on determining pseudo-total concentrations of PTE that determine quality classes for agricultural areas, permitted values for areas of children playgrounds, residential, and industrial areas. In the new Decree also, average background values of PTE in Slovenian soils are taken into account. Other legislative acts, which affect the soil policy in Slovenia, are the Decree on the limit input concentration values of dangerous substances and fertilisers in soil (Official Gazette of RS, No. 19/17 [268]), Decree on burdening of soil with waste spreading (Official Gazette of RS, No. 61/11 [269]), Decree on waste landfill (Official Gazette of RS, No. 36/16 [152]), and Decree on waste (Official Gazette of RS, No. 69/15 [270]). Excavated contaminated soil is regarded as a non-hazardous or hazardous material according to the Slovenian waste legislation. After recovery operations, remediated soil used as recycled material in civil engineering has to comply with the Slovenian policy in the field of waste, construction materials, and environment.

Chapter 2

Aims and Hypothesis

In the light of the upcoming water crisis, it is very important to develop new procedures for the purification of wastewater for its reuse. Among available alternative sources of water, the reuse of municipal wastewaters is one of the most perspective solutions. Municipal wastewaters, which are one of the biggest stressors of aquatic environments, have to be cleaned by wastewater treatment plants before being released into the environment. However, effluent water from wastewater treatment plants is not appropriate for reuse because it still contains too high concentrations of contaminants. The first part of this work consists of a study for the development of a procedure for remediation of effluent water from the SBWTP up to a suitable quality for secondary human needs. The procedure is based on the utilization of nZVI, which were proved to be efficient for water remediation in numerous scientific studies. Despite their experimentally proven beneficial characteristics, nZVI were until now not yet tested and utilised for the purpose of municipal wastewater reuse applications. Investigation of behaviour and efficiency of nZVI for the remediation of real effluent water from a SBWTP was therefore crucial for the development of the most optimal remediation procedure. Due to a complex composition and interactions between microbiological, inorganic and organic contaminants in effluent water, it is needed to carefully optimise nanoremediation up to a highest possible efficiency for simultaneous removal of multiple contaminants.

The following hypotheses were set for the water remediation study:

- Differences in physical, microstructural and chemical characteristics, which exist between differently synthesized nZVI, are reflected in efficiency and appropriateness of these nZVI for remediation of effluent water from the SBWTP.
- By understanding the mechanisms and the kinetics of disinfection, removal of PTE and change in concentration of nitrogen species, the most optimal nZVI dose and mixing time during nanoremediation can be set.
- During remediation nZVI are transformed into harmless iron oxides, which are efficiently removed from water by settling.
- Water, which is safe for reuse, can be produced for effluent water from the SBWTP according to the optimal nanoremediation procedure in combination with conventional water remediation methods.

The aims of the water nanoremediation study within the scope of the doctoral thesis were the following:

- To characterize three different nZVI materials (one synthesized in the laboratory and two commercially available) and subsequently to define physical, microstructural and chemical differences among them, due to differences in synthesis of materials.
- To determine the variability and seasonal fluctuations in composition of effluent water from the SBWTP, by analysing microbiological parameters (*Escherichia coli*, Intestinal Enterococci, *Clostridium perfringens*, and coliform bacteria), inorganic parameters (ammonia, nitrite, nitrate, Al, As, B, Cd, Cr, Cu, Fe, Hg, Mn, Na, Ni, Pb, Sb, Se and Zn), and BOD₅ and COD to evaluate operational efficiency of SBWTP.
- To determine which of differently synthesised nZVI are the most efficient for remediation of real effluent water, from the scope of dose dependent disinfection efficiency, and removal of inorganic contaminants.

- To optimize the nanoremediation with the use of the most appropriate nZVI, by further analysing the influence of different operational parameters (nanoparticle dose, mixing and settling time) on disinfection efficiency, removal of inorganic parameters, and behaviour of nanoparticles in water.
- To combine the most optimal nanoremediation procedure with conventional water remediation methods of oxidation, ion exchange and filtration through activated carbon, to produce water safe for reuse, which is confirmed by analyses of disinfection efficiency, removal of inorganic and organic parameters.

The soil contamination is a persistent problem worldwide, which has to be solved by remediation of soil in the most sustainable and economical way. Immobilization is a remediation procedure, at which soil is mixed with additives to form inert composite, which can be potentially used *in situ* for the purpose of rehabilitation of degraded area. The use of recycled materials (paper ash, fly ash from coal combustion, ladle slag from steelmaking processes and red mud from bauxite processing) for this purpose represents a sustainable alternative to the use of Portland cement. Namely, immobilization is in both cases governed by similar mechanisms. However, the optimal design of composite, in which contaminants are efficiently immobilised, is dependent on several factors. First, the content and forms in which contaminants are present in soil have to be characterised, which was from the mineralogical point of view for the first time documented for the case study of the soil from the Old Zinc-works in Celje. Secondly, physical, chemical and mineralogical characteristics of immobilization additives have to be well defined, because this determines the main mechanisms of immobilization in composite. Potential hydraulic or pozzolanic reactivity of additives that leads to the formation of new minerals that chemically incorporate contaminants and bind the composite is especially important. The use of composites from a technical point of view is determined by the basic geotechnical properties, which are optimum water content to achieve maximal compaction by basic geotechnical means, water permeability and unconfined compressive strength. The environmental acceptability of the obtained composite has to be confirmed by leaching tests with water, which is the main vector for the transfer of contaminants in the environment, where such a composite can be used.

The following hypotheses were set for the soil remediation study:

- Recycled materials, paper ash, fly ash from coal combustion, ladle slag from steelmaking processes and red mud from bauxite processing, in contact with water form new mineral phases that can potentially incorporate PTE for their chemical immobilization.
- Combination of paper ash with fly ash from coal combustion, ladle slag from steelmaking processes and red mud from bauxite processing, for the preparation of ternary composites can result in enhanced PTE and sulphate immobilization efficiency and better geotechnical properties compared to binary composites, in which only single additives are used.
- Inert geotechnical composites, according to limit values from national landfilling policy, can be prepared from soil contaminated by metallurgical residues, with the use of recycled materials as additives for PTE and sulphate immobilization.

The aims of the soil remediation study, which represents the second part of the doctoral thesis, are the following:

- To investigate physical, chemical and mineralogical characteristics of contaminated soil, especially from an environmental point of view, and to define the most contaminated soil from the Old Zinc-works site, which is used for a real-case experimental study of immobilization.
- To characterize several recycled materials for their utilization as potential immobilization additives from their mineralogical, physical, chemical characteristics and their potential hydraulic activity. Also, the aim of preliminary immobilization

experiments is to investigate the influence of low concentrations of additives and their alkalinity on immobilization of Cd, Mo, Pb and Zn.

- To investigate and compare the potential of paper ash, fly ash from coal combustion, ladle slag from steelmaking processes and red mud from bauxite processing for immobilization of PTE from contaminated soil at the addition of 25 wt.%, which was preliminary determined by empirical tests to be the most perspective ratio.
- To investigate geotechnical composites from contaminated soil and immobilization additives in terms of time-dependent trend in immobilization efficiency, determination of possible remediation mechanisms, and environmental acceptability.
- To test the possible benefits of using paper ash in combination with coal fly ash, ladle slag and red mud, with a purpose of enhancing the immobilization efficiency and basic geotechnical characteristics.
- The final aim is to investigate and compare the basic geotechnical characteristics of the composites.

Chapter 3

Structure of the Dissertation, Material and Methods

This work is divided into two separate multiphase studies:

- Optimization of the use of nanoscale zero-valent iron particles for remediation of effluent water from the small biological wastewater treatment plant in combination with complementary conventional methods for municipal wastewater reuse.
- Development of the remediation procedure for contaminated soil by the immobilization approach with the use of recycled materials from the industry for beneficial environmentally acceptable use of obtained geotechnical composite.

Although we are dealing with two different media, water and soil, several investigation approaches and analytical tools were used in both cases.

Experimental work within the scope of the water nanoremediation study, which is presented on the flow-chart in Fig. 3.1, was divided into multiple parts.

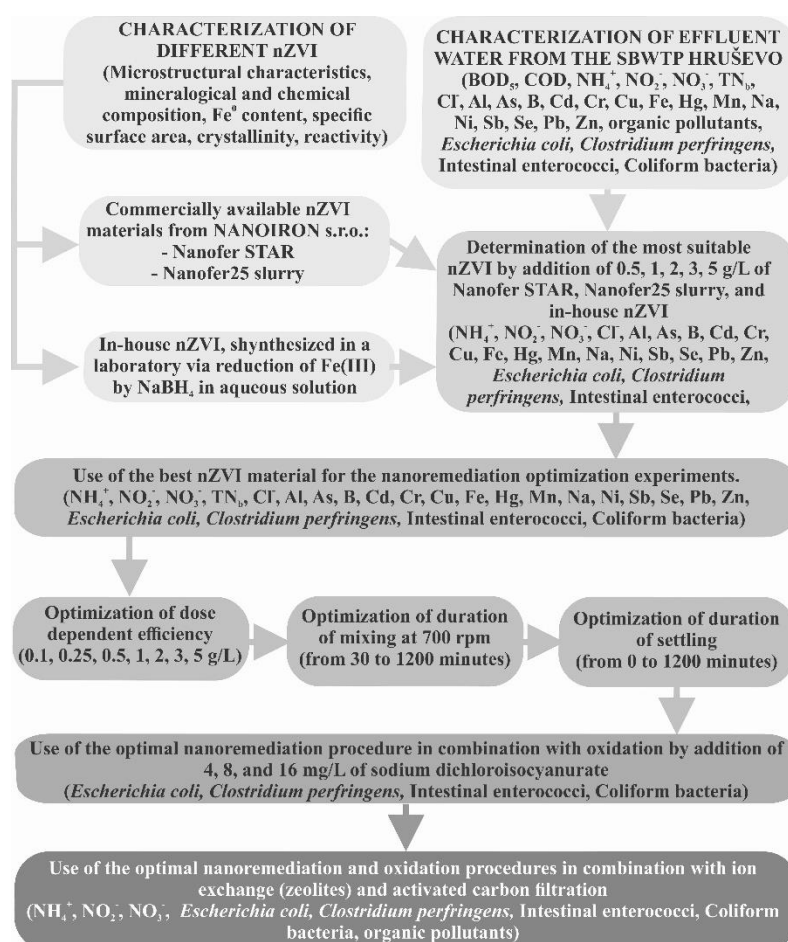


Figure 3.1: Flow-chart of work in the water remediation study.

Initially different nZVI materials were characterized, which were commercially available or synthesized in a laboratory. In parallel, effluent water from the SBWTP was analysed. This was followed by a second part of the study, water remediation experiments for water remediation and development of optimised water remediation procedure for water reuse. The ultimate goal of this study was to develop an optimized water remediation procedure for the preparation of drinking water [271] from effluent water.

Synthesis of in-house nZVI, mineralogical analyses, determination of specific surface area, and nanoremediation experiments were conducted at the Slovenian National Building and Civil Engineering Institute (ZAG), at the Laboratory for Stone, Aggregate and Recycled Materials, and at the Laboratory for Polymers. Analyses of total elemental composition of nZVI and inorganic parameters in water samples were performed at the Jožef Stefan Institute, at the Department of Environmental Sciences. Microbiological analyses, determinations of BOD₅, COD, and TN_b, analyses for the presence of organic pollutants in water were made at the National Laboratory for Health, Environment and Food, Department for Microbiologic Analysis of Food, Water and Other Environmental Samples, located in Novo mesto.

Soil remediation study was also divided in multiple parts, which are presented on the flow-chart in Fig. 3.2. In the first part, information about contamination at the Old Zinc-works site were gathered. Location of the most contaminated soil was determined at the site and further detailed characterization of soil was carried out. In the following part, multiple immobilization additives were collected and characterised in details. Finally, immobilization experiments were performed, which represented the third part of the study.

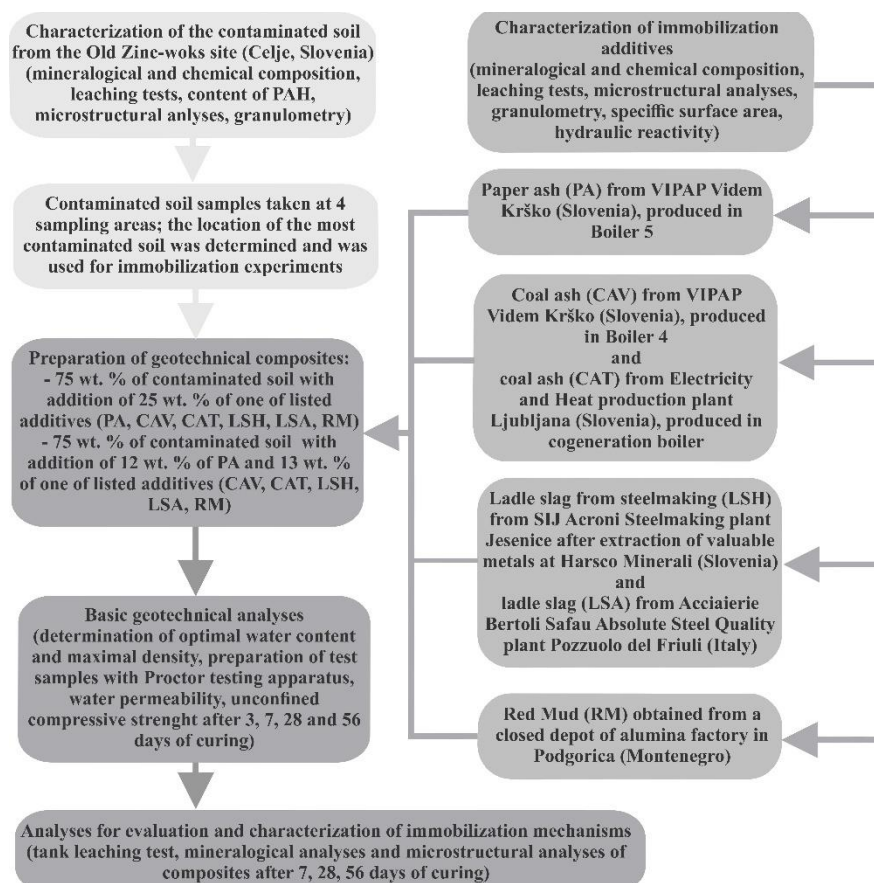


Figure 3.2: Flow-chart of work in the soil remediation study.

Mineralogical and microstructural analyses, leaching tests, grain size distribution, specific surface area, water permeability tests, Proctor compaction tests and unconfined compressive strength measurements were made at ZAG, at the Laboratory for Stone, Aggregate and

Recycled Materials, and at the Department of Geotechnics and Infrastructure, the Section for Geotechnics. The preparation of test samples was also performed at ZAG.

Analyses of eluates for different chemical parameters were performed at the Jožef Stefan Institute, Department of Environmental Sciences.

Total elemental analyses of contaminated soil and immobilization additives with the X-ray fluorescence method were carried out at the Faculty of Natural Sciences and Engineering, University of Ljubljana, Department of Geology.

Both studies also have a common point in the investigation of behaviour and remediation efficiency for a group of selected elements (Al, As, B, Cd, Cr, Cu, Fe, Hg, Mn, Na, Ni, Pb, Sb, Se and Zn), for which a common term Potentially Toxic Elements (PTE) was used.

3.1 Materials and Methods for Water Nanoremediation Study

3.1.1 Materials

The ferric chloride (FeCl_3) (98%) and sodium borohydride (NaBH_4) (98%) used for the synthesis of the in-house nZVI were supplied by Sigma-Aldrich (Steinheim, Germany). Samples of two types of commercially available nZVI (Nanofer25 slurry; stable water-based dispersion containing 20 wt.% of non-stabilized nZVI, and Nanofer STAR; air-stable powder of nZVI stabilized by inorganic stabilizers) were supplied by Nano Iron. s.r.o. (Rajhrad, Czech Republic).

Merck (Darmstadt, Germany) suprapure acids and Milli-Q water ($0.056 \mu\text{S}/\text{cm}$) obtained by means of a Direct-Q 5 Ultrapure water system (Millipore Watertown, MA, USA) were used for the preparation of the samples and the standard solutions. A Stock Multi Element XVI standard solution (100 mg/L in 5% HNO_3) (Merck, Darmstadt, Germany) was used for the preparation of working standard solutions for ICP-MS determinations.

Concentrated HCl 37% (Sigma Aldrich, St. Louis, Missouri, USA), was used in the chemical procedure for determining nZVI reactivity and Fe0 content.

Concentrated $\text{HNO}_3 \geq 65\%$ (Sigma Aldrich, St. Louis, Missouri, USA), was used for acidification of water samples prior to analyses for PTE by ICP-MS.

All water samples for the determination of inorganic parameters were, prior to the analyses, filtered through membrane filters with a pore size of $0.45 \mu\text{m}$ (syringe filter, Minisart, Sartorius Stedim Biotech GmbH, Goettingen Germany).

Sodium dichloroisocyanourate (NaDCC) (Pliva, Zagreb, Croatia), activated charcoal powder (Sigma Aldrich, St. Louis, Missouri, USA), and granular zeolite – clinoptilolite with grain size distribution of 0.7 – 1.2 mm and cation exchange capacity of 1.4 mmol/g (Zeocem, Bystre, Slovakia), were used for water remediation experiments.

3.1.2 Instrumental

Structural microanalyses of the selected nZVI were performed using a Field-Emission Scanning Electron Microscopy (FESEM, Supra 35 VP, Carl Zeiss, Oberkochen, Germany). The nZVI were dispersed in absolute ethanol, sonicated, and then drop-wise transferred onto a gold membrane under vacuum. The in-Lens detector was used at an operating voltage of 5 kV and at a working distance of 4.5 mm.

Analyses of the nZVI internal structure, measurements of the core diameter and shell thickness, and Selected Area Electron Diffraction (SAED) analyses, were performed using a Transmission Electron Microscope (TEM Jeol 2100, Tokyo, Japan) with a W filament. The nZVI were dispersed in absolute ethanol, sonicated, and then transferred onto a copper carbon-lacy grid. The accelerating voltage used for the TEM analysis was 200 kV, and in the case of the SAED analyses the camera length was 30 cm.

The specific surface area of the nZVI was determined by a Single point Brunauer-Emmet-Teller (BET) surface area analyser: Micrometrics ASAP 2020 (Micrometrics GmbH, Norcross, GA, USA), with N₂ as the adsorptive agent. Before the BET analysis, the particles were dispersed in absolute ethanol, centrifuged (CENTRIC 322A Tehnica, Železniki, Slovenia) for 15 minutes at 4000 rpm, collected with a magnet and dried in a vacuum to the constant mass. The BET analyses were performed by evacuation for 30 minutes at 2 Pa and at 110°C.

X-ray Powder Diffraction (XRD) analyses of the nZVI were performed using an Empyrean PANalytical diffractometer (PANalytical B.V., Almere, the Netherlands) with Cu K α irradiation ($\lambda = 1.54056 \text{ \AA}$) and a graphite monochromator, at 45 kV and a current of 40 mA, over the 2θ angular range from 5° to 100° , using a step size of 0.01° and a measuring time per step of 200 seconds.

Table 3.1: ICP-MS operating parameters for the determination of 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			
Carrier gas flow		1.05 L/min		0.75 L/min
He gas flow		4.5 mL/min	10 mL/min	
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			
<i>Data acquisition parameters</i>				
Isotopes monitored		¹¹ B, ²⁷ Al, ⁵² Cr, ⁵⁵ Mn, ⁵⁶ Fe, ⁶⁰ Ni, ⁶³ Cu, ⁶⁶ Zn, ⁷⁵ As	⁷⁸ Se	¹¹¹ Cd, ¹²³ Sb, 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

The samples of untreated effluent water were digested with nitric acid using a CEM MARS 5 microwave oven (CEM Corporation, Matthews, NC, USA).

The total concentrations of selected elements in nZVI (after acid digestion), and water samples were determined by an inductively coupled plasma mass spectrometer (ICP-MS), model 7700x (Agilent Technologies, Tokyo, Japan) according to SIST EN ISO 17294-2, 2005. Water samples were prior to analysis filtrated through membrane filter with $0.45 \mu\text{m}$ pores and acidified with nitric acid to $\text{pH} < 2$. The operating parameters of the ICP-MS are presented in Table 3.1. The accuracy of this method, expressed as relative standard deviation, is approximately $\pm 1\%$ [272].

River water reference material purchased from the National Research Council (Ottawa, Ontario, Canada) was used to check the accuracy of the ICP-MS analytical results. The determined concentrations agreed well with the certified values (agreement better than $\pm 3\%$).

The concentrations of ammonium cation (NH_4^+), nitrites (NO_2^-), and nitrates (NO_3^-) in water samples were determined by UV/Vis Absorption spectrophotometry (using a HACH DR/2010 Portable Data-logging Spectrophotometer, Loveland, CO, USA). All water samples were prior to analysis filtrated through membrane filter with 0.45 μm pores and were not acidified. The concentrations of NH_4^+ were determined by the Nessler Method, NO_2^- by using NitraVer powder pillows, and NO_3^- by the Cadmium Reduction Method using NitraVer powder pillows. Nessler method is based on colorimetric reaction between potassium, mercury, and iodine, to produce a yellow-brownish colour. The absorption band is in the wavelength range between 400 and 425 nm. Spectrophotometric determination of NO_2^- is based on involving p-nitroaniline and sulphanilamide with ethyl acetoacetate as the coupling agent. The absorbance is then measured at wavelengths 507 and 356 nm, respectively. Determination of NO_3^- is based on metal cadmium reduction of nitrate in the sample to NO_2^- . This is followed by a reaction of nitrite with sulfanilic acid to form an intermediate diazonium salt, which couples with gentisic acid to form an amber-coloured solution. The measurement wavelength is 500 nm for spectrophotometers. The accuracy of UV-VIS spectrophotometry, expressed as relative standard deviation, is $\pm 3\%$.

Analyses for the presence of organic contaminants in water were performed using Agilent Technologies (Santa Clara, California, USA) Gas Chromatograph (6890N, model G3171A) – Mass Spectrometer (5975) (GC-MS). Fresh effluent water and samples from remediation experiments were first filtrated through membrane filter with 0.45 μm pores, and then extracted in liquid-liquid state by dichloromethane. For chromatography column HP-5ms 30 m (Agilent, Santa Clara, California, USA) was used. SCAN mode and He as gas carrier phase were used during measurement, which was done in the temperature range from 100 to 250 $^\circ\text{C}$. Identification of organic pollutants was made on obtained chromatograms based on matchmaking with data from GC-MS chromatographic mass spectra library for organic substances of the National Institute of Standards and Technology (NIST).

Measurements of pH and conductivity in the water samples were performed by means of a WTW pH 3110 (Weilheim, Germany) meter and a Yokogawa SC8221-E (Tokyo, Japan) conductivity meter, respectively.

3.1.3 Effluent water

Effluent water samples were taken at the outflow of the SBWTP located at the village of Hruševno near Ljubljana in central Slovenia (coordinates; D48/GK Y: 454162, X: 102620). The SBWTP has a capacity of 100 PE and is of the biological aerobic Rotating Biological Contactor (RBC) type. The effluent water is released into the Gradaščica River, which belongs to the Sava River basin. A schematic presentation of this SBWTP is given in Fig. 3.3, while the picture of the SBWTP with open top covers is given in Fig. 3.4(1). Sampling (Fig. 3.4(2)) was performed 14 times, in all seasons, between 2014 and 2016. Depending on the type of analysis being performed, 4 to 20 L of effluent water was collected at the outflow of the SBWTP with a telescopic swing swivel dipper (Fig. 3.4(2)). Each time sampling was performed between 9:00 and 10:00 am to avoid variabilities between effluent water samples due to daily fluctuations in concentrations of contaminants [36]. Samples for analyses of inorganic and microbiological parameters were stored and transported in sterile plastic containers (Fig. 3.4(4)). Meanwhile, for analyses of organic parameters amber coloured glass bottles were used to transport and store the samples. Analyses were performed immediately after the delivery to the laboratory.

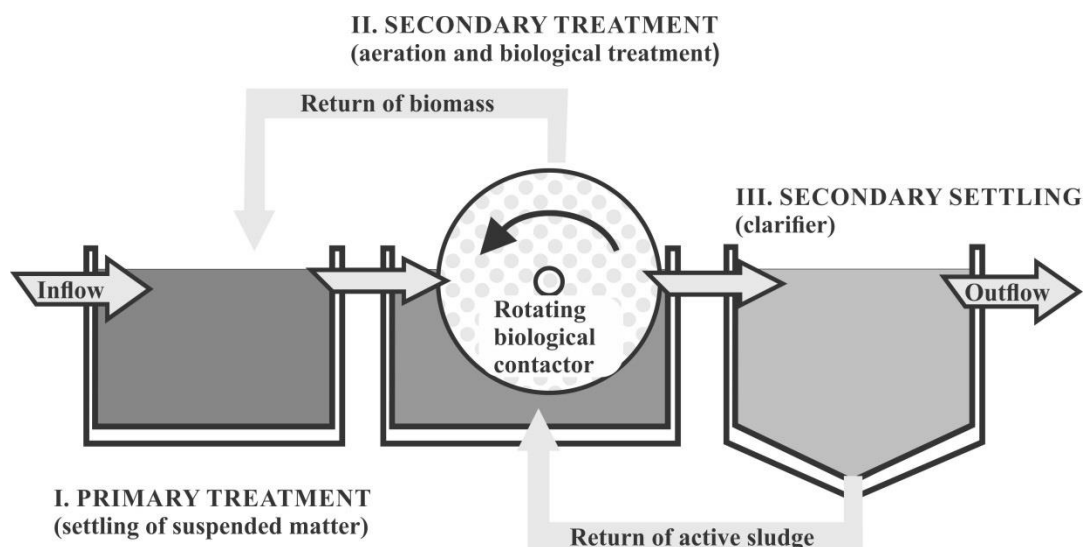


Figure 3.3: Scheme presentation of the SBWTP Hruševo.

Effluent water for remediation experiments was sampled according to the same protocol and 8 times. The characteristics of effluent samples for the experimental work ($n=8$) were each time compared with those from long-term sampling at the SBWTP ($n=14$). Student's t-test was used for statistical evaluation and comparison of mean values of results of 14 untreated effluent water samples and the individual results of 8 untreated samples intended for remediation experiments. There were no statistically significant differences between the means with when significance level $\alpha = 0.05$ was considered. Experiments were performed on fresh samples, immediately after sampling at room temperature ($22 \pm 1^\circ\text{C}$).

Biological oxygen demand (BOD_5) and chemical oxygen demand (COD) were determined in effluent water samples by the standardised methods given in SIST EN 1899-1, 2:2000 [273] and SIST ISO 6060:1996 [274], respectively.

The total concentrations of selected PTE (Al, As, B, Cd, Cr, Cu, Fe, Hg, Mn, Na, Ni, Pb, Sb, Se and Zn) in untreated effluent water were determined by ICP-MS after microwave digestion. Meanwhile, water sample from remediation experiments were analysed for the same list of PTE, filtered and acidified.

Filtrated and non-acidified effluent water samples and water samples from experiments were used for the determination of ammonium cation (NH_4^+), nitrates (NO_3^-), and nitrites (NO_2^-) by spectrophotometry, and for the measurement of total bound nitrogen (TN_b). The TN_b was determined by applying the method described in SIST EN 12260:2003 [275], following oxidation to nitrogen oxides. The total organic bound nitrogen content was determined by subtracting of the sum of the concentrations of the ammonium nitrogen (ammonium N), the nitrate nitrogen (nitrate N), and the nitrite nitrogen (nitrite N) concentrations from the concentration of TN_b .

The presence of organic contaminants was analysed by GC-MS on filtrated and non-acidified effluent water and water samples from experiments. They were transported and stored in amber coloured bottles.



Figure 3.4: The SBWTP Hruševo (1) with its top open; sample is taken with a telescopic swing swivel dipper at the outflow (2) and transferred in sterile plastic containers (3) and (4).

Microbiological analyses were performed on non-filtrated and non-acidified effluent water and samples from experiments, by following the standardized procedures. The most probable number of *Escherichia coli* and Coliform bacteria per 100 mL (MPN/100 mL) were determined according to ISO 9308-2:2012 [276], as well as the MPN of Intestinal Enterococci per 100 mL according to the Standard Methods given in 9230E:2007 [277]. The number of colony forming units (CFU) per 100 mL of the bacteria species *Clostridium perfringens* was determined following the procedure prescribed in the Directive of the European Council 98/83/ES [278].

3.1.4 Nanoparticles

The investigated nZVI materials were chosen based on literature overview, where they were most often used both for scientific studies and for real-case application.

The in-house nZVI particles were synthesised following the procedure described by Bae et al. [279] and Wang and Zhang [61]. Solutions of ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) (0.11 M) and sodium borohydride (NaBH_4) (0.9 M) were prepared with nitrogen purged demineralised water. The iron solution was intensively mixed with a magnetic stirrer, when borohydride solution was dropwise added. Nanoparticles have precipitated after exothermic reaction and the suspension was left to mix until bubbles of H_2 ceased to form. The particles were isolated by centrifugation at 4000 rpm for 15 minutes and collected by means of a magnet (Fig. 3.5 – In-house nZVI). The excess solution was decanted, and the nanoparticles were thoroughly rinsed three times with nitrogen-purged demineralised water. The in-house nZVI particles were freshly synthesised before each experiment. Prior to their use, they were dispersed in demineralised water by sonication for 10 min.



Figure 3.5: In-house nZVI in suspension and collected over a magnet, Nanofer STAR powder, and Nanofer25 slurry in a beaker.

The Nanofer STAR was used in a dry powdery form whereas the Nanofer25 slurry was dispersed by vigorous mixing for 10 min before its use (Fig. 3.5 – Nanofer STAR and Nanofer25 slurry). Both of these two commercial products were stored in airtight containers, cooled to 5 °C.

Based on detailed analyses of nZVI materials the following characteristics were compared: microstructural characteristics, mineralogical composition and crystallinity, particle size distribution, total elemental composition, Fe⁰ content and reactivity.

The, microstructural characteristics, and size distribution was determined by measurements of the diameters of the nZVI on FESEM and TEM. The shell thickness of the nZVI was determined using TEM microimages, where a clear contrast between the core and less dense shell (which is a lower Z-value material) is visible. The crystallinity of the nZVI was determined by TEM, SAED, and XRD, which was also used for analyses of mineralogical composition. The BET analysis was used for a specific surface area measurement. The available Fe⁰ content in the nZVI was determined by a modified H₂ evolution method, which is schematically presented in Fig. 3.6, based on the principle described by Liu et al. [105]. The method is based on reaction between acid (HCl) and Fe⁰, where 1 mole of elemental iron produced 1 mole of H₂ gas. The reaction is performed in airtight system. After acid is introduced into the water suspension of nZVI, H₂ is emitted and directed into the burette, where the volume is measured when it supplants water. The gas pressure in the system is equalised, with the outside air pressure. Thereby, the calculation of H₂ quantity is possible according to the ideal gas law equation (Fig. 3.6). Where P is outside air pressure, V is a volume of emitted H₂, n is the amount of H₂ in moles, R is ideal gas constant (8.314 kg m²/s² K mol), and T is air temperature (Kelvin). According to the molar ratio between Fe⁰ and generated H₂ the chemical reaction, the quantity of the former is determined.

To check the purity of the nZVI, the total concentrations of selected elements were determined by ICP-MS after their digestion in hydrochloric acid.

3.1.5 Water remediation experiments

3.1.5.1 Determination of suitable nZVI

Effluent water sample was divided in 2200 mL aliquots, which were transferred to 3000 mL sterilized glass beakers. All three nZVI materials were separately added in concentrations 0.5, 1, 2, 3, and 5 g/L. The concentrations were chosen on the basis of scientific literature reports of similar experimental studies (for example [65], [91], [280], [281]) and from reports of real-case applications [64]. The aliquots of effluent water sample were after the addition of nZVI mixed with a laboratory blender for 60 min at 500 rpm with a PTFE paddle. This was followed by 1200 min settling. Afterwards, water samples were carefully taken from top water level with a sterile syringe, without disturbing the oxidized iron sediment at the bottom. Samples were analysed for microbiological parameters (*Escherichia coli*, Intestinal Enterococci, *Clostridium perfringens*, Coliform bacteria) and inorganic parameters, including selected PTE and nitrogen

species (Al, As, B, Cd, Cr, Cu, Fe, Hg, Mn, Na, Ni, Pb, Sb, Se, Zn, NH_4^+ , NO_2^- , NO_3^- , and TN_b). The experimental results are given as a mean value from three replications.

3.1.5.2 Optimization of nanoremediation parameters

Experiments for optimization of the nanoremediation procedure were performed with the use of nZVI, which were in the previous experimental phase proved to be the most efficient. Experiments were conducted in the same manner as described in clause 3.1.5.1. Effluent water sample was divided in 2200 mL aliquots, which were transferred in 3000 mL sterilised beakers. Water samples were after each nanoremediation experiment carefully taken from a top water level with a sterile syringe, without disturbing the oxidized iron sediment at the bottom, for analyses.

In the first experiment, lower concentrations of nZVI, namely 0.1, 0.25, 0.5 g/L, were tested at mixing speed 500 rpm, at slightly extended mixing duration of 240 min, and settling time 1200 minutes.

The second experiment was devised to test remediation efficiency at different times of mixing (30, 60, 120, 240, 390, 600, 780, 960, 1200 min), with the use of 0.1 and 0.5 g/L of nZVI. Mixing speed was 500 rpm and settling time was reduced to 180 min to exclude possible effects on remediation efficiency due to a time of settling. Analyses of microbiological parameters (*Escherichia coli*, Intestinal Enterococci, *Clostridium perfringens*, Coliform bacteria), PTE and nitrogen species (As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Sb, Se, Zn, NH_4^+ , NO_2^- , and NO_3^-) were made in experiments for optimization of nZVI dose and mixing time. The experimental results are given as a mean value from two replications.

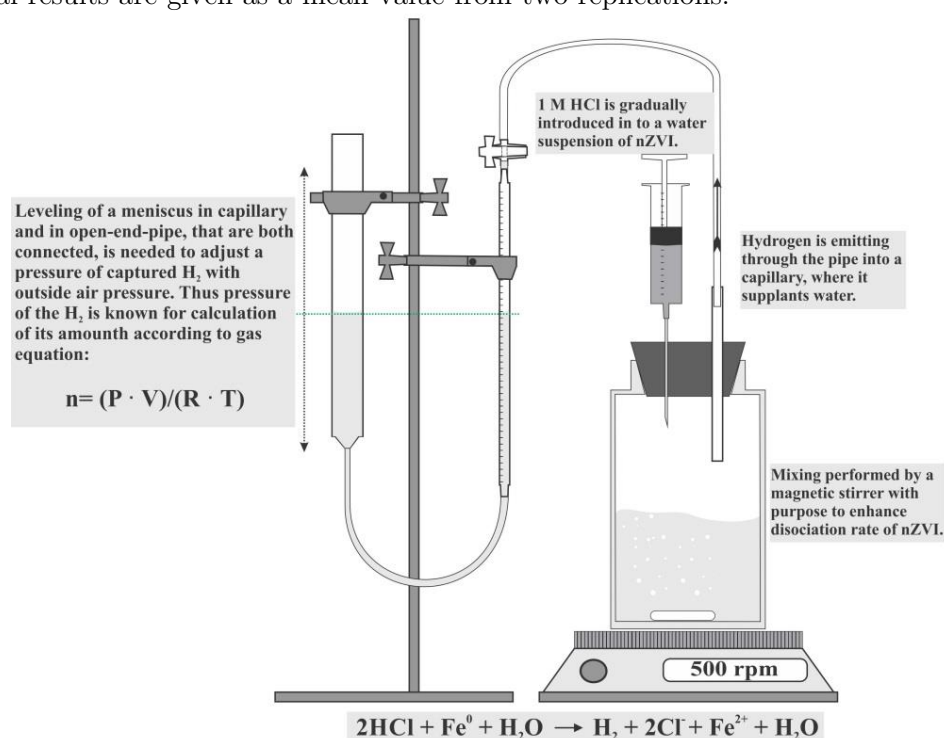


Figure 3.6: Laboratory set-up for chemical determination of Fe^0 content in fresh nZVI after effluent water remediation.

Optimal settling time and kinetics of oxidation of nZVI were tested with nZVI concentrations 0.1, 0.25, 0.5, and 1 g/L, in 2200 mL aliquots taken from the effluent water sample. Nanoremediation was conducted at mixing speed 500 rpm and mixing time 240 minutes. Then water samples were carefully taken from top water level with a syringe at 30,

60, 180, 600, and 1200 min of settling. Concentration of iron in suspended and dissolved form was determined by ICP-MS after the filtration of water samples through a membrane filter with a pore size of 0.45 μm . Content of Fe^0 in nZVI at different times of settling was determined by H_2 emission method (Fig. 3.6). Sediment of settled iron particles was analysed by XRD after it was collected at 1200 min of settling time.

3.1.5.3 Optimization of additional stages of remediation

Most of the contaminants were removed from effluent water with the use of optimized nanoremediation procedure. However, additional conventional treatment methods were needed to obtain the quality of remediated water according to criteria for drinking water. First, experimental treatments with the use of oxidizing agent were performed. Effluent water sample, divided in aliquots of 2200 mL, was treated according to the optimal nanoremediation procedure. However, three concentrations of nZVI were used, 0.1, 0.25, and 0.5 g/L, to test if the lowest concentrations of nZVI can be effectively used in combination with the oxidizing agent. Treated effluent water samples after nanoremediation were carefully taken from top water level by a sterile syringe, without disturbing the sediment of iron particles at the bottom. Samples were transferred in new 2000 mL sterile glass beakers, and treated with 4, 8, and 16 mg/L of sodium dichloroisocynourate (NaDCC). The latter is a commonly known disinfection substance [282]. Concentrations of NaDCC, which were used, are higher than recommended for disinfection of drinking water from taps at households (Clasen & Edmondson, 2006). This is because effluent water after nanoremediation is still containing bacteria, organic and inorganic contaminants that consume more free available chlorine for efficient purification. After the addition of NaDCC to nanoremediated effluent water samples, the latter were mixed with a glass stirring bar and left to stand still for 60 minutes. Disinfection efficiency was determined with results of analyses of microbiological parameters (*Escherichia coli*, Intestinal Enterococci, *Clostridium perfringens*, and Coliform bacteria). The experimental results are given as a mean value from two replications.

In the following phase partly purified effluent water was, after nanoremediation and treatment with NaDCC, filtrated through zeolite column to remove NH_4^+ and iron. Namely, zeolites are known to effectively remove NH_4^+ and metal cations from water [283]. Effluent water samples in aliquots of 2200 mL were treated according to the optimal nanoremediation procedure, with nZVI concentrations 0.1, 0.25, and 0.5 g/L. Then aliquots of 2000 mL effluent water were further treated by 8 mg/L of NaDCC. Finally, water samples were filtrated through zeolite column, which contained 400 g of granular zeolite. Concentrations of nitrogen species were analysed after every stage of remediation. The experimental results are given as a mean value of two replications.

In the final experimental phase 12000 mL of effluent water was remediated. First, the sample was treated according to the optimal nanoremediation procedure. This was followed by disinfection with an optimal amount of NaDCC. Partly remediated water was in the final stage treated by percolation through zeolite and activated charcoal column. Activated charcoal was used to remove the remaining organic contaminants [46]. Column was composed of 400 g of granular zeolite and 100 g of activated charcoal to treat 8000 ml of water. Removal efficiency for organic contaminants was determined by qualitative analyses of GC-MS spectra of effluent water, before remediation, after nanoremediation and after percolation through a column of activated charcoal. All microbial and inorganic parameters were also analysed at these stages of the remediation procedure and compared with limit values for drinking water (Official Gazette of RS, No. 51/17 [271]).

3.2 Materials and Methods for Soil Remediation Study

3.2.1 Materials

Samples of contaminated soil (CS) were obtained at 4 sampling areas at the Old Zinc-works site (Celje, Slovenia). Areas are presented in Fig. 3.7, encircled with a dashed line. They were defined according to the information from the report of Gobec [155], who has performed systematical sampling and chemical analyses of the CS from these areas.

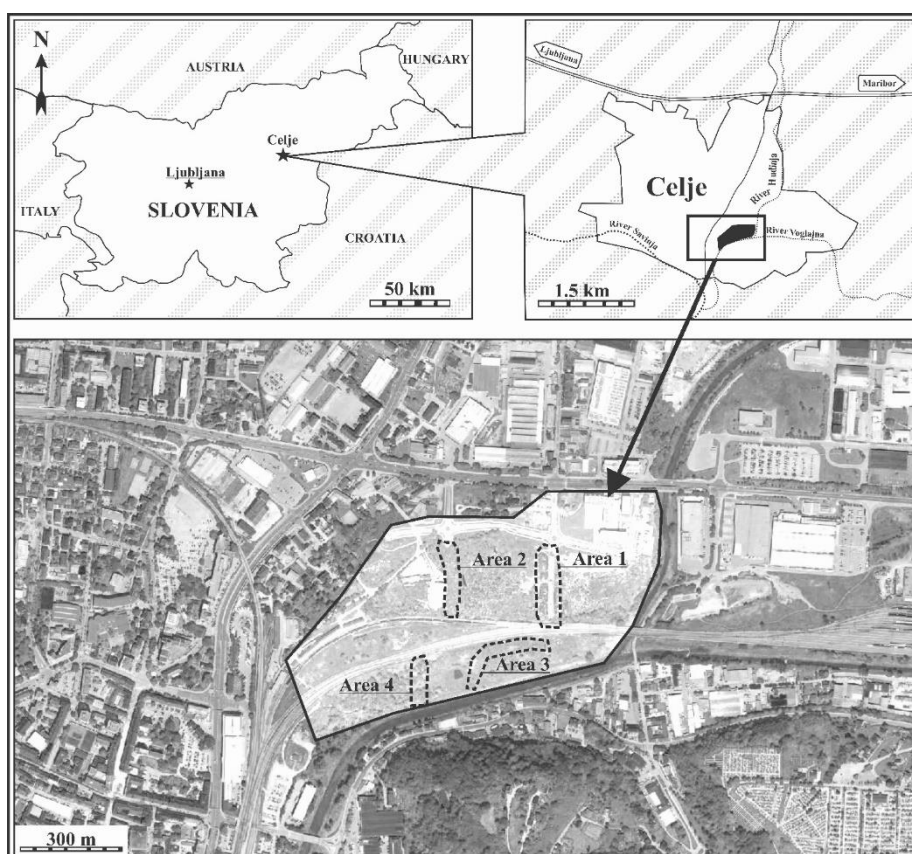


Figure 3.7: Location of the Old Zinc-works site (marked with an arrow and white shading) and sampling areas (encircled with a dashed line).

According to this report, CS from the Old Zinc-works was regarded as hazardous waste, to which code 17 05 05* "*dredging spoil containing hazardous substances*" was assigned based on high total concentrations and water-soluble concentrations of potentially toxic elements (PTE) (Official Gazette of RS, No. 69/15 [270] and No. 39/16 [152]). However, most likely, the code 17 05 03*, "*soil and stones containing hazardous substances*," according to the European Union's List of Waste [284] would be more adequate. Namely, contaminated soil at the site was not formed due to dredging.

Situation on the field and at the representative sampling points at each of four sampling areas is presented in Fig. 3.8.

In the laboratory, increments from each individual area were merged into 4 representative samples, each composed of soil from one sampling area. Samples were sieved, particles larger than 16 mm were then crushed in a jaw crusher (Retsch GmbH, BB 50, Haan, Germany), and mixed with the rest of the sample. They were stored in closed PE bags. Subsamples for analyses and experiments were taken from homogenized CS sample by quartering procedure SIST EN 932-2:1999 [285].



Figure 3.8: Sampling at Area 1 (1, 2), Area 2 (3, 4), Area 3 (5, 6), and Area 4 (7, 8).

In the first stage, the research was focused on the chemical analyses of eluates from standardised leaching tests, in order to determine in which part of the sampling area the most contaminated soil was located. For further analyses in the second stage and for immobilization experiments in the third stage of research, a sample of soil taken from the most contaminated sampling area was prepared, according to the same sampling and preparation procedures as described above. Approximately 600 kg of soil was taken and used for analyses and experiments.

Immobilization additives were sampled with a plastic scoop according to the standardized procedure SIST EN 932-1:1999 [286].

Paper ash (PA) was produced at the VIPAP mill company, located at Krško, Slovenia. It is formed in a steam boiler, where heat is gained from incineration of waste paper sludge from the de-inking process with a combination of a small quantity of bark (up to 10 wt.%). The latter is added to increase the calorific value of the feed material. Approximately 90 wt.% of the PA consists of bottom ash and 10 wt.% of fly ash. Representative sample of approximately 50 kg was collected from the 30 m³ silo. The sample was stored in an airtight closed plastic buckets.

Two coal fly ashes were used in this work. The first one was a fly ash (CAV) produced at the VIPAP Videm Krško paper mill company (Krško, Slovenia) and was formed during combustion of coal in a steam boiler. Representative sample of approximately 50 kg was collected from a silo and was stored in an airtight closed plastic buckets.

The second one (CAT) was produced at TE-TOL, the Electricity and Heat production plant Ljubljana (Slovenia) in a cogeneration boiler from combustion of medium grade Indonesian coal and a small amount of wood chips. The ash was at TE-TOL loaded on trucks by a dispensing system, which has installed a device for wetting of the ash prior its transfer to prevent dusting. Therefore, the collected sample of CAT was slightly moistened. Representative sample of ash of approximately 50 kg was collected from a temporary depot, prior to its recycling for geotechnical composites at Termit mining company, in Moravče (Slovenia). The sample of fly ash was stored in airtight closed plastic buckets.

Two ladle slags from the secondary steelmaking process were used. The first one (LSA) was produced at steel company Acciaierie Bertoli Safau, which is located near Udine (Italy), where ladle slag was stored in a semi-closed and dry depot. ABS ladle slag consisted of slag from the vacuum oxygen decarburization process (40 wt.%) and from ladle furnace (60 wt.%). Approximately 80 kg of sample was taken from a depot and stored in airtight closed plastic buckets.

Second ladle slag (LSH) was obtained from Harsco Minerali, located at Jesenice (Slovenia). Slag was primarily produced at the SIJ Acroni steelmaking plant at a ladle furnace for stainless steel production from recycled scrap steel. Extraction of valuable metals from slag was later performed by Harsco Minerali. Approximately 100 kg of slag was sampled fresh, immediately after it has exited the extraction process. Sample was stored in in airtight closed plastic buckets.

Red mud (RM) from the Bayer process was sampled from an open disposal site at alumina plant in Podgorica, Montenegro. Alumina plant in Podgorica, which is currently part of a company Uniprom-Kap, utilized the high-grade bauxite ores from deposits in Nikšić (Montenegro). Approximately 30 kg of the RM was sampled from a disposal site. RM was dried at 105 °C in a convection oven and ground to a particle size below 2 mm on the disc mill with grinding sets made from tungsten carbide in order to obtain a 0-2 mm gradation.

Subsamples of immobilization additives for analyses and experiments were taken from homogenized sample by quartering procedure described in SIST EN 932-2:1999 [285]. All samples were stored in a dry and cold place, not exposed to the light.

3.2.2 Instrumental

Gas sorption measurements, using ASAP 2020 Micrometrics equipment (Norcross, Georgia), were performed in order to determine the BET (Brunauer, Emmet and Teller) surface area of CS and additives. The samples (except RM, which was already in a dry form) were dried prior to measurements by a convection oven at 40 °C $\pm$ 1 °C in the presence of soda lime pellets until a constant mass was reached. During measurements samples were evacuated at 70 °C with a rate 0.67 kPa/s until a final vacuum of 2.7 Pa was achieved. Nitrogen was used as the adsorptive agent for the analysis.

Grain size distributions of CS and immobilization additives were determined based on the combination of dry and wet sieving methods according to SIST EN 933-1:2012 [287]. Dry sieving was applied to determine grain size distribution of particles larger than 0.4 mm. Grain size distribution of a fraction smaller than 0.4 mm was in CS determined by wet sieving and subsequent determination of hydrodynamic radius by laser diffraction in 2-propanol media by CILAS 920 Particle Size Analyser (Cilas, Orléans, France). Dry sieving for determination of grain fraction <0.4 mm and determination of grain size distribution particles <0.4 mm in 2-propanol media by CILAS 920 Particle Size Analyser was performed for additives.

Contaminated soil was classified based on granulometric data and according to SIST EN ISO 14688-2:2004 [137].

Total elemental composition of CS, and additives was studied by handheld X-ray fluorescence (XRF) analyser Niton XL 3t GOLDD 900 (Thermo Fisher Scientific Inc., Waltham, Massachusetts, USA). Analyses were performed on powdered samples in triplicate. For each sample 5 g of homogenised material with grain size <0.063 mm was compressed into the pellet. The content of the elements was measured applying pre-set modes – "Mining" (Si, Al, Fe, Mg, Ca, K, Ti, P, S, Cl, Nb, Rb, Sr, and Zr) and "Soil" (As, Cu, Hg, Mn, Pb and Zn). To ensure accuracy, the analyser was previously calibrated with 24 international standards (NIST and USGS). The accuracy of this method, expressed as relative standard deviation, is approximately $\pm 5\%$, or higher for certain elements, if they are present in low (As, Hg, P) or high concentrations (for example Ti).

Mineralogical composition of CS, additives, and geotechnical composites were defined by X-ray Powder Diffraction (XRD) on an Empyrean PANalytical diffractometer (PANalytical B.V., Almere, The Netherlands) with Cu $K\alpha$ irradiation ($\lambda = 1.54056$ Å) and a graphite monochromator, at 45 kV and a current of 40 mA, over the 2θ angular range from 4° to 70° , using a step size of 0.01° and a measuring time of 200 sec per step. Representative samples were dried at $40^\circ\text{C} \pm 1^\circ\text{C}$ by a convection oven until constant mass of a sample was achieved. Then, they were sieved and crushed in a vibrating disc crusher, made of stainless steel. Sample powders were further pulverized with an agate mortar and pestle to gain a grain size of approximately 45 μm . The interpretation of the results of XRD analysis was carried out using the HighScore v.4.x LTU (PANalytical B.V., Almere, the Netherlands) software and the PDF-4 (ICDD, USA) database. The PDF reference patterns card numbers of each mineral phase identified are given in Table 3.2. The relative mass fraction of newly formed crystalline phase ettringite in each geotechnical composite was defined by using the Reference Intensity Ratio (RIR) semi quantitative method (I/I_c).

Microstructural analyses of rough and polished sections of the samples were performed by using a scanning electron microscope JEOL 5500 LV (Tokyo, Japan) coupled with an EDS from Oxford instruments (United Kingdom). The device was set to a low vacuum mode, where 12 kPa of pressure is established in the sample chamber. Back Scattered Electrons were used for analyses, at a voltage of 20 kV and working distance between detector and sample of 20 mm. Representative samples for microstructural analyses were dried at $40^\circ\text{C} \pm 1^\circ\text{C}$ by a convection oven until constant mass of a sample was achieved. Selected samples of slag from CS and additives were investigated without any pretreatment. Meanwhile most samples of slags, CS, additives and composites were impregnated with epoxy resin, cut to produce a flat surface, and polished. Preparation procedure was done by avoiding the use of water for that reason 2-propanol was used instead. Polished samples were stored in an evacuated desiccator in a presence of silica gel and soda lime pellets.

Table 3.2: Data of mineral phases identified by XRD analysis.

Mineral phase	Designated label in this study	Chemical formula	PDF card reference number
Almandine	A	$\text{Fe}^{2+}_3\text{Al}_2(\text{SiO}_4)_3$	41-1423
Anhydrite	Ah	CaSO_4	37-1496
Anorthite	An	$\text{CaAl}_2\text{Si}_2\text{O}_8$	41-1486
Boehmite	Bh	$\text{AlO}(\text{OH})$	21-1307
Brucite	Bu	$\text{Mg}(\text{OH})_2$	7-239
Brownmillerite	Br	$\text{Ca}_2(\text{Al,Fe})_2\text{O}_5$	30-226
Calcite	C	CaCO_3	15-8258
Cerussite	Ce	PbCO_3	5-417

Mineral phase	Designated label in this study	Chemical formula	PDF card reference number
Chlorite	Cl	$(\text{Mg, Fe})_5\text{Al}(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_8$	12-242
Cordierite	Cd	$\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$	13-0294
Cancrinite	Cv	$\text{Na}_6\text{Ca}_2\text{Al}_6\text{Si}_6\text{O}_{24}(\text{CO}_3)_2$	25-776
γ - Dicalcium silicate	Gs	Ca_2SiO_4	31-297
Dolomite	D	$\text{CaMg}(\text{CO}_3)_2$	36-426
Enstatite	Es	$\text{Mg}_2\text{Si}_2\text{O}_6$	19-768
Ettringite	Et	$\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26(\text{H}_2\text{O})$	41-1451
Fayalite	Fa	Fe_2SiO_4	34-0178
Forsterite	Fo	Mg_2SiO_4	34-189
Franklinite	Fr	$(\text{Zn, Fe})(\text{Fe})_2\text{O}_4$	22-1012
Gahnite	Gh	ZnAl_2O_4	5-669
Gehlenite	Ge	$\text{Ca}_2\text{Al}(\text{Al, Si})\text{O}_7$	35-755
Gibbsite	Gb	$\text{Al}(\text{OH})_3$	33-18
Goethite	G	$\text{FeO}(\text{OH})$	29-713
Goslarite	Go	$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	9-395
Gypsum	Gy	$\text{CaSO}_4 \cdot 2(\text{H}_2\text{O})$	33-311
Hatruite	S3	Ca_3SiO_5	42-0551
Hedenbergite	Hb	$\text{CaFeSi}_2\text{O}_6$	41-1372
Hemicarboaluminate	Hc	$\text{Ca}_4\text{Al}_2\text{O}_6(\text{CO}_3)0.5(\text{OH}) \cdot 11.5\text{H}_2\text{O}$	41-0221
Hemimorphite	He	$\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2 \cdot (\text{H}_2\text{O})$	5-555
Hematite	Hm	Fe_2O_3	33-664
Hercynite	Hr	FeAl_2O_4	34-192
Hyalophane	Ha	$(\text{K, Ba})\text{Al}(\text{Si, Al})_3\text{O}_8$	19-3
Hydrocalumite	Hy	$\text{Ca}_2\text{Al}(\text{OH})_6\text{Cl} \cdot 2\text{H}_2\text{O}$	42-558
Ilmenite	Il	FeTiO_3	29-733
Larnite	La	Ca_2SiO_4	33-302
Lepidocrocite	Lp	$\text{FeO}(\text{OH})$	8-98
Lime	L	CaO	37-1497
Magnetite	Ma	$\text{Fe}(\text{II})\text{Fe}(\text{III})_2\text{O}_4$	3-863
Mayenite	My	$\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$	9-413
Merwinite	Me	$\text{Ca}_3\text{Mg}(\text{SiO}_4)_2$	35-591
Monocarboaluminate	Mc	$\text{Ca}_4\text{Al}_2\text{O}_6\text{CO}_3 \cdot 11\text{H}_2\text{O}$	41-0219
Monosulphoaluminate	Ms	$\text{Ca}_4\text{Al}_2\text{SO}_{10} \cdot 16\text{H}_2\text{O}$	44-0602
Mullite	Mu	$\text{Al}_{(4+2x)}\text{Si}_{(2-2x)}\text{O}^{(10-x)} \quad x = 0.17 \text{ to } 0.59$	15-776
Muscovite/illite	MI	$(\text{K, Na})\text{Al}_2(\text{Si, Al})_4\text{O}_{10}(\text{OH})_2 /$ $(\text{K, H}_3\text{O})\text{Al}_2\text{Si}_3\text{AlO}_{10}(\text{OH})_2$	34-0175 26-0911
Periclase	Pe	MgO	43-1022
Perovskite	Pr	CaTiO_3	42-423
Peteddunnite	Pt	$\text{Ca}(\text{Zn, Mn, Fe, Mg})\text{Si}_2\text{O}_6$	40-495
Portlandite	Po	$\text{Ca}(\text{OH})_2$	44-1481
Rutile	R	TiO_2	16-934
Talc	Tl	$\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$	29-1493
Tricalcium aluminate	A3	$\text{Ca}_3\text{Al}_2\text{O}_6$	38-1429
Quartz	Q	SiO_2	33-1161
Willemite	W	Zn_2SiO_4	37-1485
Wuestite	Wu	FeO	6-615
Zincite	Z	ZnO	36-1451

Analyses of the eluates from leaching of geotechnical composites were made by different instruments. Measurement of pH and conductivity were made by means of a WTW pH 3110 (Weilheim, Germany) meter and a Yokogawa SC8221-E (Tokyo, Japan) conductivity meter, respectively.

The concentration of selected PTE in eluates was determined by an inductively coupled plasma mass spectrometer (ICP-MS), model 7700x (Agilent Technologies, Tokyo, Japan). The operating parameters of the ICP-MS equipment are presented in Table 3.1. The accuracy of ICP-MS, expressed as relative standard deviation (RSD), is approximately $\pm 1\%$.

Concentrations of SO_4^{2-} and Cl^- were measured by UV-VIS Spectrophotometry with the HACH DR/2010 Portable Datalogging Spectrophotometer device (Loveland, CO, United States of America). The accuracy of UV-VIS Spectrophotometry expressed as relative standard deviation is $\pm 3\%$.

3.2.3 Characterization of contaminated soil and additives

The determination of the most contaminated soil out of four samples from four samples areas was based on analyses of eluates from leaching of four representative samples of CS according to SIST EN 12457-2:2004 [151] in triplicates. The ratio between dry mass of samples and volume of leaching solution – demineralized water was 1/10. The dry mass of a sample was 90 g, which was put in a 1.1 L glass bottle along with 900 mL of demineralized water. The bottle was shaken for 24 hours at 10 rpm on a mechanical shaker (SRT9D, Stuart, Staffordshire, Great Britain). After shaking, samples were centrifuged at 6000 rpm for 10 minutes by using CENTRIC 322A (Tehtnica, Železniki, Slovenia). Eluates were filtrated through a membrane filter with a pore size 0.45 μm (Membranfilter porafil, MACHEREY-NAGEL, Düren, Germany), stored in plastic PE bottles, acidified on $\text{pH} < 2$ with 0.1 M HNO_3 and deep frozen prior to chemical analyses. Selected PTE As, Ba, Cd, Cr, Cu, Hg, Mo, Ni, Pb, Sb, Se, and Zn were determined by ICP-MS, and anions SO_4^{2-} , Cl^- by spectrophotometry.

The same leaching procedure and analyses in triplicates were used for the characterization of immobilization additives.

Analyses of the CS from the most contaminated sampling area, and immobilization additives by XRF were done on dry powdered samples in triplicates.

The basic characterization of CS from the most contaminated sampling area, and immobilization additives included analyses of a specific surface area by N_2 sorption (BET), determination of grain size distribution according to SIST EN 933-1:2012 [287] and by laser particles size analyser, and determination of particle density by Pycnometer method in petroleum according to SIST EN 1097-7:2008 [288].

Quantitative analysis of selected elements in CS from the most contaminated sampling area and in additives was done by XRF and mineral composition by XRD. Different grain size fractions of soil were analysed separately (8 – 16, 2 – 8, 0.25 – 2, 0.125 – 0.25, 0.063 – 0.125, and < 0.063 mm) as well as 8 different types of slag, which were identified in CS. The XRD analyses were supported by SEM/EDS analyses of polished sections of soil, slag, and additives.

The potential formation of hydration products of immobilization additives was investigated by the preparation of pastes. Additives were mixed with water in a water/additive dry mass ratio 1/1 to form a paste and left to cure in a climatic chamber at 20 °C and 98% humidity. The first set of pastes was prepared from PA, CAV, CAT, LSH, LSA, and RM. The second set was made from PA in combination with every single other additive individually (CAV, CAT, LSH, LSA, and RM) in a dry mass ratio 1/1, and the same addition of water. Hydration products were determined by XRD and SEM/EDS after 7, 28 and 56 days of curing.

3.2.4 Soil remediation experiments

The preliminary immobilization experiments were made on CS from the most contaminated sampling area. Individual additives (PA, CAV, CAT, LSH, LSA, RM) were mixed with CS in dry mass ratios 1, 2, 3, 4, and 5 wt.%, followed by admixture of water of 30 wt.%. Composites were left to cure for 28 days in closed plastic vessels. Then they were subjected to leaching according to SIST EN 12457-2:2004 [151]. PTE Cd, Mo, Pb, and Zn were determined in eluates by ICP-MS and pH was measured.

3.2.4.1 Preparation of composites and basic geotechnical analyses

Remediation experiments were conducted in such a way that geotechnical composites containing 75 wt.% of CS from the most contaminated sampling area, and 25 wt.% immobilization additives in dry mass ratio were produced. Eleven geotechnical composites were investigated, the composition of which is given in Table 3.3.

Table 3.3: Composition of binary and ternary geotechnical composites included in immobilization experiments.

Designation	Content of CS (wt.%)	Mass content of additive I. (wt.%)	Mass content of additive II. (wt.%)
SC/PA	75	Paper ash VIPAP 25	/
SC/CAV	75	Coal ash VIPAP 25	/
SC/CAT	75	Coal ash TETOL 25	/
SC/LSH	75	Ladle slag Harsco 25	/
SC/LSA	75	Ladle slag ABS 25	/
SC/RM	75	Red mud 25	/
SC/CAV/PA	75	Coal ash VIPAP 13	Paper ash VIPAP 12
SC/CAT/PA	75	Coal ash TETOL 13	Paper ash VIPAP 12
SC/LSA/PA	75	Ladle slag ABS 13	Paper ash VIPAP 12
SC/LSH/PA	75	Ladle slag Harsco 13	Paper ash VIPAP 12
SC/RM/PA	75	Red mud 13	Paper ash VIPAP 12

The used dry mass ratio of immobilization additive was chosen on the basis of practical experiences from the past real-case projects at ZAG and preliminary laboratory experiments. Similar concentrations of additives were also reported in scientific literature for coal fly ash [220], [222], [221], and ladle slag [289], [290], [291]. Lower concentrations were reported for red mud for the purpose of remediation of soil [248]. Also, paper ash in lower concentrations was used only for geotechnical stabilization of soil [238]. Similar or higher concentrations of red mud as in this study were rarely reported and were mostly used for the preparation of other types of geotechnical composites [292]. Also, higher or similar concentrations of paper ash were reported for the preparation of geotechnical composites with other different recycled materials [232], [239].

To our best knowledge there were, until now, no described cases of soil remediation with the use of combination of PA with ladle slag or red mud as the immobilization additives in ternary composites. There were attempts to combine RM, for example with lime [293] apatite [294], gypsum [238], and fly ash from coal combustion [295]. Also, combinations of ladle slag with lime [244] were reported.

Homogenization of composites was performed in a planetary mixer (Gostol 171, Gostol Nova Gorica, Slovenia), at speed of 300 rpm and time of 5 minutes. The Modified Proctor Compaction Test (according to SIST EN 13286-2:2005 [296]) was employed to determine maximum dry density and optimum water content of geotechnical composites. The test was

conducted with the use of cylindrical mould A (diameter 10.01 cm and height 11.66 cm, volume 915 cm³), rammer B (4.5 kg), and compacting energy of 2.66 MJ/m³. Compaction was performed in 5 layers, where 25 blows were delivered to each layer with a rammer.

Water acts as a softening agent on particles in composite so that they can slip over each other and move into a more densely packed position. Compacted composite is prepared in the Proctor test apparatus with different initial water contents. Dry density of composite is then measured. Water content, at which the maximum dry density is achieved, is regarded as the optimal water content [136].

Test samples of binary and ternary composites were prepared with the optimal water content and compacted in the Proctor test apparatus. Monolithic cylindrical test samples were extracted from mould undamaged by a press. More than 210 test samples were prepared for experiments and analyses within the scope of soil remediation study.

Test samples were cured in a climatic chamber at 20 °C and 98% humidity for 3, 7, 28 and 56 days before they were analysed.

The unconfined compressive strength was investigated on test samples of composites according to SIST EN 13286-41:2004 [297]. The loading speed was between 0.02 and 0.08 MPa/sec. The results are given as a mean value of two parallel analyses.

The water permeability coefficient of the geotechnical composites was performed after 28 days of curing on monolithic samples confined within PE mould, and according to falling head principle as described in SIST-TS CEN ISO/TS 17892-11:2004 [298]. The method is used to determine the coefficient of permeability of water through water-saturated material. The test was conducted at laboratory conditions (at temperature 25 °C) and with the use of demineralized water.

3.2.4.2 Mineralogical, microstructural and chemical analyses

Mineralogical analyses of composites were performed by XRD after 7, 28, and 56 days of curing. Samples for the analyses were carefully taken from the central part of a test sample, dried until constant mass at 40 °C, and ground into powder.

Microstructural analyses of the composites were made on polished sections by SEM/EDS after 28 days of curing. Semiquantitative chemical composition analyses were performed by EDS.

The environmental acceptability or immobilization efficiency is the most important factor in remediation experiments. Therefore, it is necessary to use appropriate tests to confirm the effectiveness of immobilization of contaminants within newly formed composites. The environmental acceptability of composites was evaluated by leaching test SIST EN 1744-3:2002 [299], which was slightly modified. Leaching was performed on monolithic test samples of composites after 7, 28, and 56 days of curing in duplicates. Samples were placed on a screen, which was put inside a tank, submersed in demineralized water. The ratio between dry mass of a test sample and volume of leaching solution was 1/10. Leaching was performed by mixing with a motor-driven dip stirrer at 700 rpm for a period of 24 hours. The leaching procedure is based on the assumption that the state of chemical equilibrium is established between the liquid and water-soluble solid phases. The purpose of the leaching test was to simulate natural leaching behaviour under a short period of exposure to water saturated conditions. Concentrations of PTE As, Ba, Cd, Cr, Cu, Hg, Mo, Ni, Pb, Sb, Se, and Zn in eluates were measured by ICP-MS. Anions SO₄²⁻ and Cl⁻ were determined by spectrophotometry. Results are given as an average value of two parallel chemical analyses.

Chapter 4

Results and Discussion of Water Nanoremediation Study

4.1 Nanoparticles of Zero-Valent iron

The basic parameters of the in-house nZVI, Nanofer STAR, and Nanofer25 slurry are presented in Table 4.1. Their size distribution, determined by measurements of the diameters of the nZVI on FESEM and TEM, show that in-house nZVI, Nanofer STAR, and Nanofer25 slurry have radii between 30 and 100 nm, 30 and 80 nm, and 20 and 80 nm, respectively. Only individual nZVI have diameters larger than 200 nm. Size distribution of in-house nZVI is similar as reported by Nurmi et al. [71] for nZVI synthesized with a borohydride reduction method, while the average size of Toda Kogyo Corp. nZVI, which is synthesized according to the same procedure as Nanofer nZVI, is slightly larger. The literature data for the particle size distribution of the same Nanofer nZVI as used in this study show very similar values [300]. Slightly smaller size distribution of nZVI, synthesized via borohydride reduction as in this study, was reported by [301].

The data from the BET analysis indicate that a specific surface area of the in-house nZVI, the Nanofer STAR, and the Nanofer25 slurry amounted to 83, 17 and 44 m²/g, respectively (Table 4.1). This is in a range of values as reported by a scientific literature for nZVI synthesized via thermal reduction of nano-iron oxides at elevated temperatures with the use of H₂, the same way as both Nanofer products. Nanofer25 slurry has an almost twice as high value and Nanofer STAR almost 10 m²/g larger BET value than reported for Toda Kogyo Corp. nZVI, which is their equivalent material to Nanofer STAR and Nanofer25 slurry, commonly used in scientific literature [71]. Meanwhile, BET surface area of in-house nZVI measured in this study was twice as high as that reported in literature for these types of nanoparticles [301].

Table 4.1: Basic parameters of in-house nZVI, Nanofer STAR and Nanofer25 slurry.

Parameter	In-house nZVI	Nanofer STAR	Nanofer25 slurry
Size (nm)	30 - 100	30 - 80	20 - 80
Shell thickness (nm)	4 - 6	5 - 8	4 - 6
Crystallinity	disordered	crystalline	crystalline
BET (m ² /g)	83.0 ± 4.1	17.0 ± 0.8	44.0 ± 2.2
Available Fe ⁰ (wt.%)	88.0 ± 4.4	69.0 ± 3.4	85.0 ± 4.2
Hydrophobicity (KA _{OW})	0.0954	0.0212	0.0956

The shell thickness of the nZVI was determined on the basis of measurements made on TEM microimages, where a clear contrast between the core and less dense shell is visible (Fig. 4.1, third column, marked by arrows). As can be seen in Fig. 4.1 and Table 4.1, the in-house nZVI and the Nanofer25 slurry had a slightly smaller shell thickness (4 – 6 nm) than that of the Nanofer STAR (5 – 8 nm). Same results were reported by scientific literature [301].

As can be further seen from Fig. 4.1 (the first and second column), the in-house nZVI exists in the form of chain-like aggregates of µm length of spherical particles. The Nanofer STAR and

Nanofer25 slurry consist of angular shaped particles with rounded edges that form gelated irregular aggregates of μm size. Both the in-house nZVI and the Nanofer STAR have smooth surfaces without any needle- or leaf-like structures, which are present on the rough surface of the Nanofer25 slurry particles (Fig. 4.1, first column - C). These structures represent the shells of secondary iron corrosion products, namely lepidocrocite of hematite, which are formed due to oxidation during the process of preparation of the sample. The crystallinity of the nZVI was determined by TEM, SAED (Fig. 4.1, the third and fourth column) and XRD (Fig. 4.2). As can be seen in TEM microimages, the Nanofer STAR and the Nanofer25 slurry both have well-defined crystalline core structures and shell, as lattice fringes can be observed in Fig. 4.1 (column 3 – B and C). The SAED patterns of the Nanofer STAR and the Nanofer25 slurry consist of spots and visible rings (Fig. 4.1 column 4 – B and C) which correspond to electron diffraction on mono-crystals and on the polycrystalline material, respectively [301].

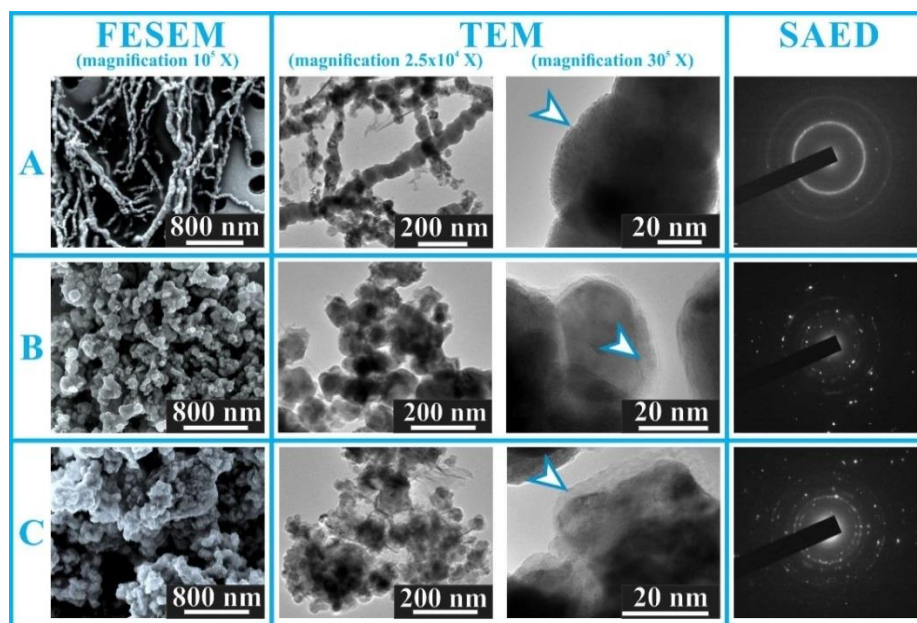


Figure 4.1: FESEM and TEM images (shell structures are marked by arrows), and SAED patterns of in-house nZVI (A), Nanofer STAR (B) and Nanofer25 slurry (C).

Sharp narrow peaks, with high intensities, can be seen on the XRD patterns of Nanofer STAR and Nanofer25 slurry at 44.7° , 65.02° , and 82.3° 2θ , which represent $\alpha\text{-Fe}^0$ body centred cubic cell (bcc) phase (Fig. 4.2B and C). This supports SAED analyses by confirming the well crystalline nature of the core of both Nanofer materials. Less pronounced are the peaks of the maghemite phase ($\gamma\text{ Fe}_2\text{O}_3$), which is present in the oxide shell of the nZVI.

Broad, less pronounced peaks, corresponding to $\alpha\text{-Fe}^0$ and of $\gamma\text{ Fe}_2\text{O}_3$, can be seen on the XRD pattern of in-house nZVI (Fig. 4.2A). The background is higher compared to the patterns of the Nanofer nZVI. Based on the literature data [302], it was concluded that the positions of some of the minor peaks corresponded to the pattern of the ferro-boride phases (Fe-B alloys), which are bound within the structure of the in-house nZVI. In the TEM microimages, the lattice fringes were less pronounced for in-house nZVI than for the Nanofer materials. The SAED pattern consists of less sharp and more diffuse rings (Fig. 4.1 column 1 – A). All of these qualitative data imply that the in-house nZVI has a disordered, amorphous to microcrystalline internal structure, which was also reported by [301].

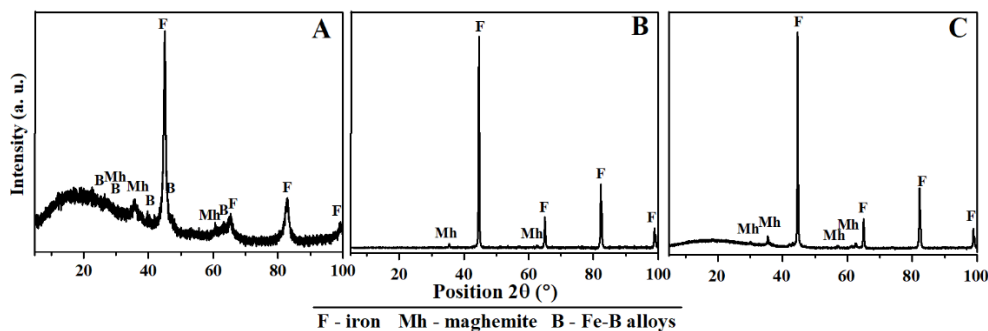


Figure 4.2: Powder X-ray diffraction patterns of in-house nZVI (A), Nanofer STAR (B) and Nanofer25 slurry (C).

The available Fe^0 content in the nZVI was determined by a modified H_2 evolution method based on the principle described by [105]. It was found that the in-house nZVI and the Nanofer25 slurry had similar available Fe^0 contents of 88 and 85 wt.% respectively, whereas the Nanofer STAR contained 69 wt.% of Fe^0 (Table 4.1). The literature data for the content of Fe^0 in Nanofer nZVI show very similar values as reported by [303]. Also, Liu et al. [301] reported only 1% higher Fe^0 content in their nZVI obtained via borohydride reduction as in the in-house nZVI from this study. The in-house nZVI and the Nanofer25 slurry released a comparable amount of H_2 at the beginning of the reaction (from 0 to 20 minutes). Cumulatively, in-house nZVI emitted the highest volume of H_2 , which indicated that it contains the highest amount of Fe^0 . On the other hand, the Nanofer STAR released H_2 less intensively and more than 30% smaller amount, indicating its lower reactivity and lowest content of Fe^0 among the three nZVI materials (Fig. 4.3). It is also known that nZVI from borohydride reduction have higher reactivity than nZVI from thermal reduction by H_2 [105].

The hydrophobicity of the investigated nZVI was determined by measuring the octanol-water affinity coefficient (KA_{ow}), as described by Xiao and Wiesner [304]. When the determined value of KA_{ow} is larger than 1 (i.e. when hydrophobic material is accumulated in the octanol phase) the nanoparticles are hydrophobic, whereas a value of less than 1 indicates hydrophilic characteristics. The data show that all of the analysed nZVI are hydrophilic (Table 4.1).

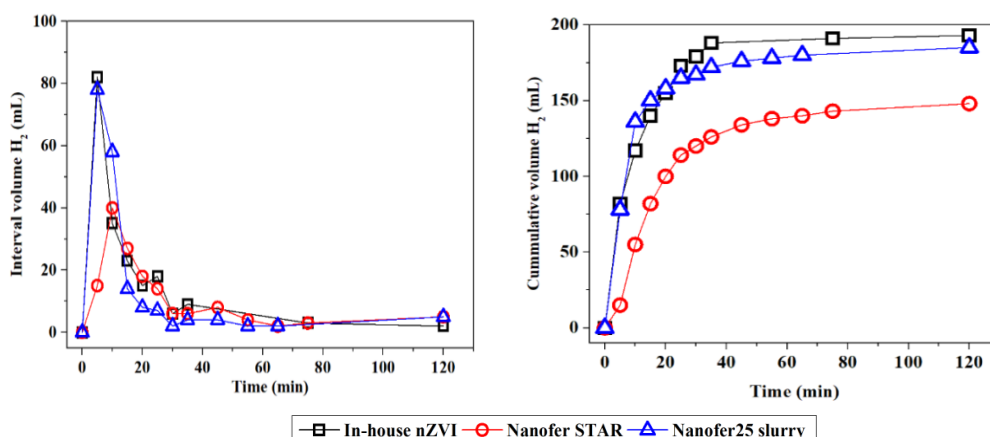


Figure 4.3: Volumes of the released H_2 during the reaction of in-house nZVI, Nanofer STAR and Nanofer25 slurry with HCl .

The total concentrations of selected PTE in samples of HCl digested nZVI were determined by ICP-MS to check their purity of nanoparticles (Table 4.2). The data from Table 4.2 also indicate that both the Nanofer STAR and the Nanofer25 slurry were contaminated with Cr, Cu, and Mn. Additionally, the Nanofer25 slurry was found to contain Al, Na, and Ni in relatively high concentrations. The PTE in Nanofer nZVI are originating from iron oxide

nanoparticles used as a basis for thermal reduction into nZVI. The in-house nZVI was found to contain relatively high amounts of B and Na (4100 and 8500 $\mu\text{g/L}$, respectively), originating from the use of NaBH_4 . Similar content of B in nZVI synthesized via reduction by NaBH_4 was reported by [105]. However, removal of B, which is adsorbed or structurally incorporated as a ferro-boride phase, by intensive rinsing, leads to the passivation of in-house nZVI rendering them noneffective [305]. Elevated Mn concentration (2000 $\mu\text{g/L}$) determined in the in-house nZVI arose from contaminated FeCl_3 used in its synthesis.

Contamination of nZVI materials by PTE evidently occurred during synthesis from used precursors. When nZVI are applied for the treatment of environmental waters, the possibility exists that the PTE from nanoparticles are released into water being remediated [306].

Table 4.2: Total element concentrations in digested samples of in-house nZVI, Nanofer STAR and Nanofer25 slurry determined by ICP-MS. Results represent mean values of three parallel determinations.

Element ($\mu\text{g/g}$)	In-house nZVI	Nanofer STAR	Nanofer25 slurry
Al	370	510	2900
As	3.90	35	41
B	4100	<10	<10
Cd	0.70	2.50	3.70
Cr	250	1100	1400
Cu	260	2000	3000
Hg	<2	<2	<2
Mn	2000	780	1000
Na	8500	0.90	860
Ni	200	330	550
Pb	2.90	33	80
Sb	3.80	10.4	11
Se	<2	<2	<2
Zn	<1	490	550

Analyses of particle have shown differences between nZVI materials used in this study. Also, comparison with literature data revealed that differences exist between nZVI materials, even though they are synthesized according to a similar procedure. The absolute comparison of data from water remediation studies is thus not possible. Namely, water remediation processes and efficiency are highly dependent on the physical, microstructural and chemical properties of nZVI [307].

4.2 Effluent Water from the Small Wastewater Treatment Plant

Effluent water samples ($n = 14$) were collected during a longer time period for the purpose of the SBWTP Hruševno observation. Sampling was each time performed during the same time of the day, between 9:00 and 10:00 am, which is the period when contaminants are present in the highest concentrations in the effluent water [36]. This effect is due to a high inflow of municipal wastewater from connected households. This shortens the hydraulic retention times, which are usually needed for a more efficient removal of contaminants, in the flow-through regime of the SBWTP. The analyses of the effectiveness of the SBWTP operation were thus independent of the variations due to daily cycles. The data that represent basic water quality indicator parameters (pH, conductivity, COD, and BOD_5), concentration of N in the form of

different species, and selected elements are given in Tables 4.3, 4.4, and 4.5, respectively. The high buffer capacity of the wastewater is indicated by small variations of pH, which extends over one unit from neutral to slightly pH alkaline range. Electrical conductivity, which is related to the concentration of charged ions, significantly varied with regard to the composition of effluent water. Values of COD and BOD₅ are the main indicators for the operation of SBWTPs. At the SBWTP Hruševno they were constantly below limit values according to the Slovenian legislation (Official Gazette of RS, No. 98/15), which are 150 and 30 mg O₂/L for COD and BOD₅, respectively. Efficiency of biochemical removal of organic substances is very high if we consider literature data that report the ranges in the municipal wastewater at the inflow to SBWTP, which are 250 – 1000 for COD, and 100 – 300 for BOD₅ [36]. Concentrations of the TN_b, N in the form of NH₄⁺, NO₂⁻, and NO₃⁻ were analysed to follow efficiency of the removal of nitrogen species from the effluent water. The municipal wastewater contains a variety of nitrogen species like proteins, amino acids, amino sugars, urea, uric acid, purines and pyrimidines. Organic N in SBWTP is converted to NH₄⁺ by different pathways: a) the degradation of proteins to amino acids and their further deamination, b) the enzymatic decomposition of purines to uric acid, which is then aerobically broken down, and c) by the hydrolysis of urea in aqueous solutions [308].

Table 4.3: Ranges for the relevant parameters determined in effluent water samples (n=14) from the SBWTP.

Parameter	Min	Arithmetic mean	Max
pH	7.0	7.4	8.0
Conductivity (μS/cm)	31	635	920
COD (mg/O ₂ L)	23	43	54
BOD ₅ (mg/O ₂ L)	3.7	6.8	13

Ammonium cation is highly toxic to aquatic organisms and humans and contributes to eutrophication of surface waters. To prevent its excessive release from municipal effluents into the aquatic environment, in SBWTP NH₄⁺ is oxidised under aerobic conditions by nitrification bacteria to NO₃⁻, with NO₂⁻ as an intermediate product [41], [309]. Low concentrations of NO₃⁻ and NO₂⁻ are commonly present in the effluent water, while the amount of NH₄⁺ greatly depends on the concentration of the total N in the receiving waters from households, as well as on the nitrification efficiency that depends on the temperature and pH of water [309]. The pH value of the effluent water (from 7 to 8) indicates that conditions on the SBWTP are favourable for the nitrification. Therefore, variations in concentrations of nitrogen species were a consequence of air temperature variations and quality of water inflow to the SBWTP. The effluent water contains also residual organic N species, which were not removed during the clean-up of wastewater on SBWTP. Therefore, significant variations in concentrations of inorganic N species were observed in the effluent waters during the period investigated (Table 4.5, Fig. 4.4).

Concentration ranges for selected elements in the effluent water (n = 14) are presented in Table 4.5. Great differences were observed in concentrations of the particular elements determined in the effluent water samples analysed, indicating the variable composition of the receiving waters from households (Table 4.5). The retention of elements from wastewater by the SBWTP is influenced by multiple factors. Formation of complexes with suspended organic matter can on one hand lead to the removal of PTE from water by settling, and on the other hand to discharge by effluent water into nature if the sludge retention ability of the SBWTP is limited (for example at high inflow of municipal wastewater).

Table 4.4: Concentration ranges for TN_b , organic N, nitrate N, nitrite N, and ammonium N determined in effluent water samples (n=14) from the SBWTP.

Parameter	Min (mg/L)	Arithmetic mean (mg/L)	Max (mg/L)
TN_b	9.4	20.1	42
Organic N	1.85	8.29	23.7
Nitrate N	0.8	2.63	7.16
Nitrite N	0.07	0.2	0.4
Ammonium N	2.8	9.0	28

Very mobile complexes can also be formed with dissolved organic matter or chelates. Biotransformation processes by bacteria can lead to PTE mobilization (for example by methylation) or to immobilization in organic matter (by bioaccumulation), which settles in the form of active sludge [310]. Therefore, the variability in the concentrations of individual element in the effluent water can be attributed to the complex biochemical reactions and composition of organic substances in waters treated by the SBWTP. Possible relations between microbial activity and concentrations of soluble elements can be seen in Fig. 4.4. Relatively low concentrations of NO_2^- and NO_3^- in samples taken on 13/02/2014 and 09/12/2014 can be related to the decrease of nitrification activity due to low temperatures in the winter time. Meanwhile, several elements, which do not bioaccumulate and remain in the form of soluble species, exhibit a peak in concentrations; for example, Cu, Cd, Hg, and B on 13/02/2014, and Al, Fe, Ni, Cd, Sb, and slightly Cu, Pb, B, on 09/12/2014. However, the influence of low temperatures cannot be confirmed, as the influence of intrusions of storm-water can also be possible due to rainy seasons in the investigated period. Also, a high concentration of NH_4^+ on 19/06/2014 is attributed to the inhibited microbial nitrification activity, which can be correlated to peak concentrations of Al, Mn, and Fe. The latter can be caused either by a high concentration of these elements in receiving water or due to resuspension of sediment and disruption of nitrification cycle due to the maintenance of the SBWTP.

Table 4.5: Concentration ranges of selected elements determined in effluent water samples (n=14) from the SBWTP.

Parameter	Min ($\mu\text{g/L}$)	Arithmetic mean ($\mu\text{g/L}$)	Max ($\mu\text{g/L}$)
Al	0.868	51	148
As	0.17	0.327	0.466
B	8.6	102	272
Cd	0.004	0.282	2
Cr	0.05	0.671	1.1
Cu	1.6	79	974
Fe	0.861	105	224
Hg	0.001	0.307	1.19
Mn	5.07	23.8	54.2
Na	8950	34690	80000
Ni	0.264	5.26	19.6
Pb	0.07	1.67	13.1
Sb	0.017	0.138	0.443
Se	0.067	0.101	0.152
Zn	1.17	30.4	161

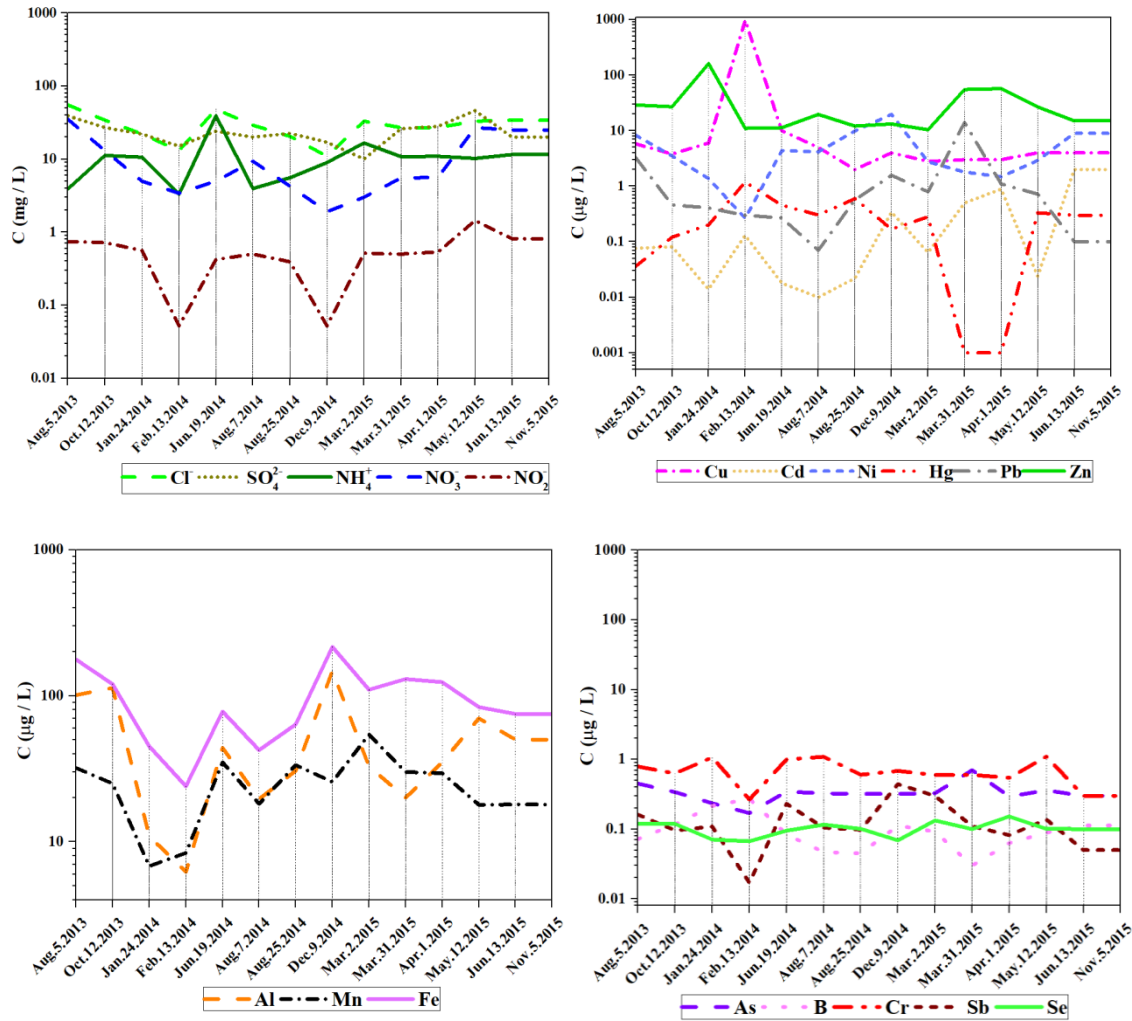


Figure 4.4: Fluctuations of concentrations of inorganic parameters in effluent water from the SBWTP in 14 samplings from August 2013 to November 2015.

Nevertheless, PTE were present in low concentrations and did not represent an environmental threat. Wastewater treatment plants that receive discharge from households provide favourable conditions for the growth of microorganisms, including faecal pollution indicator bacteria: Coliform bacteria, *Escherichia coli*, Intestinal Enterococci and *Clostridium perfringens* [43]. They are monitored and quantified in wastewater treatment plants effluent water, from which pathogens must be efficiently removed, in order to prevent any release of pathogenic bacteria to the surface waters and their potential entry into drinking water supplies. The content of investigated faecal bacteria in receiving municipal wastewaters can vary substantially, from 10^4 CFU/100 mL of *Clostridium perfringens* to more than 10^7 MPN/100 mL of Coliform bacteria. The reported efficiency of SBWTPs for the removal of microorganisms from wastewater is more than 90%, although there is no special mechanism for that purpose in the SBWTP [311].

Average Colony Forming Units for *Clostridium perfringens* and the Most Probable Number for the *Escherichia coli*, Intestinal Enterococci and Coliform bacteria in effluent water samples for all the experiments performed the period of monitoring of the SBWTP efficiency ($n = 14$) are presented in Table 4.6.

Table 4.6: Concentration ranges for microbiological parameters in effluent water samples (n=14) from the SBWTP.

Parameter	Min	Arithmetic mean	Max
<i>Escherichia coli</i>	860	19900	326000
Intestinal Enterococci	620	11791	77000
<i>Clostridium perfringens</i>	230	988	4400
Coliform bacteria	3260	255010	1980000

In Fig. 4.5, the boxes represent 25 to 75% of all determined values, small squares represent the arithmetic mean, line in the middle of the boxes represents the median value, while “X” specifies the minimum and maximum determined values as outliers. In the samples analysed, the highest was the content of Coliform bacteria (median value of 84000 MPN per 100 mL), *Escherichia coli* and Intestinal Enterococci were present in lower amounts (median values of 19850 and 5500 MPN per 100 mL, respectively) and the lowest was the bacteria population of *Clostridium perfringens* (median value of 680 CFU per 100 mL). Variations between the minimum and maximum determined values for the population of all bacterial species can be explained by the dependence of the bacteria growth on the existing conditions at the SBWTP, like temperature, the amount of oxygen and the availability of nutrients, as was demonstrated by [312].

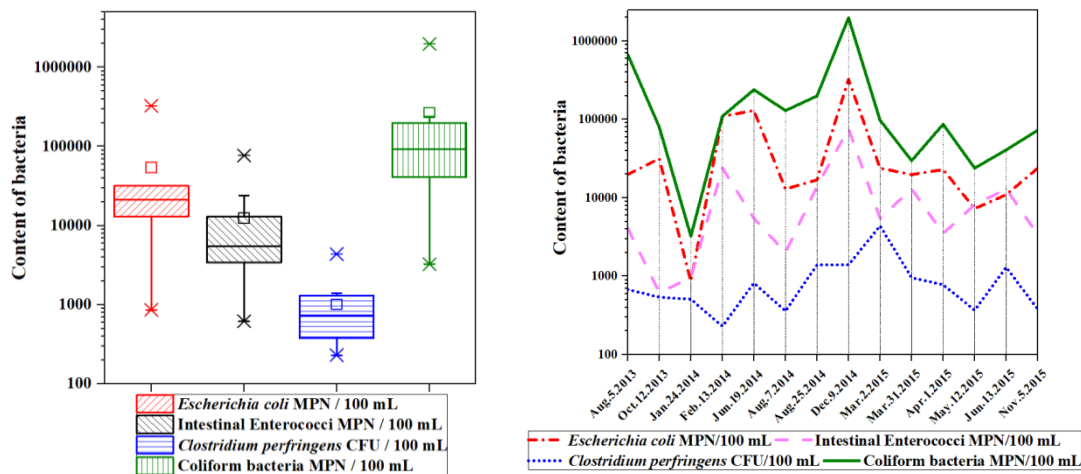


Figure 4.5: Fluctuations and ranges of concentrations of microbiological parameters in effluent water from the SBWTP in 14 samplings from August 2013 to November 2015.

The relatively low concentration of all four bacterial parameters in 24/01/2014 has no apparent correlation with the concentrations of inorganic contaminants in effluent water (Fig. 4.5). The mechanism for a very efficient removal of faecal bacteria cannot be described as there is no general negative impact on the bacterial community, which could also potentially be indicated by less efficient denitrification efficiency. The relatively high concentrations of bacteria on 19/06/2014 can be, similarly as inorganic parameters, correlated with the maintenance of the SBWTP, which was performed a few days before the sampling. Meanwhile, high concentrations detected on 09/12/2014 can be a result of a wash out of organic material due to intrusions of storm-water during a rainy season. Namely, suspended or re-suspended organic matter can mobilize a high number of pathogenic organisms in effluent water [43].

The high concentrations of nitrogen species, occasional high concentration values of PTE, and the presence of pathogenic bacteria in high numbers are preventing the reuse of effluent water. Therefore, additional treatment is needed to achieve appropriate water quality for reuse.

Achieving the strictest criteria, which are set for drinking water (Official Gazette of RS, No. 51/17), would enable unrestricted use of the treated effluent water. The ultimate goal of this study was thus to purify the effluent water from the SBWTP up to a quality of drinking water, by the utilization of nZVI and complementary methods. However, extensive optimization of the nanoremediation procedure and additional stages of remediation was needed and is described here.

4.3 Effluent Water Nanoremediation

4.3.1 Differences between nZVI

The most appropriate nZVI particles for efficient and safe nanoremediation of effluent water were chosen first with laboratory experimental work. Differences between the three nZVI materials were evaluated on the basis of removal efficiency of PTE, nitrogen species, and bacteria from effluent water samples. The influence of increasing iron loads of in-house nZVI, Nanofer STAR and Nanofer25 slurry were investigated by applying 60 min of mixing and the settling time of 1200 min.

All nZVI undergo rapid oxidation of Fe^0 core upon contact with water. During this process soluble Fe^{2+} is released and alkalinity is formed due to hydrolysis [90]. Fig. 4.6 clearly indicates that an increase of pH, after introduction of nZVI into effluent water samples, is dose dependent. However, the increase is almost 1 pH unit higher in the case of using an in-house nZVI and Nanofer25 slurry than for the use of Nanofer STAR. This is in line with the data of the Fe^0 content, which is the lowest in Nanofer STAR, and comparably higher in the in-house nZVI and Nanofer25 slurry. Conductivity of effluent water samples treated with nZVI is showing the same trends. In-house nZVI and Nanofer25 slurry produce a similar conductivity regardless of the concentration of added nZVI. Meanwhile, effluent water samples treated with Nanofer STAR have a lower conductivity, which can be related to the fact that less Fe^{2+} was released during oxidation. Also, a dose-dependant decrease of conductivity can be attributed to surface adsorption of ions from the effluent water.

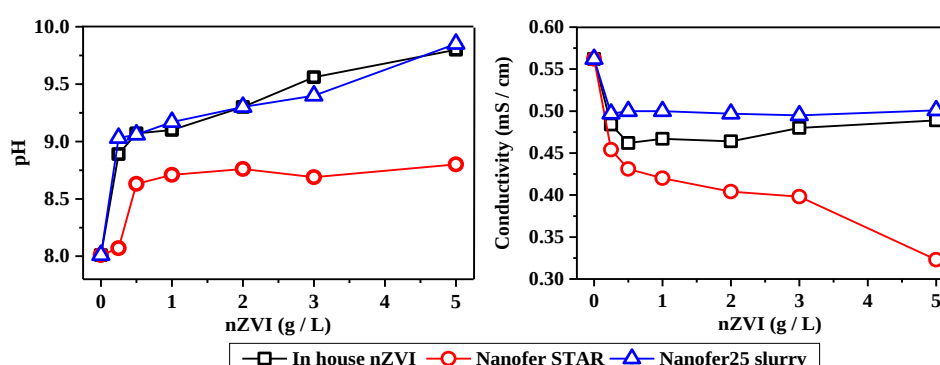


Figure 4.6: Influence of increasing nZVI concentrations from in-house nZVI, Nanofer STAR and Nanofer25 slurry (mixing time 60 min; settling time 1200 min) on the pH and conductivity of remediated effluent water samples.

Comparative data for the removal of PTE from effluent water are given in Fig. 4.7. Under alkaline pHs, the mechanism of divalent and trivalent metal cation removal is mainly attributed to their co-precipitation with iron corrosion products. On the other hand, elements present as oxyanions like CrO_4^{2-} , AsO_4^{3-} and SeO_4^{2-} can be, by the action of nZVI, first reduced and then adsorbed on the surface of the iron corrosion products. Co-precipitation of AsO_4^{3-} and SeO_4^{2-} with Fe^{2+} can also substantially contribute to their removal from the effluent water [70], [72]. However, the use of nZVI demonstrated not only removal but also contamination of

effluent water. Namely, water remediated with the in-house nZVI contained very high amounts of B and Na, whose concentrations were dose dependent with increasing the in-house nZVI concentrations. Concentrations of B and Na in non-remediated effluent water (70 and 41800 $\mu\text{g/L}$, respectively) were, after the addition of 0.5 g/L of in-house nZVI, increased to 65000 and 170000 $\mu\text{g/L}$, respectively. By applying higher amounts of nZVI, concentrations of B and Na in the remediated water were additionally increased. So, extensive contamination was caused by a release from the in-house nZVI due to the use of NaBH_4 in their synthesis. This assumption was confirmed by intensive washing of nZVI with Milli-Q water. This on one hand eliminated B and Na contaminants from nZVI, but on the other, such washing caused passivation of nZVI, which were oxidised. This was mainly manifested in the loss of their bactericidal properties. In general, it can be seen that in-house nZVI effectively removed most of the PTE investigated.

After the treatment of the effluent water with Nanofer STAR, Mn and Cu were found in much higher concentrations than initially present in effluent water or in water treated with in-house nZVI and Nanofer25 slurry (Fig. 4.7). It is most likely that both PTE formed strong soluble complexes with the organic substances present in the effluent water. Thus, desorption and mobilizations of Cu and Mn, which were present as contaminants in these nanoparticles (Table 4.2), occurred. Interestingly, during the use of increasing concentrations of Nanofer25 slurry the immobilization efficiency for Mn decreased, indicating possible inputs from the contaminated nZVI. Similar observations were reported by Peeters et al. [306] who investigated the processes during the remediation of landfill leachate with nZVI. The pH of the effluent water after the treatment with Nanofer STAR (pH around 8.6) was, depending on nZVI load, 0.5 up to 1.3 units lower than the pH of the in-house nZVI and Nanofer25 slurry (Fig. 4.6). As a result of lower pH and its lower reactivity, Nanofer STAR exhibited a slightly lower efficiency of element removal.

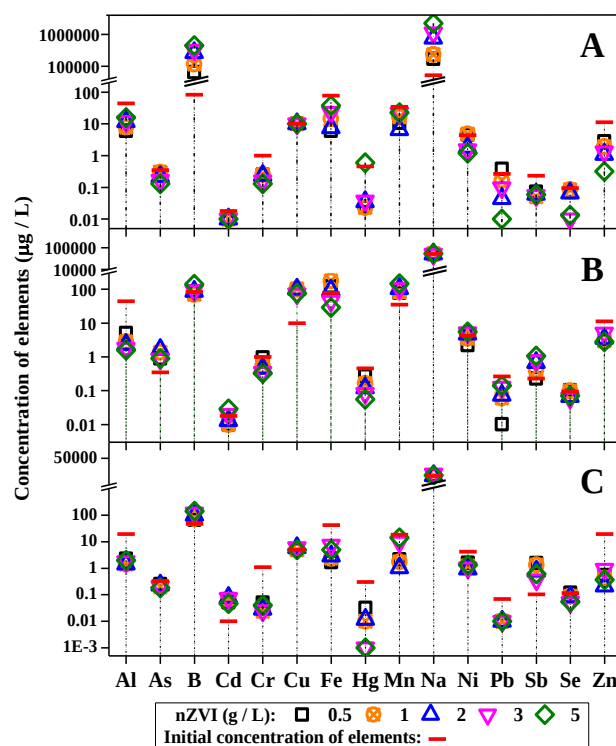


Figure 4.7: The influence of increasing nZVI concentrations from the in-house nZVI (A), Nanofer STAR (B), and Nanofer25 slurry (C) (mixing time 60 min; settling time 1200 min) on the concentration of elements determined in remediated water samples from the SBWTP.

Among nZVIs investigated, the lowest concentrations of elements in the remediated effluent water were found after the treatment with Nanofer25 slurry (Fig. 4.7). In general, highly reactive Nanofer25 slurry effectively removed elements already at the lowest nZVI concentration applied (0.5 g/L). The pH of the non-remediated effluent water (pH 8.0) was after application of 0.5 g/L of Nanofer25 slurry raised to pH 9.2 and with increasing nZVI concentrations up to pH 9.9 (Fig. 4.6). These alkaline conditions favoured co-precipitation of the majority of metals with iron corrosion products. Both, Fe initially present in the effluent water and the iron corrosion products formed from Nanofer25 slurry were also efficiently removed from the effluent water by settling. Data from Fig. 4.7 further demonstrate that the remediated water was not additionally contaminated by the elements released from impurities present in Nanofer25 slurry. The exceptions are Cd and Sb, but their concentrations were already very low, below 1 µg/L. It can also be seen that B, which is present in the form of negatively charged borate ion, was not removed. Beside borate, the removal of Na was also inefficient. This element exists in aqueous media at alkaline pHs as a highly soluble hydroxide, which cannot be co-precipitated with iron corrosion products. Removal of multiple PTE from contaminated water by nZVI was already reported to be possible with high and dose-dependent efficiency [65], [280]. Although, PTE are present in effluent water in low concentrations (Fig. 4.7, Table 4.4), their removal efficiency was relatively low at concentrations of nZVI <3 g/L. Reported adsorption capacities of nZVI for selected PTE (except B and Na) are higher than the concentrations in effluent water. However, competitiveness between multiple ions and dissolved organic matter present in effluent water significantly influences removal efficiency of PTE [313].

Data from the above experiments demonstrated that in-house nZVI introduced huge amounts of B and Na into the remediated water. Due to high toxicity of B the use of in-house nZVI in environmental applications is restricted [314].

The influence of increasing nZVI concentrations of in-house nZVI, Nanofer STAR and Nanofer25 slurry (60 min of mixing, 1200 min of settling) on the behaviour of nitrogen species was also studied. The data for TN_b , organic N, nitrate N, nitrite N and ammonium N is presented in Fig. 4.8. As can be seen, the overall removal of TN_b (about 25% of its initial concentration) is the highest when applying Nanofer STAR. This nZVI, which is the least reactive among those investigated in the present study, exhibits weak interaction with organic N. Concentration of organic N slightly decreased only when iron loads from Nanofer STAR were higher than 3 g/L. On the other hand, Nanofer STAR removed nitrate N the most efficiently if we consider nZVI dose dependency. This effect is related to a great chemical reduction efficiency of nZVI for transformation of the NO_3^- and NO_2^- to NH_4^+ [315]. Since at lower pHs the reduction is more pronounced, Nanofer STAR (pHs of remediated water around 8.6) reduced NO_3^- to NH_4^+ more effectively than in-house nZVI or Nanofer25 slurry (pHs of remediated water between 9.2 and 9.9) (see data of Fig. 4.6). It is evident that about 35% of the amount of ammonium N, initially present in the effluent water, and NH_4^+ formed by the reduction of the NO_3^- , is removed by the Nanofer STAR. Removal of NH_4^+ by adsorption and co-precipitation with iron corrosion products is limited due to high solubility of the latter in aqueous solutions. However, the removal efficiency by Nanofer STAR is much greater than that of the in-house nZVI or Nanofer25 slurry, since at lower pHs, more NH_3 molecules are converted to NH_4^+ , which is removed by adsorption on the negatively charged surface of iron corrosion products. This can also be correlated by measurements of conductivity (Fig. 4.6), which showed the highest nZVI dose-dependent drop during the use of Nanofer STAR compared to the in-house nZVI and Nanofer25 slurry. From the data in Fig. 4.8 it can be further seen that a similar degree of removal of TN_b (about 15% of its initial concentration) is obtained by both, in-house nZVI and Nanofer25 slurry. One of the important constituents of organic N in municipal wastewater are proteins [308]. They are, by the action of nZVI, degraded to amino acids and ammonium. The interactions of these highly reactive nZVI with

organic N resulted in the formation of ammonium N species and thus, in substantial decrease in concentration of organic N (about 40 and 80% of initial concentration of in-house nZVI and Nanofer25 slurry, respectively). Additional, but much smaller amount of ammonium N is generated by the reduction of NO_3^- , while the formation of NH_4^+ by the reduction of NO_2^- is almost negligible.

By the formation of ammonium N from organic N and nitrate N, its initial concentration in the effluent water was increased for about 18% or 25% when in-house nZVI or Nanofer25 slurry, respectively, were used for the remediation. At alkaline pHs (9.2 up to 9.9, Fig. 4.6) the adsorption of ammonium N is hindered. However, the amount that is equivalent to newly formed NH_4^+ species is removed at the use of in-house nZVI. So, its concentration in the remediated water remained approximately the same. On the contrary, after the Nanofer25 slurry application, the amount of ammonium N was slightly increased with increasing the nZVI loads. More efficient removal of ammonium N by the use of in-house nZVI in comparison to Nanofer25 slurry is related to its higher surface area (surface area 83 m^2/g and 44 m^2/g for in-house nZVI and Nanofer25 slurry, respectively, Table 4.3).

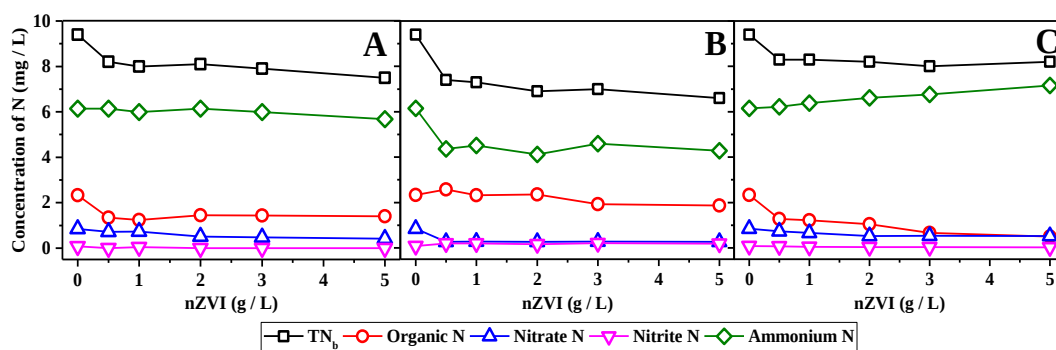


Figure 4.8: Influence of increasing iron loads from in-house nZVI (A), Nanofer STAR (B) and Nanofer25 slurry (C) (mixing time 60 min; settling time 1200 min) on the concentration of N species determined in remediated water samples from the SBWTP.

Data presented in Fig. 4.8 clearly demonstrate that the amount of organic N and inorganic N species presented in the remediated effluent water depends strongly on the reactivity and physical properties (surface area) of the nZVI tested. The pH of effluent water after the remediation also has a significant influence on the overall removal of N species by adsorption with iron corrosion products [314].

However, due to a low reactivity and presence of competing chemical species from the effluent water, the observed effects of NO_3^- and NO_2^- reduction into NH_4^+ were not as intensive as reported by the literature for simple artificial water matrices [315]. The effect of removal of NH_4^+ from water can be, beside adsorption to nZVI and its corrosion products, at least partly contributed to the effect of ammonia air stripping. This process is also intensified with the increase of pH to alkaline values as observed at the use of all three nZVI materials. Thus NH_4^+ is deprotonated and transformed into NH_3 , which is stripped from water and emitted into air by bubbles [316]. Namely air bubbles were introduced into water during intensive mixing at aerobic conditions at the nanoremediation procedure. The effect of ammonia stripping, lowering of NH_4^+ concentrations in water despite its evident formation due to a reduction of NO_3^- and NO_2^- , was reported by Hwang et al. [315]. They observed the removal effect of more than 80 wt.% of total N from artificial water solution of NO_3^- (100 mg/L) treated by 0.1 g/L nZVI (NaBH_4 reduction synthesis). However, the results of this study are not fully comparable with the described findings due to a more complex composition of used effluent water, lower pH increase at application of nZVI, and lesser air bubbles introduction.

Influence of the increasing iron loads from in-house nZVI, Nanofer STAR and Nanofer 25 slurry, on the disinfection efficiency of effluent water from the SBWTP was further investigated. The results are presented in Fig. 4.9. Data demonstrate that among the nZVI investigated in-house nZVI inactivated bacterial species the most effectively. The disinfection efficiency (C_x/C_i) was almost independent of the nZVI concentration, and was very effective even at the lowest iron load (0.5 g/L). Nanofer STAR was efficient only at iron load of 5 g/L, while Nanofer25 slurry was effective at iron loads from 1 g/L, if we consider disinfection effectiveness of $> 90\%$. The highest disinfection efficiency of in-house nZVI, in comparison to Nanofer STAR and Nanofer25 slurry, can be related to its highest specific surface area (83, 17 and 44 m^2/g , respectively), the available Fe^0 content (88, 69, 85 wt.%, respectively) (Table 4.1) and the highest reactivity (Fig. 4.3).

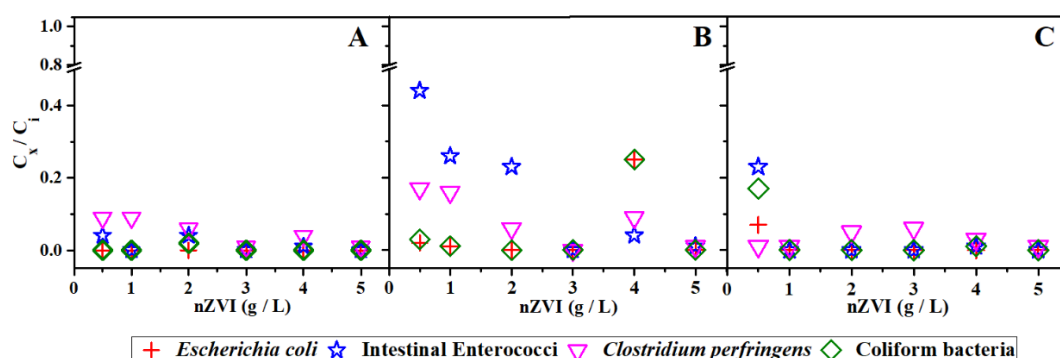


Figure 4.9: Influence of increasing iron loads from in-house nZVI (A), Nanofer STAR (B) and Nanofer25 slurry (C) (mixing time 60 min; settling time 1200 min) on the disinfection efficiency (C_x/C_i) of effluent water from the SBWTP (C_i = before remediation; C_x = after remediation).

Despite the fact that the most efficient disinfection of the effluent water was achieved by in-house nZVI, this type of nZVI was found not to be suitable for the remediation as it released high amounts of B and Na into water being remediated (see data in Fig. 4.7). B released as a contaminant from in-house nZVI may also contribute to the disinfection of the effluent water. Its bactericidal properties against microorganisms were reported [317].

In-house nZVI effectively interacts with the microbial cell surface, which results in cell membrane disruption and oxidative stress, eventually leading to cell death [90]. The nZVI dose-dependent efficiency, which can be observed for all three nZVI materials, is in line with the findings from the scientific literature [91]. The disinfection of effluent water by Nanofer STAR in this study is comparable to the use on Toda Kogyo Corp. nZVI at the same nZVI concentrations for *Escherichia coli* [89]. The disinfection efficiency at the treatment of effluent water by using in-house nZVI is lower than reported by literature [91] at the same concentrations. This can be attributed to the effect of organic substances present in the effluent water that prevents the interactions of nZVI with bacterial cells, by sterically stabilizing the nanoparticles [93]. The efficiency of Nanofer STAR was less pronounced than for Nanofer25 slurry, despite the fact that both have similar microstructural characteristics and particle size distribution. The difference in disinfection efficiency between both Nanofer products clearly indicates that physical interactions with the bacteria cells are not the only factors affecting disinfection. The higher reactivity of Nanofer25 slurry compared to Nanofer STAR results in higher ROS yields and higher cytotoxicity towards bacteria [318].

The results presented in Fig. 4.9 also confirm that generally Gram-negative bacteria (*Escherichia coli*, Coliform bacteria) are more susceptible to disinfection effects by nZVI than Gram-positive species (Intestinal Enterococci, *Clostridium perfringens*) [91], which is visible at the use of Nanofer STAR. This can be attributed to thicker and more resistant peptidoglycan cell wall of Gram-positive species, which can better resist the direct interactions with nZVI.

However, the trend is not pronounced when Nanofer25 slurry was used, which could also imply that it forms more ROS, which can inactivate bacteria regardless of cell wall resistivity.

4.3.2 Optimization of nanoremediation

Nanofer25 slurry was selected for further investigation of water nanoremediation study for multiple reasons that pointed out its use as more appropriate than in-house nZVI and Nanofer STAR:

- In-house nZVI released high amounts of toxic B into the water during remediation.
- The use of in-house nZVI is hardly feasible for real-case use due to a complexity of large-scale production, which would generate high amounts of wastewaters containing toxic B (both from synthesis and washing of the particles), controlling of exothermic reaction that also generates gaseous H_2 is very demanding and dangerous, sustaining highly reactive in-house nZVI in an inert atmosphere is costly, and the material is hard to handle.

The use of Nanofer STAR was proved to be less efficient for water remediation both from the view of removal of PTE and for the disinfection.

Nanofer25 slurry has showed the best dose-dependant remediation efficiency, without additional side effects in the form of additional contamination by PTE.

4.3.2.1 Optimization of disinfection efficiency

Initial study showed that Nanofer25 slurry type of nZVI was not effective for bacterial inactivation, when iron load of 0.5 g/L was applied at a mixing and settling time of 60 and 1200 min, respectively (Fig. 4.9). However, literature data [89], [93] and previously published research work [314] show that disinfection efficiency not only depends on the concentration of used nZVI but also on the time of mixing. Therefore, this parameter was prolonged to 240 min, while the settling time was kept the same (1200 min). On the other hand, the effectiveness of disinfection at lower concentrations of nZVI (0.25 and 0.1 g/L) was also tested (Fig. 4.10). From the data in Fig. 4.10 it is evident that a prolonged mixing time (240 min) increased the disinfection efficiency of Nanofer25 slurry at iron load of 0.5 g/L and that its disinfection efficiency at a lower iron load (0.25 g/L) worsened and became almost ineffective at iron load of 0.1 g/L (Fig. 4.10). Very similar dose-dependent disinfection efficiencies were reported by [318]. However, their work was based on the use of nZVI synthesized by borohydride reduction, exposure of 60 min, which is more comparable with the use of in-house nZVI (Fig. 4.9), which in this study achieved higher efficiency.

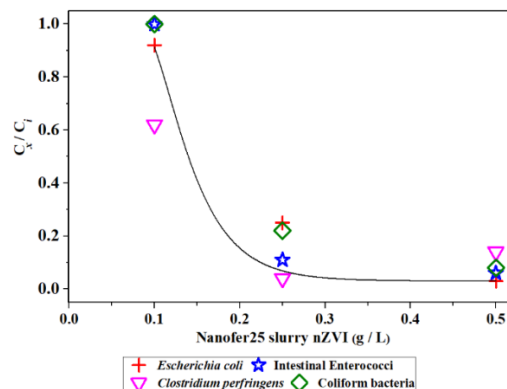


Figure 4.10: Influence of increasing iron loads from Nanofer25 slurry (mixing time 240 min; settling time 1200 min) on the disinfection efficiency (C_x/C_i) of effluent water from the SBWTP (C_i = before remediation; C_x = after remediation).

The results of disinfection efficiency in the experiment with prolonged times of mixing indicate that the enhancement in efficiency can be on account of higher yields of ROS. Namely, mixing can aerate water, thus providing O_2 for ROS by oxidation of nZVI. The process of ROS formation and consequently disinfection is thus far more effective under aerated conditions [319], [95]. Therefore, the influence of mixing time on the disinfection efficiency of Nanofer25 slurry was further systematically studied in a time interval from 30 to 1200 min at nZVI concentrations 0.1 and 0.5 g/L and settling time of 180 min, the latter being short enough to avoid the possibility of bacterial regrowth during settling. The results are presented in Fig. 4.11.

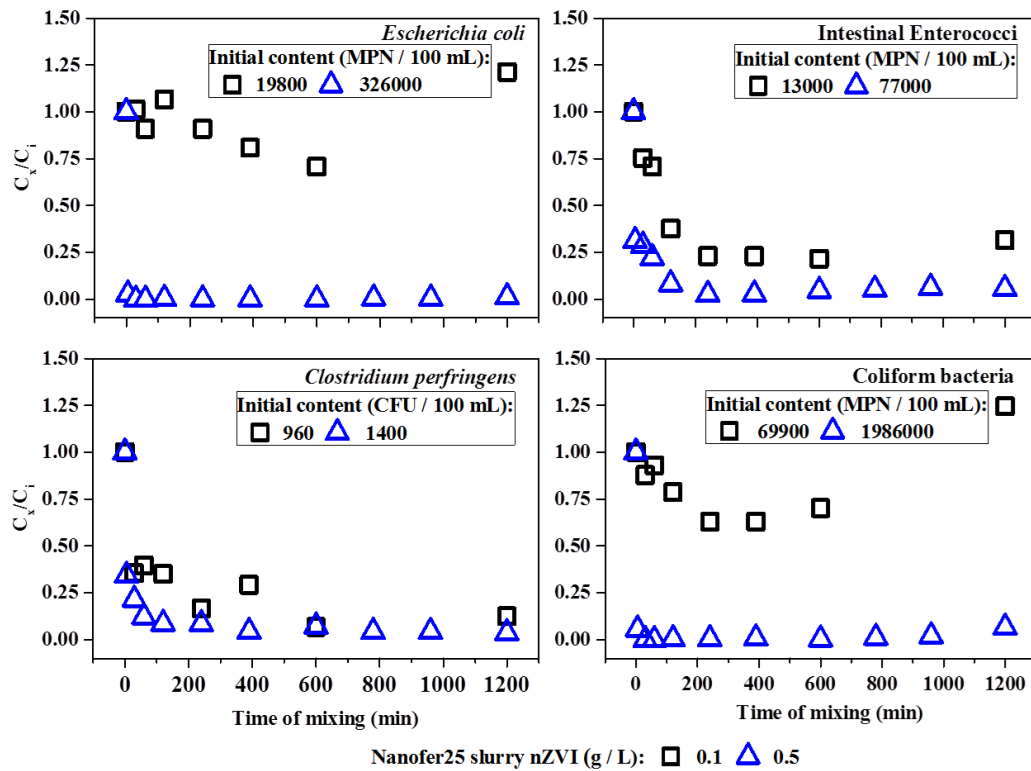


Figure 4.11: Influence of increasing mixing time from 30 to 1200 minutes (at concentrations 0.1 and 0.5 g/L Nanofer25 slurry) on the disinfection efficiency (C_x/C_i) of effluent water from the SBWTP (C_i = before remediation; C_x = after remediation).

Time-dependent disinfection of *Escherichia coli* was performed on samples, which on average contained approximately 16.5 times lower initial concentrations of bacteria, when 0.1 g/L nZVI was applied compared to the case of 0.5 g/L nZVI application. Despite the initial difference, low nZVI concentration had a negligible effect on bacteria, with approximately 35% maximum efficiency at 600 min of mixing. After 1200 min of mixing the concentration of *Escherichia coli* even increased over the initial value. This indicates that mixing and laboratory conditions during the experiment favoured regrowth of bacteria in effluent water after all nZVI were oxidised. The efficiency of Nanofer25 slurry for disinfection of *Escherichia coli* at 0.5 g/L was substantially higher and almost independent of the mixing duration. Namely, approximately 98% efficiency was achieved after 30 min of mixing, and no regrowth was seen even after 1200 min of mixing.

The average initial concentration of Intestinal Enterococci was approximately 6 times lower in the experiments with the use of 0.1 g/L Nanofer25 slurry as for 0.5 g/L. Nevertheless, disinfection efficiency was constantly at least 10% lower at 0.1 g/L nZVI dosage. Maximum efficiency at 0.1 g/L, 78%, was achieved at 390 min of mixing. Slight regrowth of bacteria after 1200 min of mixing was observed as disinfection efficiency dropped below 75%. At the

application of 0.5 g/L nZVI maximal efficiency, 98%, was achieved between 390 and 600 min of mixing, with no regrowth even after 1200 min.

The lowest average initial concentrations were measured for *Clostridium perfringens*, which were approximately 500 CFU higher when 0.5 g/L nZVI was used compared to the experiments with the use of 0.1 g/L nZVI. The maximum efficiency at the use of 0.1 g/L nZVI was for *Clostridium perfringens* 95% achieved at 600 minutes of mixing. At the use of 0.5 maximal disinfection efficiency was approximately 96% between 120 and 240 min of mixing.

The highest difference in average initial concentrations of bacteria between experiments was for Coliform bacteria. The concentration of bacteria at the application of 0.1 g/L of nZVI was 28 times lower than at 0.5 g/L nZVI. However, maximal disinfection efficiency at a low nZVI concentration was less than 50% at 390 min of mixing. On the other hand, at 0.5 g/L concentration disinfection maxima was achieved already at less than 60 min of mixing, without regrowth that was observed at 0.1 g/L nZVI concentration.

There are only a few studies that dealing with the kinetics of disinfection with the use of nZVI. However, they were performed in artificially prepared laboratory water matrices. For example, more than 80% disinfection efficiency of approximately 2×10^6 CFU of *Escherichia coli* in artificial and simple water matrix prepared in laboratory after less than 20 min of mixing under aerobic conditions, with 0.1 g/L nZVI containing just 25 wt.% of Fe^0 [95] was reported. For comparison, in real natural effluent water, less than 30% disinfection efficiency was achieved, for approximately 50 times lower *Escherichia coli* concentration, with the use of 0.1 g/L Nanofer25 slurry nZVI, which contains 85 wt.% of Fe^0 , at 600 min of mixing.

Chen et al. [93] observed more than 80% reduction of *Escherichia coli* at nZVI concentration 1 g/L, after 60 min of mixing, which is less efficient than in this study. The same authors also observed that disinfection efficiency dropped to less than 20%, when 10 mg/L of soluble organic matter was present in the water. However, the disinfection efficiency maxima were apparently not achieved after 240 min of mixing as seen from the data. Differences in the efficiency between literature reports and this study again imply that mixing conditions are crucial for efficient disinfection. Namely, in this study, mixing was performed in an open beaker with a blender and thus more O_2 can enter the system for ROS generation compared to closed mixing conditions in the study of [93], where O_2 is rapidly used up for chemical processes. The presence of O_2 due to aerobic conditions in combination with soluble organic matter – chelates can even enhance the yield of ROS, thus enhancing the disinfection efficiency [320].

The difference in disinfection efficiency between Gram-positive and -negative bacteria, which is reported by literature [91], is only minor in the results of this study. It is observed, at the use of 0.5 g/L nZVI concentration, that disinfection maxima was achieved at longer mixing times for Intestinal Enterococci and *Clostridium perfringens* (both Gram-positive) as for *Escherichia coli* and Coliform bacteria (Gram-negative), despite much lower initial concentrations of the former.

When longer mixing time was applied for *Escherichia coli*, Coliform bacteria, and slightly for Intestinal Enterococci, regrowth of bacteria was observed. Multiplying of bacteria, which remained after incomplete disinfection during nanoremediation, can be related to favourable growth conditions: water is aerated and still contains enough nutrients to support growth. Also, the reactive component of nZVI (Fe^0) as well as ferrous iron is oxidized to iron hydroxides or oxides, which do not have bactericidal effects [91]. Recovery of bacterial community was reported to happen in a matter of a few hours after oxidation of nZVI [83]. This is also in line with the results of this study. Also, changes in equilibrium between microbial species can be observed, as confirmed by this study and literature [90].

Disinfection efficiency for nanoremediation of effluent water by Nanofer25 slurry was optimized at the nZVI concentration of 0.5 g/L and time of mixing between 180 and 240 min. The optimal nZVI concentration used for achieving > 90% disinfection efficiency for *Escherichia coli*, Intestinal Enterococci, *Clostridium perfringens*, and Coliform bacteria, is

lower than those reported by most of the scientific literature [83], [90]. This concentration cannot be further decreased, if the same efficiency ($> 90\%$) is required, as a sharp drop in disinfection efficiency is observed already at 0.25 g/L concentration of nZVI (Fig. 4.10). However, additional disinfection of effluent water is needed for safe water reuse or to achieve drinking water limit values (Official Gazette of RS, No. 51/17 [271]).

4.3.2.2 Optimization of PTE removal

Concentrations of selected PTE in effluent water are already low, below limit values for drinking water (Official Gazette of RS, No. 51/17). Nevertheless, they were analysed to monitor possible changes in concentrations of water soluble species of PTE due to remediation with nZVI. The influence of mixing time was systematically studied in time interval from 30 to 1200 min at nZVI concentrations 0.1 and 0.5 g/L and settling time of 180 min. The results for elements that show the most significant changes are presented in Figs. 4.12 and 4.13. Elements Al, B, Hg, and Na did not show any trends dependent on nZVI concentrations 0.1 and 0.5 g/L , or the time of mixing, therefore they are not included here.

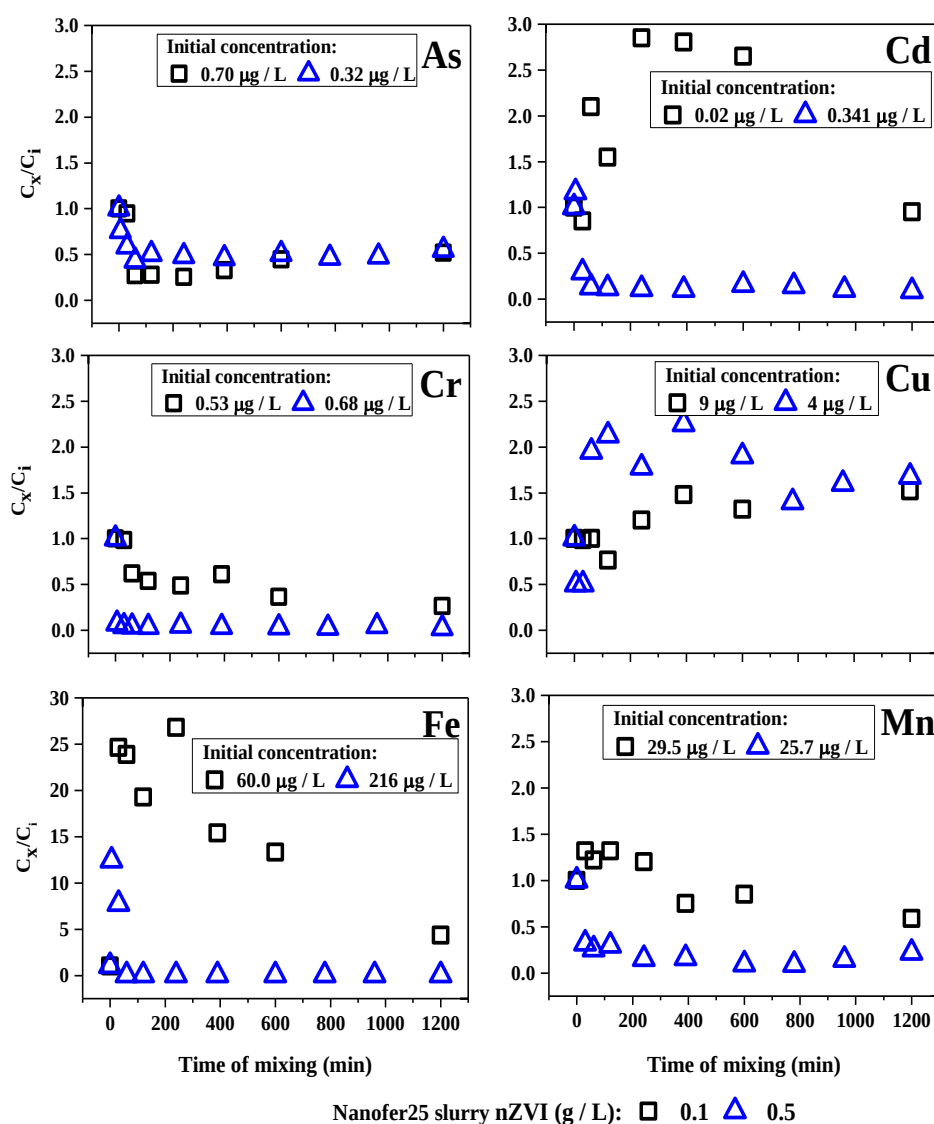


Figure 4.12: Influence of increasing mixing time from 30 to 1200 minutes (at concentrations 0.1 and 0.5 g/L Nanofer25 slurry) on the removal efficiency (C_x/C_i) of Fe, Cd, Cr, Cu, As, and Mn from effluent water from the SBWTP (C_i = before remediation; C_x = after remediation).

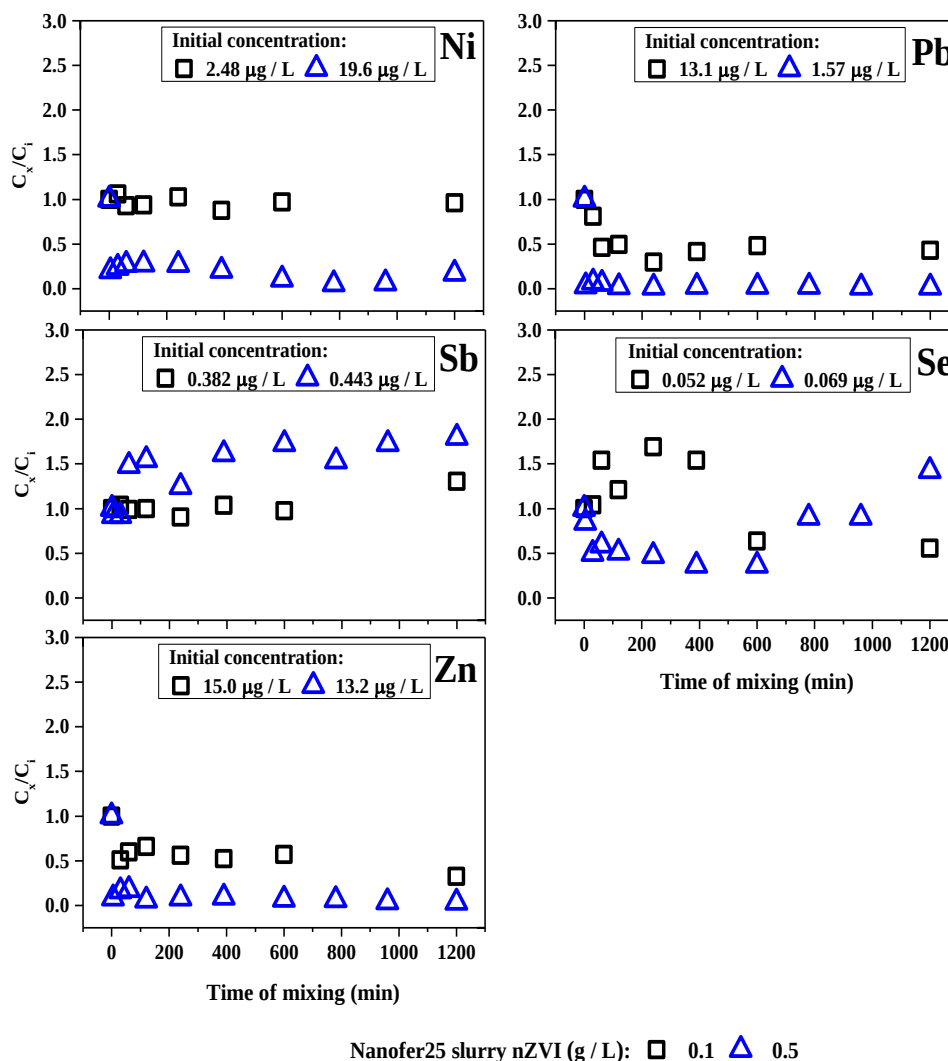


Figure 4.13: Influence of increasing mixing time from 30 to 1200 minutes (at concentrations 0.1 and 0.5 g/L Nanofer25 slurry) on the removal efficiency (C_x/C_i) of Fe, Cd, Cr, Cu, As, and Mn from effluent water from the SBWTP (C_i = before remediation; C_x = after remediation).

The pH of effluent water during nanoremediation is one of the most important parameters that determines the immobilization of PTE. Therefore, changes in pH were also measured and are given in Fig. 4.14. After the addition of nZVI into effluent water pH increased rapidly from 7.5 to 8.3 after 240 min of mixing, regardless of the nZVI dose. Similar increase of pH from neutral values to approximately 9 after the addition of nZVI were reported to happen in the first few hours in some simple artificial water matrices [85]. With prolonged mixing, pH of effluent water with 0.1 g/L nZVI further increased to 8.7. However, with the use of 0.5 g/L nZVI pH dropped to approximately 8.0. This could indicate that at higher concentrations of nZVI, more alkalinity was consumed for the transformation of iron into hydroxide minerals.

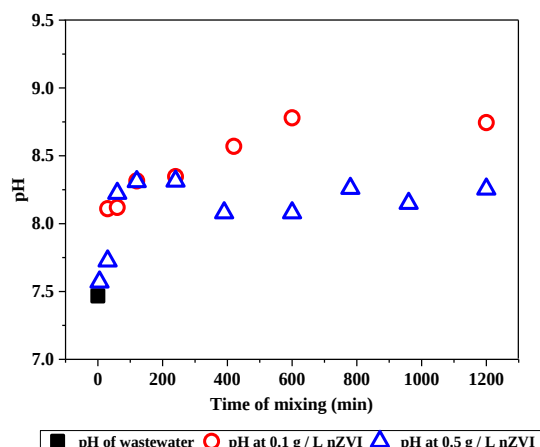


Figure 4.14: Influence of increasing mixing time from 30 to 1200 minutes (at concentrations 0.1 and 0.5 g/L Nanofer25 slurry) on the pH of effluent water from the SBWTP.

The average initial concentration of As in effluent water, which was treated with 0.1 g/L of nZVI, was more than twice higher than for experimental treatment with 0.5 g/L nZVI. The concentration of As in effluent water was very low. However, nZVI lowered initial concentration slightly less efficiently with the use of 0.5 g/L nZVI, where approximately 50% of As was removed, compared to the use of 0.1 g/L nZVI where approximately 65% of As was removed. Adsorption maximum in both cases achieved between 120 and 240 minutes of mixing. Desorption was observed afterward, which can be connected with a gradual increase of pH towards slight alkaline values (Fig. 4.14), at which adsorption of As oxyanion is hindered. Also, it is reported by scientific literature that As is less efficiently removed by nZVI in aerated conditions in the presence of dissolved oxygen, than in the case of this study [321].

Cadmium in effluent water, which was treated by 0.1 g/L of nZVI, was present in very low concentrations, which was on average more than 100 times lower than in the experiment where 0.5 g/L nZVI was used. Therefore, the removal kinetics are not fully comparable. Namely, the former experiment indicated desorption of Cd from nZVI with an initial rise of concentrations by almost 300% after 240 min of mixing, followed by a drop to the initial concentration after 1200 min of mixing. Gradual removal of Cd after desorption can be related to gradual increase of pH at prolonged mixing times (Fig. 4.14) which favours immobilization of Cd [281]. At the use of 0.5 g/L nZVI the removal of Cd was rapid, reaching its maximum of 98% at 120 min of mixing. Literature data for the removal of Cd by nZVI reported that the presence of competing ions that are also present in effluent water, especially Cl^- , can substantially decrease the removal efficiency. In simple artificial water matrices more than 20% and 90% removal of 100 mg/L Cd was achieved at 0.1 and 0.5 g/L nZVI dosage, respectively [281]. However, much longer time of 15 hours was reported to achieve reaction equilibrium, compared to this study.

The average initial concentrations of Cr in effluent water were similar in the case of use of 0.1 and 0.5 g/L nZVI. The maximal removal of Cr at 0.1 g/L nZVI was 65%, achieved at 1200 min of mixing. Meanwhile, at 0.5 g/L nZVI, 98% of removal was achieved after 30 min of mixing. Much lower efficiency of Cr removal at 0.1 g/L of nZVI can also be a consequence of higher pH compared to when 0.5 g/L was used (Fig. 4.14). More alkaline pH of effluent water, when 0.1 g/L nZVI was used, is namely unfavourable for efficient adsorption of Cr oxyanion by iron minerals [70].

The average concentration of Cu was more than twice higher in the effluent water treated by 0.1 g/L of nZVI than by 0.5 g/L. At the application of both concentrations of nZVI a removal of Cu from effluent water at low mixing times, from 30 to 240 min for 0.1 g/L of nZVI and from 30 to 60 min for 0.5 g/L nZVI, was observed. However, desorption from nZVI occurred at longer mixing times, which caused an increase in Cu concentrations in effluent

water to approximately 200% of average initial concentrations in effluent water treated by 0.5 g/L nZVI. Similar dose dependent release of Cu can be observed in Fig. 4.7.

The average initial concentrations of Fe were approximately 4 times higher in effluent water treated with 0.5 g/L of nZVI compared to the effluent water sample treated with 0.1 g/L nZVI. However, the concentration of Fe was lowered by 98% of its initial concentration after 60 min of mixing, despite the use of 0.5 g/L of nZVI. On the other hand, when 0.1 g/L nZVI was applied, the concentration of Fe increased by up to 25 times of initial concentration at 240 min of mixing. With longer mixing times the concentration of Fe dropped to approximately 5 times the initial concentration. This effect can be related to the behaviour of nZVI in effluent water. It is reported by scientific literature that at higher concentrations of suspended nZVI, their agglomeration and sedimentation is faster and more intensive due to a higher density of attractive magnetic electrostatic forces generated by nZVI [322]. Due to a lower agglomeration rate at lower nZVI concentrations, their stabilization by dissolved organic matter from effluent water is possible during mixing. The effects of stabilization of nZVI by dissolved organic matter from treated water that enhanced their mobility was also described in scientific literature [93]. The stabilized nZVI remained in the suspension, thus contributing to the concentrations of iron until they were oxidised by prolonged mixing.

Manganese was present in effluent water in similar concentrations in experiments with treatment by 0.1 and 0.5 g/L nZVI. However, when a lower nZVI concentration was used, the concentration of Mn has increased by up to 130% with a mixing time up to 240 min and decreased with prolonged mixing times. This implies that Mn is bound to nZVI, which remained suspended due to above-described effects. Meanwhile, at the application of 0.5 g/L nZVI, the concentration of Mn decreased gradually until 240 minutes of mixing by up to 90%.

Almost two times higher average initial concentrations of Ni were present in effluent water treated by 0.5 g/L nZVI compared to the effluent water treated by 0.1 g/L nZVI. However, there was no time-dependent removal or release at 0.1 g/L nZVI. At higher nZVI dose removal efficiency of approximately 95% was achieved rapidly after 30 min of mixing. Rapid adsorption of Ni was reported from simple artificial water matrices, where removal efficiency was much higher. Namely, 99% removal efficiency was achieved by 0.1 g/L nZVI from water with 500 mg/L concentration of Ni [323].

Approximately 10 times higher average initial concentrations of Pb were present in the effluent water treated by 0.1 g/L of nZVI than in effluent water treated by 0.5 g/L nZVI. The maximum efficiency of Pb removal with 0.1 g/L nZVI was 70% at 240 min of mixing. Then desorption was observed at longer times of mixing, which resulted in a drop of efficiency to 50% at 1200 min of mixing. With the use of 0.5 g/L nZVI, a rapid removal of Pb from effluent water was observed, reaching 98% efficiency after 30 min of mixing.

Average initial concentrations of Sb in effluent water samples treated by 0.1 and 0.5 g/L nZVI were roughly the same. Gradual desorption of Sb from nZVI was observed in both cases with prolonged mixing and depending of the nZVI dose, as it can also be seen in Fig. 4.7. Maximum increase of initial Sb concentration in effluent water was 180%, when 0.5 g/L of nZVI was used at 1200 min of mixing.

Approximately the same concentrations of Se were present in effluent water samples treated by 0.1 and 0.5 g/L nZVI. However, at a lower nZVI dose, desorption of Se occurred, reaching 170% of its initial concentration. This was followed by a gradual lowering of Se concentration, reaching 45% removal efficiency at 1200 min of mixing. At the application of 0.5 g/L nZVI, rapid removal occurred at 30 min of mixing followed by a gradual desorption and increase, which resulted in reaching 140% of initial concentration of Se in effluent water after 1200 of mixing. The behaviour of Se during nanoremediation by nZVI is similar as for Mn and Fe. Therefore, the former can also be bounded or very connected to nZVI behaviour in effluent water. Literature data on the other hand report rapid removal of Se from simple artificial water matrices, reaching 99% after less than 60 min [79]. However, Se is in nature present as

oxyanion, therefore its removal in alkaline environment of effluent water during nanoremediation (Fig. 4.14) is limited, similarly as for As and Cr.

The average initial concentrations of Zn in effluent water were also very similar in both cases, treatment with 0.1 and 0.5 g/L nZVI. As seen in Figs. 4.7 and 4.13, removal of Zn is dose dependent. It reached 70% efficiency at 1200 min of mixing, when 0.1 g/L nZVI was used. On the other hand, it reached 95% efficiency at 120 min of mixing, when 0.5 g/L nZVI was applied. Comparable trends in removal efficiency were reported by [324]. On the one hand they observed less than 30% removal efficiency in simple artificial water solution treated by 0.1 g/L nZVI, however, at much higher initial Zn concentration (100 mg/L) than measured in effluent water of this study. On the other hand, they achieved more than 80% efficiency with the use of 0.6 g/L nZVI within 120 min reaction time under aerated conditions, which is a very similar efficiency as presented in this study.

The dose dependent efficiency for the removal of PTE from water was usually reported at higher removal efficiencies (>99%) than observed in this study. However, higher concentrations of nZVI >0.5 g/L and PTE concentrations 100 mg/L were tested in simple artificially prepared water matrices [325]. Much higher concentrations of nZVI were used in a similar study for nanoremediation of industrial wastewaters [65]. The authors treated wastewater contaminated by multiple PTE that reached more than 1000 times higher concentrations than in effluent water of the presented study. They achieved more than 90% removal efficiency for As, Cu, Ni, and Zn, with the use of 4 g/L nZVI, after 60 min of mixing, and no desorption effects were observed.

Calderon and Fullana [280] used higher concentrations of nZVI (1, 2.5, and 5 g/L) to treat artificially prepared water solution containing 100 mg/L Zn, Cd, Ni, Cu, and Cr (VI). They observed higher removal efficiencies (>90%) as in this study for all elements by using nZVI concentrations 1 and 2 g/L. However, they observed maximal removal efficiency at similar reaction times as in this study, between 30 and 300 minutes. They also reported desorption effect after reaction times longer than 600 minutes, which can be in this study observed for As, Mn and Se. Otherwise, the removal kinetics and behaviour of PTE in presented study is very different than reported by Calderon and Fullana [280]. Namely, lower concentrations of PTE are present in a very complex matrix of effluent water, which was treated by 2 to 10 times lower nZVI concentrations. The presence of dissolved organic matter, competition for adsorption sites between ions, high ionic strength and buffering capacity of effluent water, not only caused desorption of PTE, which are initially present in nZVI (Mn, Cu, Se) (reported by [306]), but also mobilization of PTE that were already removed from effluent water at short reaction times (As, Pb, Se). Desorption of PTE from nZVI due to exposure to high ionic strength water solution was also reported by Efecan et al. [323]. Much more complex behaviour of PTE during nanoremediation of effluent water compared to simple artificial water matrices can also be confirmed by comparing the results of Eglal and Ramamurthy [300] with results of this study. Namely, they reported negligible effects on removal kinetics of PTE on nZVI due to the presence of multiple metal ions, with time of maximal removal less than 120 min.

Optimal parameters for optimal removal efficiency of PTE from effluent water are similar as determined for optimal disinfection efficiency, with optimal nZVI dose of 0.5 g/L and mixing time between 180 and 240 min. These parameters not only enable the most efficient removal of PTE, but also prevent later mobilization due to a complex interaction between complex matrix of effluent water and nZVI.

4.3.2.3 Behaviour of nitrogen species during nanoremediation

Concentrations of nitrogen species in effluent water are higher than limit values for drinking water (Official Gazette of RS, No. 51/17). Their transformation and chemical interactions with nZVI are complex. Therefore, the influence of mixing time on concentrations of NH_4^+ , NO_3^- , and NO_2^- was systematically studied in a time interval from 30 to 1200 min at nZVI

concentrations 0.1 and 0.5 g/L and settling time of 180 min. The results are presented in Fig. 4.15.

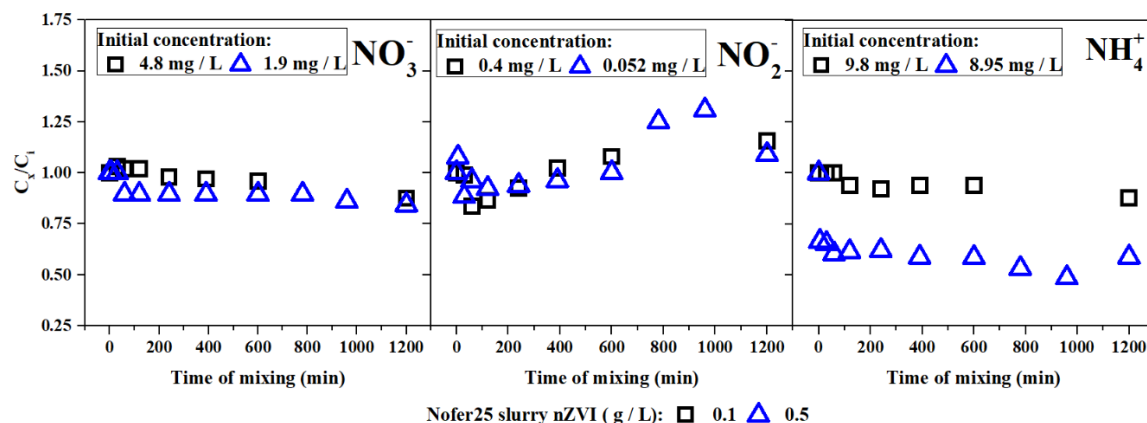


Figure 4.15: Influence of increasing mixing time from 30 to 1200 minutes (at concentrations 0.1 and 0.5 g/L Nanofer25 slurry) on the removal efficiency (C_x/C_i) of NO_3^- , NO_2^- , and NH_4^+ from effluent water from the SBWTP (C_i = before remediation; C_x = after remediation).

Approximately 2.5 times higher average concentrations of NO_3^- were initially present in effluent water sample, which was treated by 0.1 g/L nZVI compared to the sample treated by 0.5 g/L nZVI. Almost no change in the concentration of NO_3^- was observed, when 0.1 g/L nZVI was used, and only minor (approximately 10%) reduction in its concentration was observed, when 0.5 g/L nZVI was used. The observed effects are completely opposite than reported for kinetics of nitrate reduction in artificial water samples, for example by Hwang et al. [81] or by authors who recommend nZVI as an agent for removal of NO_3^- from water [321]. However, the scientific literature also reports high inhibition of NO_3^- by nZVI due to the presence of different ions in water solution, for example Cl^- , SO_4^{2-} , PO_4^{3-} , BO_4^{4-} , oxalate, citrate, etc. [326]. The same effect can be observed in the results of this study, as effluent water contains relatively high concentrations of ions, for example Cl^- and SO_4^{2-} (Fig. 4.15).

The average initial concentration of NO_2^- in effluent water sample treated by 0.1 g/L nZVI was approximately 7.5 times higher than in effluent water sample treated with 0.5 g/L nZVI. However, negligible differences in changes of NO_2^- concentrations between the use of both concentrations of nZVI were observed. Rapid decrease of NO_2^- concentration by 10% happened in the first 120 min of mixing. This was followed by a gradual increase of NO_2^- concentration to approximately 120% of its initial content at a prolonged time of mixing, at 1200 min. During reduction of NO_3^- by Fe^0 from nZVI, NO_2^- is formed as an intermediate nitrogen species, before reduction into NH_4^+ . The initial decrease of NO_2^- at a mixing time up to 120 min indicates that it was consumed for reduction into NH_4^+ , during oxidation of nZVI, as initial concentrations in effluent water are relatively low. Increase of the NO_2^- concentrations that followed indicates its formation due to a reduction of NO_3^- by Fe^0 from remaining nZVI. At longer mixing times most of the nZVI was already oxidized and thus reducing NO_2^- to NH_4^+ was less efficient, causing an increase in its concentrations.

Comparable average initial concentrations of NH_4^+ were present in both samples of effluent water, treated by 0.1 and 0.5 g/L nZVI. In the case, when a lower nZVI concentration was applied, only slight time-dependent reduction of NH_4^+ was seen. At a mixing time of 1200 min it reached 13% reduction of initial concentration. On the other hand, rapid reduction of NH_4^+ by 35% of initial concentration was observed after 60 min of mixing, when 0.5 g/L nZVI was applied. The concentration was further reduced for more than 50%, when the mixing time reached 1200 min. The results contradict literature data for reduction kinetics of NO_3^- into NH_4^+ by the use of nZVI [81], where an increase of the latter was observed. However, this effect is not visible due to multiple reasons. Inhibition of NO_3^- due to the presence of competing ions

in effluent water was already mentioned above. The cause for lowering NH_4^+ concentrations can also be due to adsorption to iron corrosion products, which have negatively charged surface sorption groups at slightly alkaline values during the nanoremediation procedure (Fig. 4.14). This can also be correlated with the results of this study, where higher removal of NH_4^+ from effluent water was observed at a higher dosage of nZVI (0.5 g/L) compared to low nZVI dosage (0.1 g/L) (Fig. 4.13). Third option for removal of NH_4^+ from water can be ammonia gas stripping effect, which was described in the previous section and was also suggested by literature [315]. Namely, alkaline pH of effluent water during nanoremediation is favourable for this process. Intensive mixing at nanoremediation experiments is introducing air bubbles that enable the gas stripping. Therefore, time dependent increase removal efficiency of NH_4^+ is observed in the results of this study.

Although nZVI removed a small fraction of NO_3^- and NH_4^+ was partly removed during the nanoremediation procedure, the concentrations of NH_4^+ remain above limit values for drinking water. Therefore, additional water treatment is needed to lower the concentration below limit values for drinking water (Official Gazette of RS, No. 51/17).

4.3.2.4 Optimization of settling duration

The most simple and effective removal of oxidised iron particles from remediated water is by sedimentation or settling. However, this process is governed by multiple factors that influence the behaviour of nZVI in water, such as magnetic properties, surface oxidation, precipitation of corrosion products, interactions with contaminants from effluent water etc. Especially problematic can be the presence of dissolved organic matter in effluent water, which can cause electrostatic stabilization of nZVI [307]. The efficient removal of iron (nano)particles from water is crucial for successful nanoremediation of water. Therefore, optimal settling time was optimised after the treatment of effluent water sample by 0.1, 0.25, 0.5, and 1 g/L nZVI (Nanofer25 slurry). A basic measure for the successful removal of iron particles from water suspension was measuring the concentration of Fe at different times of settling. In parallel, the concentration of Fe^0 was determined by H_2 emission method to evaluate the ratio of non-oxidised nZVI present in effluent water after nanoremediation.

Aggregation of nZVI in water is a very rapid process, which is driven by electromagnetic attractive forces between nanoparticles [322]. This leads to the formation of micro- and millimetre sized aggregates in a matter of minutes, as was also observed during nanoremediation experiments. Interestingly, more iron remained suspended when lower concentrations of nZVI were used for nanoremediation. This can already be seen in Fig. 4.12. and was further confirmed by experiments for the optimization of the settling time. In Fig. 4.16 analyses of Fe concentrations in effluent water after nanoremediation, at different settling times are presented.

As can be seen in Fig. 4.16, the highest concentrations of Fe during settling were measured in effluent water treated with the lowest nZVI concentration (0.1 g/L), which shows the slowest settling rate. Similar but slightly faster sedimentation of iron was observed when 0.25 g/L nZVI was applied. In both cases, a rapid decrease in Fe concentrations was observed in the first 3 hours of settling time, followed by a slower settling up to 10 hours settling time. After that, approximately 2 mg of Fe per litre remained in effluent water. However, this concentration dropped to less than 2 mg/L after 20 hours of settling. When 0.5 and 1 g/L concentrations of nZVI were applied, the drop in Fe concentrations in effluent water was fast in the first hour of settling, followed by a slightly slower settling in a period from 1 to 3 hours. At that point Fe concentrations already dropped to 1.5 and 2.4 mg/L for 1 and 0.5 nZVI application, respectively. After 10 hours of settling concentrations of Fe were in both cases below 2 mg/L.

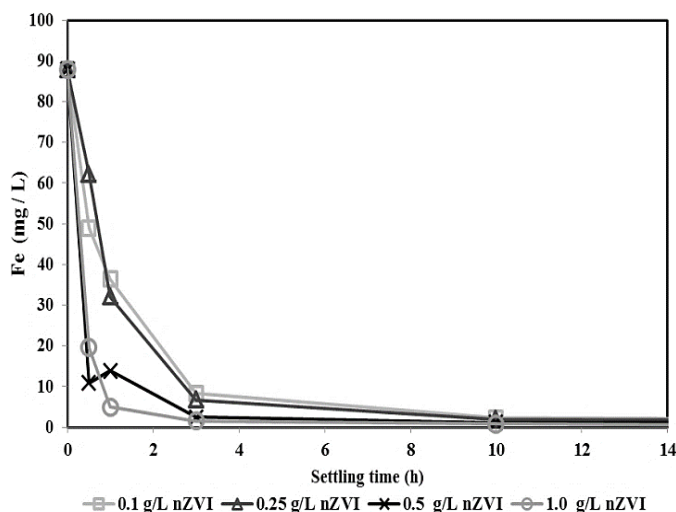


Figure 4.16: Concentrations of Fe in effluent water after nanoremediation (0.1, 0.25, 0.5, and 1.0 g/L nZVI; 180 min of mixing) at different settling times.

Explanation why the settling rate of iron is slower at a lower application of nZVI is that nanoparticles tend to aggregate faster when higher density electromagnetic attraction forces are present, which is when they are present in higher concentrations [322]. Since nZVI stay in the form of smaller particles for a longer time, when they are applied at low concentrations (0.1 or 0.25 g/L), they do not settle as they are stabilised by dissolved organic matter from effluent water. This further enhances their mobility and stability in suspension [327].

Under aerobic conditions, like in the case of nanoremediation experiments in this study, nZVI tend to oxidize fast as it was observed by the determination of Fe^0 content (Fig. 4.17). Namely, less than 30% of initial Fe^0 remained in iron particles after remediation (application of 0.25 g/L nZVI; 180 min of mixing). However, the concentration of Fe^0 did not drop for more than 4 days after nanoremediation, due to a stabilization of nZVI by organic matter from effluent water.

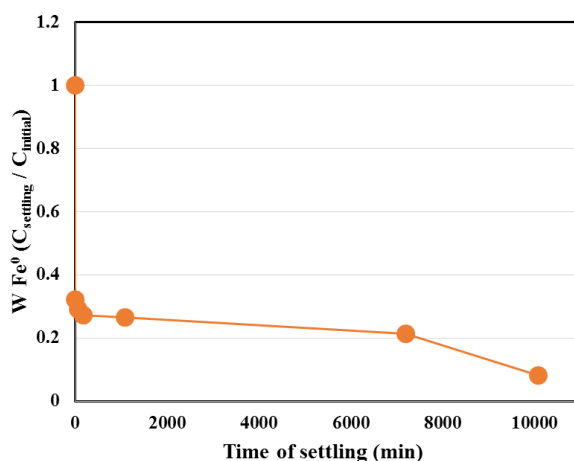


Figure 4.17: Change in the concentration of Fe^0 in nZVI during remediation (application of 0.25 g/L nZVI; 180 min of mixing), and at different times of settling.

Namely, stabilization of nZVI during the remediation process did not only enhance their persistence in effluent water, as was also confirmed by scientific studies [328], but has also prevented their oxidation. This was confirmed by XRD analysis of iron sediment after 20 hours of settling time (Fig. 4.18). It was revealed that iron sediment was composed mostly of unoxidized nZVI, when 0.1 and 0.25 g/L nZVI were applied (Fig. 4.18 A and B). On the other

hand, when 0.5 and 1 g/L nZVI were applied, typical iron corrosion products were formed (lepidocrocite, goethite, hematite), which are characteristic for the oxidation of nZVI under aerobic conditions (Fig. 4.18 C and D) [329].

nZVI tend to agglomerate and settle in effluent water during nanoremediation. However, there is a threat that a stable suspension will be formed after stabilisation by dissolved organic matter from effluent water and thus it will remain in unoxidized, reactive, form. It was proved by this study that this phenomena can occur when low concentrations of nZVI (less than 0.25 g/L) are applied for treatment of effluent water from SBWTP. In this case additional water treatment would be needed. Namely, for its safe reuse it is needed to remove the remaining iron particles from suspension and to oxidise all Fe^0 that was left in nZVI into inert form of iron oxides. Settling time optimization study has nevertheless revealed that optimal settling time after nanoremediation of effluent water is between 10 and 20 hours.

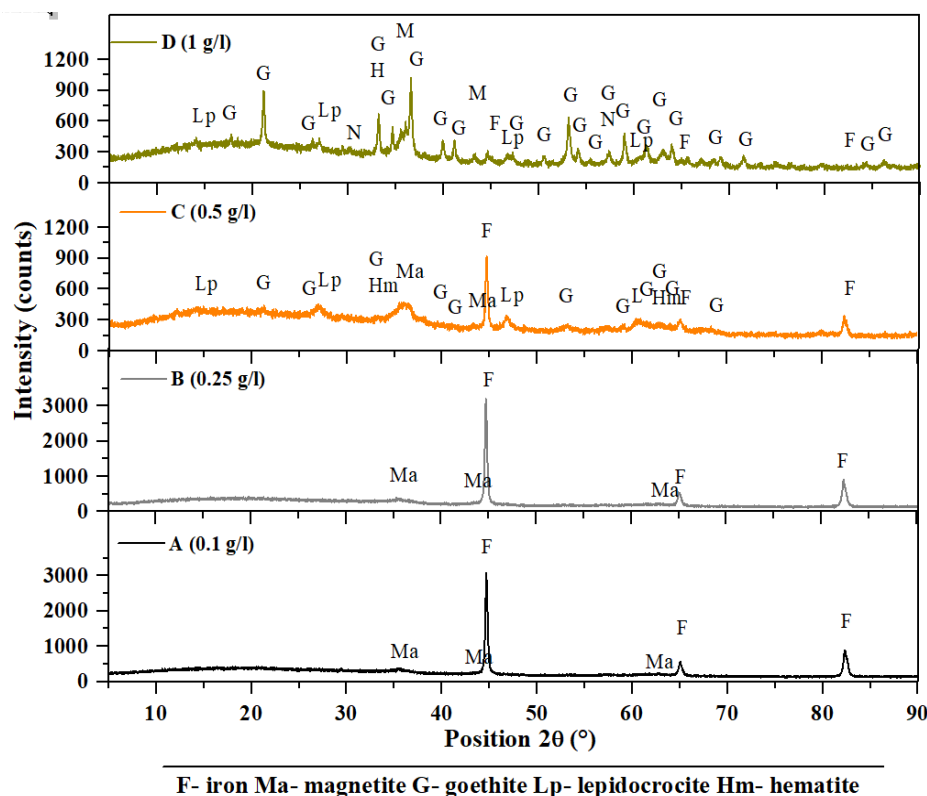


Figure 4.18: Powder X-ray Powder Diffraction patterns of iron sediment samples after 20 hours of settling from effluent water after nanoremediation with the application of 0.1 (A), 0.25 (B), 0.5 (C), and 1.0 (D) g/L nZVI (180 min of mixing).

4.3.3 Additional stages of remediation

Despite the use of optimized nanoremediation procedure of effluent water additional treatment is needed to ensure safe reuse. Although nZVI removed > 90% of bacteria, lowered concentrations of PTE and nitrogen species, they are not capable of purifying water up to a quality of drinking water, which is the goal of this study. Therefore, additional means were tested to remove any remaining contaminants and to remove any possible nano-threat.

First, treatment by an oxidizing agent sodium dichloroisocyanurate (NaDCC) was applied to remove pathogenic bacteria [282], [330] and to oxidize any remaining nZVI in effluent water after nanoremediation. NaDCC was tested in concentrations 4, 8, and 16 mg/L on effluent water samples, which were preliminary treated by 0.1, 0.25 and 0.5 g/L nZVI, according to the optimized nanoremediation procedure; 240 min of mixing, followed by 600 min of settling.

Concentrations of nZVI 0.1 and 0.25 g/L are far less effective for disinfection, as proved in previous sections of this study. Nonetheless, they were tested in combination with oxidation. Namely, lowering of the dose of nZVI for effective remediation, due to an optimal combination with the use of oxidising agent, could make the whole remediation procedure substantially more economical. The current cost of NaDCC is nearly 6000 times lower than the cost of nZVI on the market (data from December, 2017).

Influence of the increasing concentrations of nZVI in the form of Nanofer 25 slurry in combination with the use of increasing concentrations of NaDCC on the disinfection efficiency of effluent water is presented in Fig. 4.19.

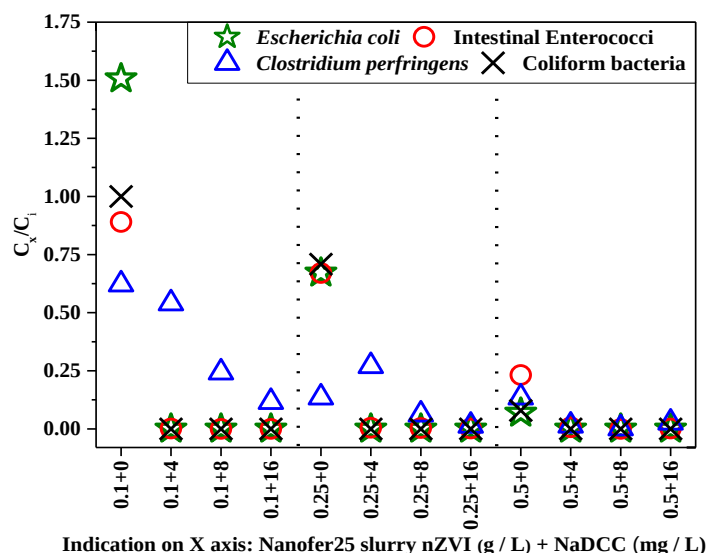


Figure 4.19: The influence of increasing concentration of Nanofer25 slurry (mixing time 180 min; settling time 600 min) and increasing NaDCC concentrations on disinfection efficiency (C_x/C_i) in remediated water samples from the SBWTP (C_i = before remediation; C_x = after remediation).

The results of disinfection efficiency show that the use of 0.1 g/L nZVI in combination with the NaDCC was not successful. Even when the highest dose of NaDCC was used (16 mg/L), disinfection efficiency did not achieve more than 90% for all parameters. However, gradual dose dependent increase in efficiency can be observed (Fig. 4.19). Better results were obtained, when nanoremediation with 0.25 g/L nZVI was combined with the NaDCC treatment. More than 90% disinfection efficiency was achieved when 8 and 16 mg/L of NaDCC were used, while 4 mg/L addition was not effective. When 0.5 g/L nZVI nanoremediation was combined with NaDCC treatment, more than 95% disinfection efficiency at all three combinations for all parameters was achieved. Almost 99% disinfection efficiency was achieved when 8 and 16 mg/L NaDCC were used.

The use of NaDCC for the preparation of drinking water was already recommended by WHO as one of the most efficient and cost-effective disinfection agents. NaDCC gradually releases free available chlorine in the form of HOCl (hypochlorous acid). For example, HOCl is released in effluent water after its depletion to restore chemical equilibrium [330]. Similar dose dependent disinfection efficiency of NaDCC as in this study was already described in scientific literature [282].

Nitrogen species, especially NH_4^+ were not effectively removed from effluent water during the nanoremediation procedure. Therefore, additional treatment by filtration through zeolite column was chosen to remove this contaminant. Effluent water samples were first treated by 0.1, 0.25, and 0.5 g/L nZVI according to the optimized nanoremediation procedure (240 min of mixing, 600 min of settling). Then, the same samples were treated by oxidizing agent NaDCC

in dosage of 8 mg/L and filtrated through zeolite column. The chosen concentration of NaDCC was the least effective for disinfection. Removal efficiency for nitrogen species was analysed after every stage of remediation and is given in Fig. 4.20.

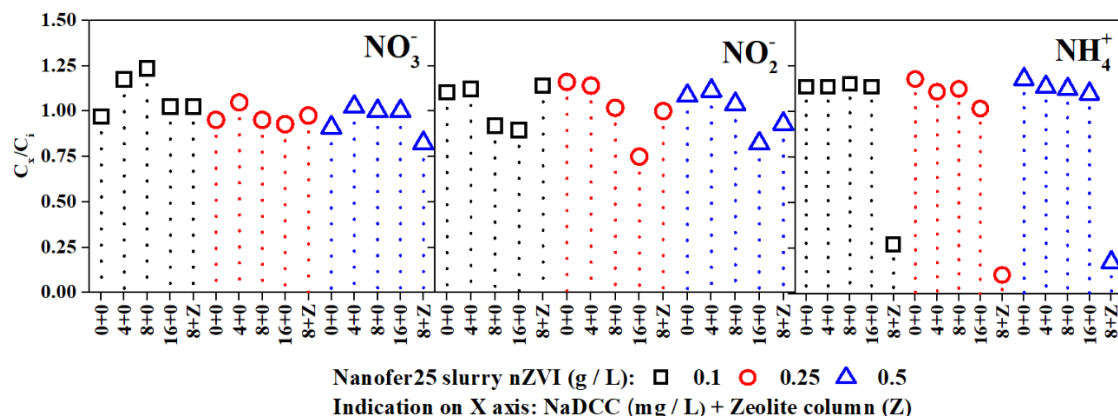


Figure 4.20: The influence of increasing nZVI of Nanofer25 slurry (mixing time 180 min; settling time 600 min) and increasing NaDCC concentrations, combined with zeolite column filtration on removal efficiency (C_x/C_i) for nitrogen species determined in remediated water samples from the SBWTP (C_i = before remediation; C_x = after remediation).

The changes in NO_3^- and NO_2^- concentrations exhibit complex chemical interactions with nZVI and NaDCC. After nanoremediation, concentrations of NO_3^- in effluent water were slightly reduced ($< 10\%$). Changes in NO_3^- concentrations were observed after the application of NaDCC, which did not indicate any trends. However, increase in its concentrations can be related to degradation of organic substances by HOCl [331], which is followed by the release of organic bound nitrogen that is further transformed into NO_3^- . This phenomenon was observed at the application of 0.1 g/L nZVI with 4 and 8 mg/L NaDCC, and at the application of 0.25 g/L nZVI with 4 mg/L NaDCC. Removal of NO_3^- after filtration through the column can be related to the use of natural zeolite material, which is usually a mixture of different aluminosilicate minerals, although zeolites are the prevailing mineral phase [332]. Namely, aluminosilicates minerals, like phyllosilicates and clays, have negative sorption sites, which enable adsorption of anions.

The concentrations of NO_2^- were slightly increased after the nanoremediation stage. After that a dose-dependent decrease in concentrations occurred with the applications of NaDCC. This can be related to oxidation of NO_2^- to NO_3^- [333]. Increase in NO_2^- concentrations after filtration through zeolite column can potentially be a result of oxidation of NH_4^+ into NO_2^- due to a prolonged reaction time with dissolved oxidant.

Changes in concentrations of NH_4^+ indicate a slight increase after nanoremediation due to a reductive transformation of NO_3^- and NO_2^- . On the other hand, dose dependent trend in lowering of concentrations was observed as a cause of oxidation due to the use of NaDCC. The trend was more pronounced at the application of NaDCC after the use of 0.25 and 0.5 g/L of nZVI than at 0.1 g/L nZVI. This can be related to the fact that more unreacted stabilised nZVI was left in the suspension after nanoremediation with the lowest nZVI concentration. Therefore, HOCl from NaDCC was mainly used up for oxidation of remaining suspended nZVI rather than for NH_4^+ .

Removal efficiency of NH_4^+ by zeolites with ion exchange process was very effective, as initial concentrations were lowered by more than 75% so that they reached drinking water limit values. The effluent water from the SBWTP still contains numerous persistent organic pollutants, which were not removed by the SBWTP and by nanoremediation. Therefore, filtration through activated charcoal column was applied at the final stage of the remediation procedure. Effluent water sample was first treated according to the optimized nanoremediation

procedure, with the use of Nanofer25 slurry in concentration 0.25 g/L, mixing time 240 min, and settling time 600 min. This was followed by treatment with NaDCC in the concentration of 8 mg/L. Finally, water was filtrated through the column made of zeolites and activated charcoal. The presence of organic contaminants was analysed in fresh effluent water sample, after nanoremediation and after treatment. The GC-MS spectra for described analyses are given in Fig. 4.21.

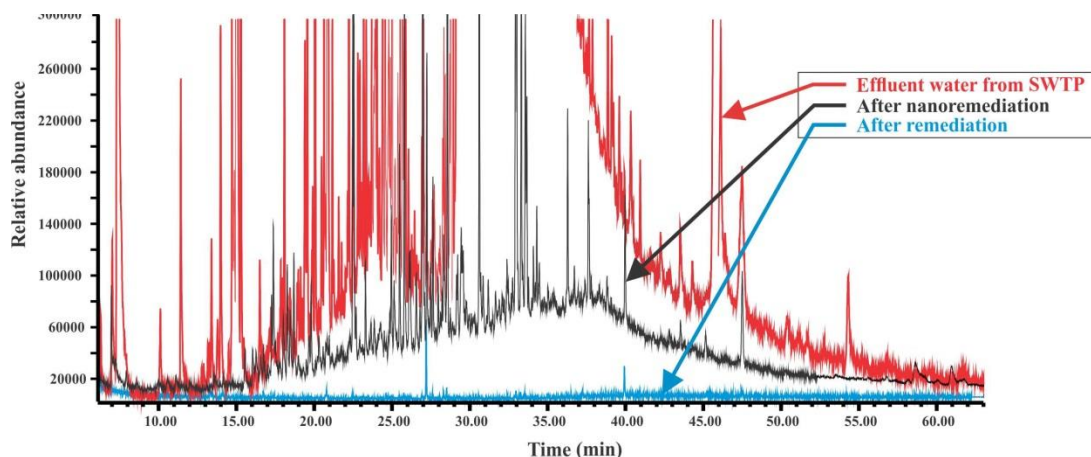


Figure 4.21: GC-MS spectra indicating the presence of organic pollutants in effluent water samples (fresh, after nanoremediation, and after multistage remediation procedure).

The peaks on GC-MS spectra indicate the presence of organic substance. In relative comparison, high measured abundance is related to the high concentration of detected substance. Petroleum products and derivatives are most abundantly present organic contaminants in effluent water. Substances, which were detected with relatively high abundances are also Butyldiglycol, Nonanoic acid, Tridecanal, 2,4-Di-tert-butylphenol, phthalates, Tetradecanal, Tetradecanoic acid, Isopropyl myristate, Palmitic acid, squalene, carbamazepine, cholestenol, tramadol, Fluoranthene, Pyrene, Bisphenol A, Galaxolide, Triethyl citrate. Abundance of all organic pollutants was reduced in GC-MS spectra of effluent water after nanoremediation. This indicates that nZVI substantially decreased the concentrations of organic pollutants in effluent water. Scientific data have confirmed that nZVI are able to degrade organic pollutants through multiple mechanisms [334]. The most important is oxidative degradation by ROS. The latter can be formed under aerated conditions, when nZVI are in contact with organic chelates or organic acids (for example ascorbic acid) from effluent water via mechanisms described by Lee et al. [320]. However, no secondary degradation products could be detected on GC-MS spectra after nanoremediation, which would indicate degradation of organic pollutants [334]. On the other hand, organic pollutants are in effluent water present in relatively high concentrations and in the form of many different compounds. Therefore, the main mechanism for the removal of organic pollutants from effluent water by nZVI in this study is probably adsorption to oxidised iron particles followed by sedimentation. The second mechanistic process for removal can be co-precipitation, coagulation, and sedimentation of organic pollutants with iron corrosion products. Namely, during corrosion of Fe^0 core in nZVI, Fe^{2+} is released into effluent water, where it can act as a coagulation agent. Ferrous iron is oxidised to Fe^{3+} and precipitated as hydroxide minerals, in which organic pollutants are bounded and removed from effluent water [335].

GC-MS spectra of water after filtration through activated charcoal indicate that the majority of organic contaminants were successfully removed. Only traces of phthalate, to which the remaining peaks correspond on the spectra, were present. However, they could be removed by additional treatment. Activated charcoal is the most effective mean for the removal of organic pollutants [46], which was used in the remediation procedure. At least part of organic

pollutants could also be removed by zeolites [283]. However, their contribution was not evaluated, as their primary purpose in water remediation procedure was to remove NH_4^+ .

Effluent water from the SBWTP, which was in the final experiment treated according to the optimal remediation procedure, has reached very high quality. As can be seen from Table 4.7., all parameters, except *Clostridium perfringens*, are below limits for drinking water. However, a low number of remaining bacteria can easily be removed by raising the concentration of NaDCC disinfection agent. Nonetheless, water after remediation according to optimised procedure is suitable for reuse for all secondary human purposes.

Table 4.7: Parameters measured in effluent water before remediation, after nanoremediation, and after complete remediation procedure.

Parameter	Outflow water	Nanoremediation	After remediation	Limit value for drinking water*
<i>Escherichia coli</i>	24000	2,400	0	0
Intestinal Enterococci	3400	350	0	0
<i>Clostridium perfringens</i>	380	15	3	0
Coliform bacteria	73000	10000	0	0
NH_4^+ (mg/L)	10.9	10.5	0.45	0.50
NO_3^- (mg/L)	25.6	28.5	30	50
NO_2^- (mg/L)	0.534	1.32	0.43	0.5
SO_4^{2-} (mg/L)	28	41	56	250
Cl^- (mg/L)	27	41	41	250
Sb ($\mu\text{g/L}$)	0.082	1.03	1.24	5.0
As ($\mu\text{g/L}$)	0.294	1.02	3.37	10
Cu (mg/L)	0.0030	0.0261	0.0036	2
B (mg/L)	0.063	0.059	0.060	1
Cd ($\mu\text{g/L}$)	0.883	0.052	0.016	5.0
Cr ($\mu\text{g/L}$)	0.543	0.559	0.161	50
Ni ($\mu\text{g/L}$)	1.48	5.07	1.29	20
Se ($\mu\text{g/L}$)	0.152	0.080	0.081	10
Pb ($\mu\text{g/L}$)	13.1	0.714	0.289	10
Hg ($\mu\text{g/L}$)	<0.001	0.074	0.032	1.0
Al ($\mu\text{g/L}$)	35.0	15.6	4.96	200
Mn ($\mu\text{g/L}$)	29.5	15.0	3.05	50
Na (mg/L)	26.3	52.6	67.2	200
Fe ($\mu\text{g/L}$)	124	927	175	200

* Official Gazette of RS, No. 51/17.

Chapter 5

Results and Discussion of Soil Remediation Study

5.1 Contaminated Soil from the Old Zinc-works Site (Celje)

The composition of each sample of CS collected from four different sampling areas was very variable. Homogenized samples are shown in Fig. 5.1, along with selected larger pieces collected at each sampling area.



Figure 5.1: Representative CS samples and larger pieces of material from the sampling area one (1), two (2), three (3) and four (4) from the Old Zinc-works site. Larger pieces of slag (S), tar-impregnated slag (tS), refractory materials impregnated with slag (rS), concrete with slag (SC), and brick with slag (bS) are also presented.

The most distinctive feature of CS from all four sampling areas was the variable content of different types of metallurgical slags. They were present in different quantities in all grain size fractions; therefore, it was not possible to determine the exact mass ratio of slag in CS. However, if we take into consideration the composition of grains larger than 16 mm, in CS from all four sampling areas, the content of slag particles varied from 40 to 70 (± 5) wt.%. The remaining part of the CS was represented by construction and demolition wastes (bricks, concrete, and wood), parent geological bedrock, which is silty clay and silty sand. In order to define which of four contaminated areas contained the most contaminated soil, chemical analysis of CS samples was conducted. The results of pH and conductivity measurements in eluates from CS from four sampling areas are given in Table 5.1, while results of chemical

analyses of eluates are given in Table 5.2. Eluate from CS from area 1 contained elevated concentrations of SO_4^{2-} , Cd, and Zn, which exceeded limits for inert materials, because they were determined to be 7780, 0.63, and 13.78 mg/kg d. m., respectively. Therefore, CS from the sampling area 1 was regarded as a non-hazardous waste according to the Decree on the landfill of waste (Official Gazette of RS, No. 36/16 [152]). The CS from sampling area 2 contained water-soluble concentrations of Cd, 0.08 mg/kg d. m., which exceeded the limit value for inert materials. Thus, it was also regarded as a non-hazardous waste. The most contaminated soil, according to the results of chemical analyses of eluates from the leaching test, was determined to be the CS from sampling area 3. The water-soluble concentration of SO_4^{2-} was 8090 mg/kg d. m., of Cd 0.42 mg/kg d. m., of Pb 0.5 mg/kg d. m. and of Zn 66.46 mg/kg d. m., which according to the Decree on the landfill of waste (Official Gazette of RS, No. 36/16 [152]) classified the CS from sampling area 3 as a hazardous waste. The CS from sampling area 4 contained 0.11, and 4.99 mg/kg d. m. of Cd, and Zn, respectively, which exceeded the limit values for inert materials. Therefore, it was regarded as a non-hazardous waste. Other inorganic parameters listed in the Decree on the landfill of waste were not exceeding the limit values. The investigation of CS, from the same four sampling areas, and by the same leaching procedure performed by Gobec [155], showed higher values of SO_4^{2-} , Cd, Pb, and Zn. For example, Gobec reported Zn concentrations in aqueous eluates 36, 8.2, 100, and 12 mg/kg d. m. compared to 13.78, 2.36, 66.46, and 4.99 mg/kg d. m. in this study for CS from sampling areas 1, 2, 3, and 4, respectively. Leaching test was also performed on representative samples of larger pieces of slag, collected during sampling. The size of slag was reduced by crushing to < 16 mm prior to the leaching procedure, with the aim of simulating the deterioration of slag due to weathering. The analysis of eluates showed that average concentrations of Cd, Pb, and Zn were 1.35, 8.22, and 388.2 mg/kg d. m., respectively. This pointed out that the metallurgical slag was the most hazardous waste, which was mixed with soil on the Old Zinc-works site.

Table 5.1: pH and conductivity of eluates from CS given as average values of three analyses.

Parameter	Area 1	Area 2	Area 3	Area 4
pH	7.65	8.01	7.14	7.54
Conductivity (mS/cm)	1.02	1.14	1.82	0.91

The total concentrations of elements of CS from the two most contaminated areas, namely 1 and 3 (Table 5.2), were determined by XRF. The concentrations of almost all selected PTE measured in CS from area 1 (except Ba, Cd, Cr, and Ni) were lower in comparison to concentrations in CS from area 3. Extremely high concentrations of Pb, and Zn, from 9905 to 22,489, and from 58,282 to 109,300 mg/kg d. m., were determined in CS from sampling Area 1 and 3, respectively. Also, very were high total concentrations of As, Cd, Cu and Ni were determined in CS from Area 1 and 3. Gobec [155] reported very similar concentrations for Pb (13,000 and 21,000 mg/kg d. m.) and Zn (63,000 and 120,000 mg/kg d. m.) after *Aqua regia* extraction from soil samples from Area 1 and 3. Chemical analysis after this type of extraction is considered to be pseudo total concentration of elements (for example [336]) therefore absolute comparison with the results of this study, obtained by XRF, is not possible. Also, current legislation on soil quality in Slovenia is based on limit values, which were set according to the aqua regia extraction procedure (Official Gazette of RS, No. 68/96 [147]). Therefore, values for Limit, Warning, and Critical concentrations of elements in soil in Table 5.1, represent only indicative values for comparison of total concentrations in CS from areas 1 and 3.

Table 5.2: Concentrations of selected elements, sulphate, and chloride in eluates from CS samples from 4 sampling areas. Total concentrations of selected elements in CS samples from sampling areas 1 and 3 ("/" indicates that there is no data).

Parameter (mg/kg d. m.)	Area 1		Area 2	Area 3		Area 4	Limit values ²		Limit values ³
	Total ¹	Eluate ¹	Eluate ¹	Total ¹	Eluate ¹	Eluate	Inert	Non-Hazardous	Critical
SO ₄ ²⁻	/	7780	5260	/	8090	2930	6000	20,000	/
Cl ⁻	/	21	21	/	15	15	800	15,000	/
As	652	0.036	0.04	1422	0.052	0.017	0.5	2	55
Ba	13624	0.54	0.43	13226	1.29	1.2	20	100	/
Cd	107	0.63	0.08	53	0.42	0.11	0.04	1	12
Cr	180	0.0037	0.0039	86	0.0032	0.00075	0.5	10	380
Cu	415	0.044	0.028	3675	0.11	0.032	2	50	300
Hg	0.79	0.00086	0.00033	2.28	0.00033	0.00033	0.01	0.2	10
Mo	27.7	0.051	0.11	31	0.03	0.04	0.5	10	200
Ni	1051	0.024	0.012	419	0.032	0.0072	0.4	10	210
Pb	9905	0.21	0.094	22,489	1.02	0.26	0.5	10	530
Sb	18	0.01	0.013	68	0.0055	0.006	0.06	0.7	/
Se	1	0.0048	0.0031	2.18	0.0039	0.0032	0.1	0.5	/
Zn	58,282	13.78	2.36	109,300	66.46	4.99	4	50	720
Major elements (wt.%) and in oxide form (%)									
Al (Al ₂ O ₃)	5.37 (10.15)		/	5.39 (10.18)		/			
Fe (Fe ₂ O ₃)	5.32 (7.6)		/	14.62 (20.9)		/			
Si (SiO ₂)	15.08 (32.26)		/	9.61(20.56)		/			
K (K ₂ O)	0.08 (0.09)		/	0.49 (0.6)		/			
Ca (CaO)	8.56 (12)		/	2.67 (3.74)		/			
Mg (MgO)	2.17 (3.6)		/	2.38 (3.95)		/			
P (P ₂ O ₅)	0.0154 (0.01)		/	0.0540 (0.12)		/			
S (SO ₃)	1.95 (4.88)		/	2.92 (7.28)		/			

¹ Mean value of 3 measurements. ² Official Gazette of RS, No. 36/16 ³ Official Gazette of RS, No. 68/96).

Comparison of total concentrations and limit values in Slovenian Soil Decree shows that CS from areas 1 and 3 contains As, Cd, Cu, Ni, Pb, and Zn in concentrations that indicate critical presence of these PTE in soil and thus a very high degree of contamination (Official Gazette of RS, No. 68/96). Higher total concentrations of As, Cu, Ni, Pb, and Zn in CS from area 3 compared to total concentrations of these PTE in CS from area 1 are reflected in much higher concentrations of the latter in eluates, if we compare CS from both sampling areas. The content of water-soluble fraction of selected PTE in CS from sampling area 3 was relatively low, accounting 0.004%, 0.8%, 0.003%, 0.008%, 0.004%, and 0.06% of total content for As, Cd, Cu, Ni, Pb, and Zn, respectively. It was evident that Cd was the most mobile PTE in CS, followed by a Zn. This is in line with the scientific findings, which point out Cd as one of the most mobile PTE, which was the most abundantly present in the water-soluble fraction [337]. Content of water-soluble fraction of Zn in CS from sampling area 3 was 3 times higher compared to CS from sampling area 1 which had 0.02% water-soluble fraction of Zn. This was in line with the findings, which indicate that with increasing of total content of Zn in soil the content of water-soluble fraction is also increasing exponentially [338].

Variable composition of CS from areas 1 and 3 was further reflected in total concentrations of major elements (except Al, which was in both cases approximately 5 wt.%). The concentration of elements Ca, Fe, K, Mg, P, S, Si in CS from area 1 were 8.5, 5.3, 0.08, 2.1, 0.01, 1.9, and 15 wt.%, respectively. On the other hand, the concentrations of Ca, Fe, K, Mg, P, S, Si in CS from area 3 were 2.6, 14.6, 0.49, 2.38, 0.05, 2.9, and 9.6 wt.%. Differences, especially in a content of Fe and S, confirmed that metallurgical residues content in CS from area 3 was higher.

Further analyses of mineralogical, microstructural and physical characteristics were performed on CS from sampling area 3, which was proved to be the most contaminated. This CS was also used for remediation experiments in the following research work.

The mineralogical composition of CS from sampling area 3 is shown in Fig. 5.2 where XRD patterns of different grain fractions of the sample, namely 0 to 0.063 mm, 0.063 to 0.5 mm, 0.5 to 2 mm, 2 to 8 mm, and from 8 to 16 mm are presented.

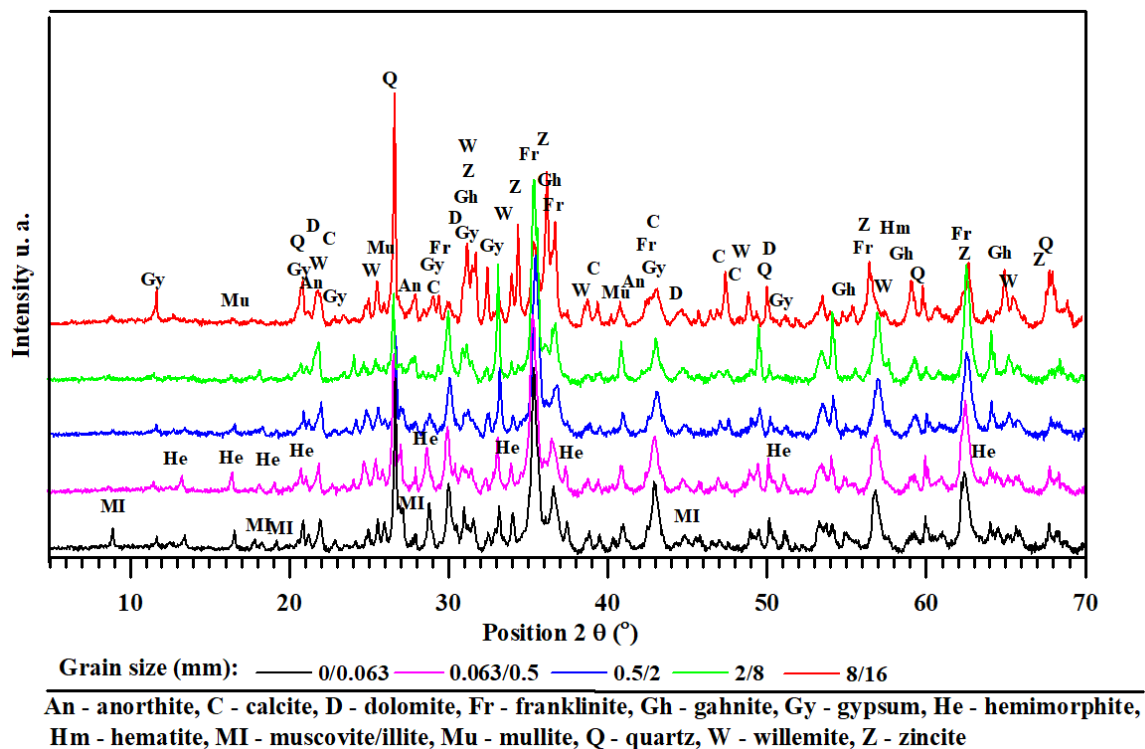


Figure 5.2: XRD pattern of different grain size fractions of CS from sampling area 3.

The mineral phases originating from primary soil were quartz, dolomite, calcite, muscovite/illite, and feldspar. Different mineral phases, corresponding to the remnants of the metallurgical activity (eg. metallurgical slags, tailings) were identified. Those were anorthite, franklinite, gahnite, gypsum, hemimorphite, mullite, willemite and zincite. There was no major difference in mineralogical composition between different gradations of CS (0.5 to 2 mm, 2 to 8 mm, and from 8 to 16 mm). Interestingly the highest relative abundance of gypsum was detected in the largest grain fraction that was in the majority composed of slag, which indicate that gypsum was mainly associated with the latter. Characteristic peaks of zinc mineral hemimorphite have the highest intensities in XRD pattern of smallest grain size fractions. This could be interpreted that hemimorphite has formed in the form of small crystals during chemical weathering of primary Zn mineral from slag, willemite [170].

Because slag fragments were the major contributors to the contamination of soil from the Old Zinc-works site, 8 different types of slag were additionally investigated by XRD (Fig. 5.3). Gypsum was present in all, except one, slag samples in relatively variable abundancy. The analyses have further showed that all slag samples contained at least one Zn-containing mineral. This implies that all investigated slag samples originated from Zn production and processing. Gahnite ($(\text{Zn}, \text{Fe})\text{Al}_2\text{O}_4$), franklinite (ZnFe_2O_4) and willemite (Zn_2SiO_4) were prevailing among Zn bearing phases. Meanwhile, hemimorphite ($\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$), as a secondary Zn mineral, zincite (ZnO) and petedunnite ($\text{Ca}(\text{Zn}, \text{Mg}, \text{Fe}^{2+})\text{Si}_2\text{O}_6$), represented minor mineral phases. Cerussite (PbCO_3) was as a minor and only Pb containing mineral phase detected by XRD in slag sample S8. The latter is commonly present in Pb contaminated soils as a secondary mineral [339]. Iron oxide minerals magnetite, hematite, and hydroxide minerals goethite, lepidocrocite, were abundantly present in slags. Apart from that petedunnite, pyroxenes enstatite and hedenbergite were also determined as minor phases. Anorthite and Ca feldspar ($\text{CaAl}_2\text{Si}_2\text{O}_8$) were abundantly present in all slags except in S7 and S8 (Fig. 5.3). The content of quartz was very variable in all slags, from minority in S1 and S8, to a major phase in S5 and S3. Mullite most probably represents the remains of the furnace lining or other parts of the metallurgical furnace, which was fused with slag, and/ or was formed parallelly with quartz due to the high temperatures in the smelter [173]. The elevated background in a range from 5° to 35° 2θ is evident on XRD spectrums of slags S2, S4, S6, and S7. This was correlated with the content of amorphous glassy phase.

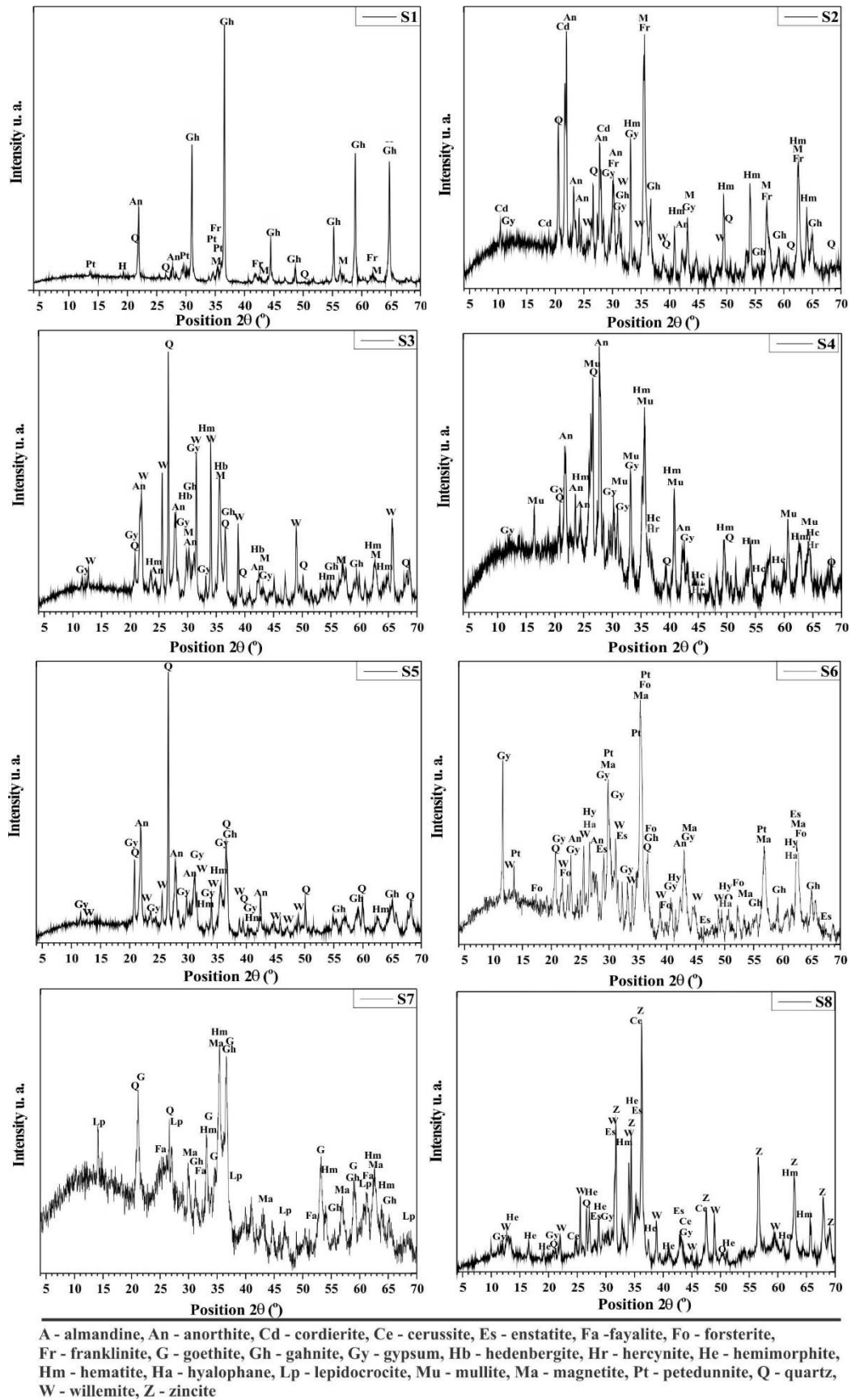


Figure 5.3: XRD patterns of 8 different slag types from the Old Zinc-works site.

The general composition of CS from sampling area 3 was very heterogeneous, as can be seen in microimage in Fig. 5.4 (1). Irregular particles of organic material (possibly tar?) can be visible, enveloped with iron hydroxides (Fig. 5.4(2)). Grains of primary soil minerals were mostly found in the shape of agglomerates consisted of quartz and phyllosilicate minerals (Fig. 5.4(3)).

Iron oxides and hydroxide minerals (in Fig. 5.4(5)), which usually contained traces of Zn, were found in slag. Franklinite was the most abundantly Zn bearing mineral phase, which was present in the form of euhedral crystals (in polished section in Fig. 5.4(6) and crystal on a surface of slag in Fig. 5.5(1) marked as Fr). It was also determined in XRD patterns of slag samples S1 and S2 (Fig. 5.3). A microimage of gahnite in well crystalline slag polished section is given in Fig. 5.6(1) (marked by Gh). The Zn and Al element distribution (EDS mapping analysis) in Fig. 5.6(1) demonstrates the position of euhedral gahnite crystals, where the largest crystal is zoned as it gradually transits into ferrochromite spinel (as seen from mapping of Cr). Small crystals of willemite (marked as W) are also shown in the central part of microimage (white spots). Between Zn bearing minerals Fe was mainly concentrated in ferrosilite phase. Zincite was commonly found in needle shaped forms encrusted by gypsum (Fig. 5.5(2)). Occasionally the zincite was present in the form of layers on slag (in Fig. 5.5(3) – indicated by marking Z). Zn was only rarely found in the form of Zn sulphate – goslarite ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$), appearing as needle-shaped crystals (in Fig. 5.5(4) – indicated by a marking Go). Due to its chemical instability and solubility, this can be one of the phases responsible for Zn leaching [177]. Important secondary Zn mineral was hemimorphite (in Fig. 5.5(5) marked as He), found on a surface of slag particles as a rosette of plate-like orthorhombic crystals. Certain type of slag contained Zn in its elementary form (Fig. 5.5(6)). Rarely found zinc ore residues were indicated by the presence of sphalerite (ZnS), which is presented in Fig. 5.5(7).

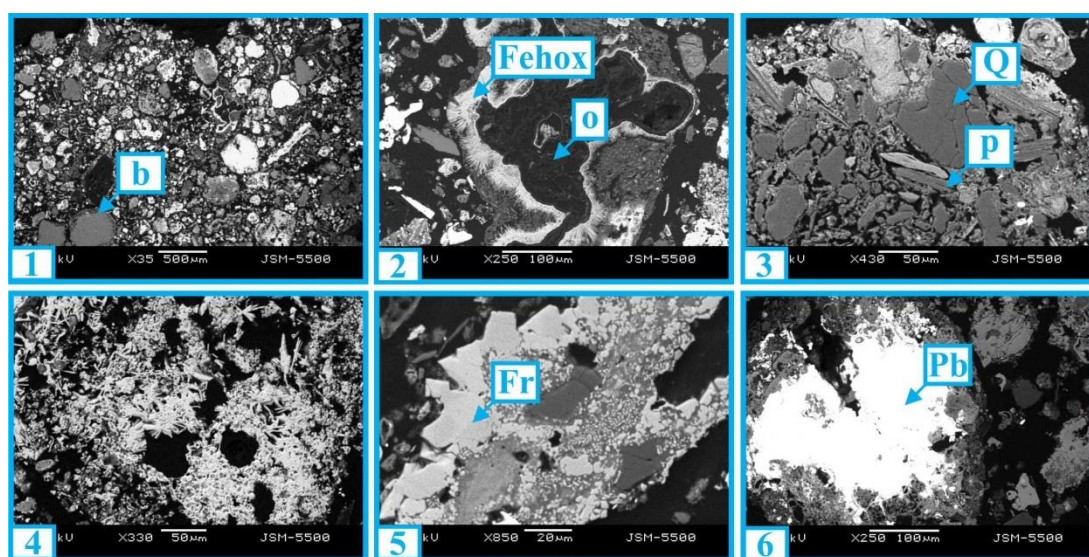


Figure 5.4: General microimage of CS (1) with marked and magnified spots (from 2 to 6), where markings represent brick (b), franklinite (Fr), iron (hydr)oxides (Fehox), lead (oxide) (Pb), organic material (o), phyllosilicate minerals (p), and quartz (Q).

Lead was found in the form of Pb oxides or as elementary Pb in irregularly shaped grains (Fig. 5.4(4)) or parts within the slag. In Fig. 5.5(8) it also included euhedral crystals of iron oxide mineral. Lead was also found as a mineral cerussite (Fig. 5.5(9)), which was defined also by XRD analysis (Fig. 5.3 (S8)). A very rare form of Pb was mineral mimetite ($\text{Pb}_5(\text{AsO}_4)_3(\text{OH})$), which can be seen in Fig. 5.6(2) (marked by a mi), where results of mapping analysis of elements Pb and As are given for better visualization. This is secondary

mineral, which was reported to form during weathering of metallurgical slags at sites contaminated by smelting [340].

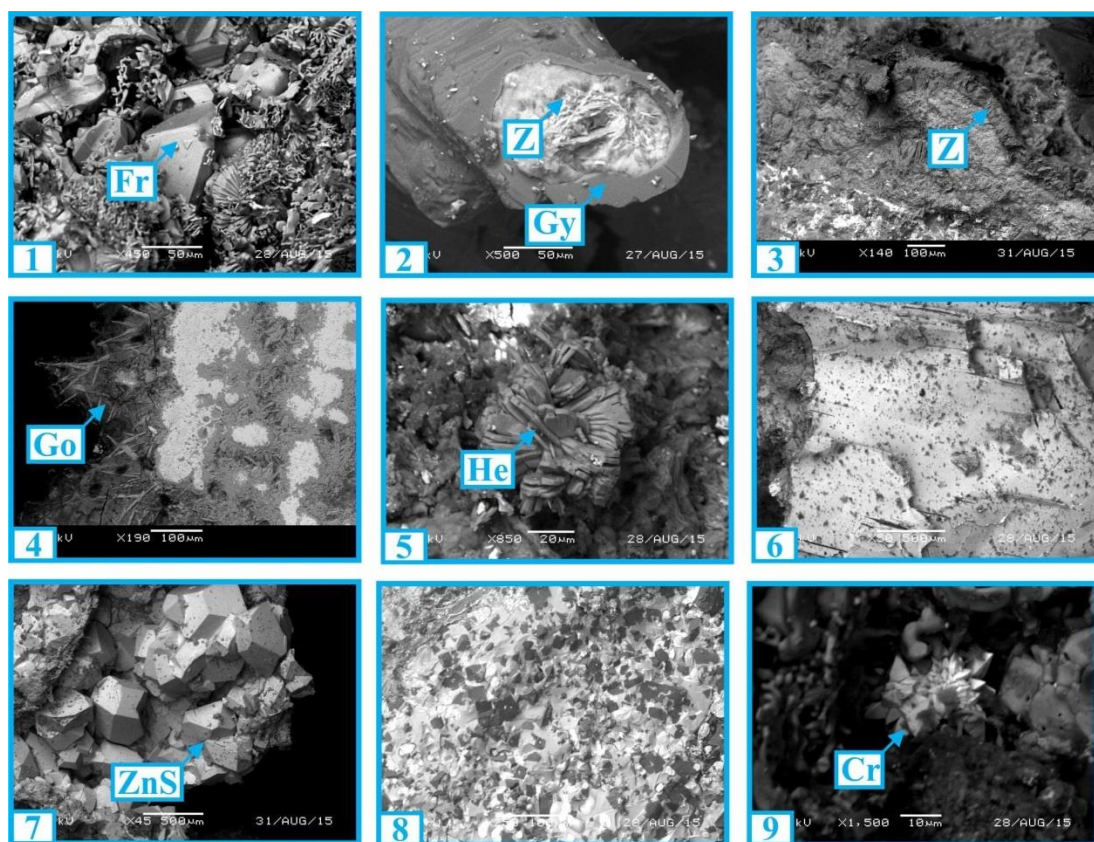


Figure 5.5: Microimages of different forms of Zn (from 1 to 7) and of Pb mineral phases (8, 9), where markings represent cerussite (Cr), franklinite (Fr), goslarite (Go), gypsum (Gy), hemimorphite (He), sphalerite (ZnS) and zincite (Z).

Distribution of Ba and S presented in microimage of polishes section in Fig. 5.6(3) indicated the presence of barite (BaSO_4). Besides barite Ba feldspar hyalophane ((K, Ba)[Al(Si, Al)Si₂O₈]) was also identified by XRD (Fig. 5.3 (S6)). In microimage in Fig. 5.6(3) areas where Fe and Zn were more concentrated indicate the presence of the franklinite phase, while Ca and Si form a microcrystalline matrix with the chemical composition similar to anorthite. Gypsum in slag was very abundantly present in the form of encrustations, where crystals grow on the surface of slag as visible in Fig. 5.6(4). The layer of gypsum (also marked by Gy) is evident from the mapping analysis, where the distribution of S and Ca is manifested. Compared to slags presented in Figs. 5.6(1 and 3), the slag displayed in Fig. 5.6(4) consists of a porous glassy phase.

Mineralogical composition of investigated CS and of metallurgical slags picked from CS was similar to those reported by different authors, who have investigated sites contaminated by zinc and lead smelting processes [170], [173], [341], [340]. They reported that franklinite, gahnite and willemite were the primary Zn bearing mineral phases in metallurgical slag. Vanaecker et al. [170] also reported the presence of Zn containing pyroxenes, which was confirmed also in slags from this study (petedunnite). The elementary Pb (which could not be directly confirmed in this study), lead oxides and cerussite were the main Pb bearing mineral phases in contaminates soils reported by scientific literature [176] similarly as in this study. All these authors have reported a porous glassy matrix of the metallurgical slag, which was transitioning into the microcrystalline anorthite phase ($\text{CaAl}_2\text{Si}_2\text{O}_8$). This phase was also defined by SEM/EDS and XRD analyses of the slag particles from CS.

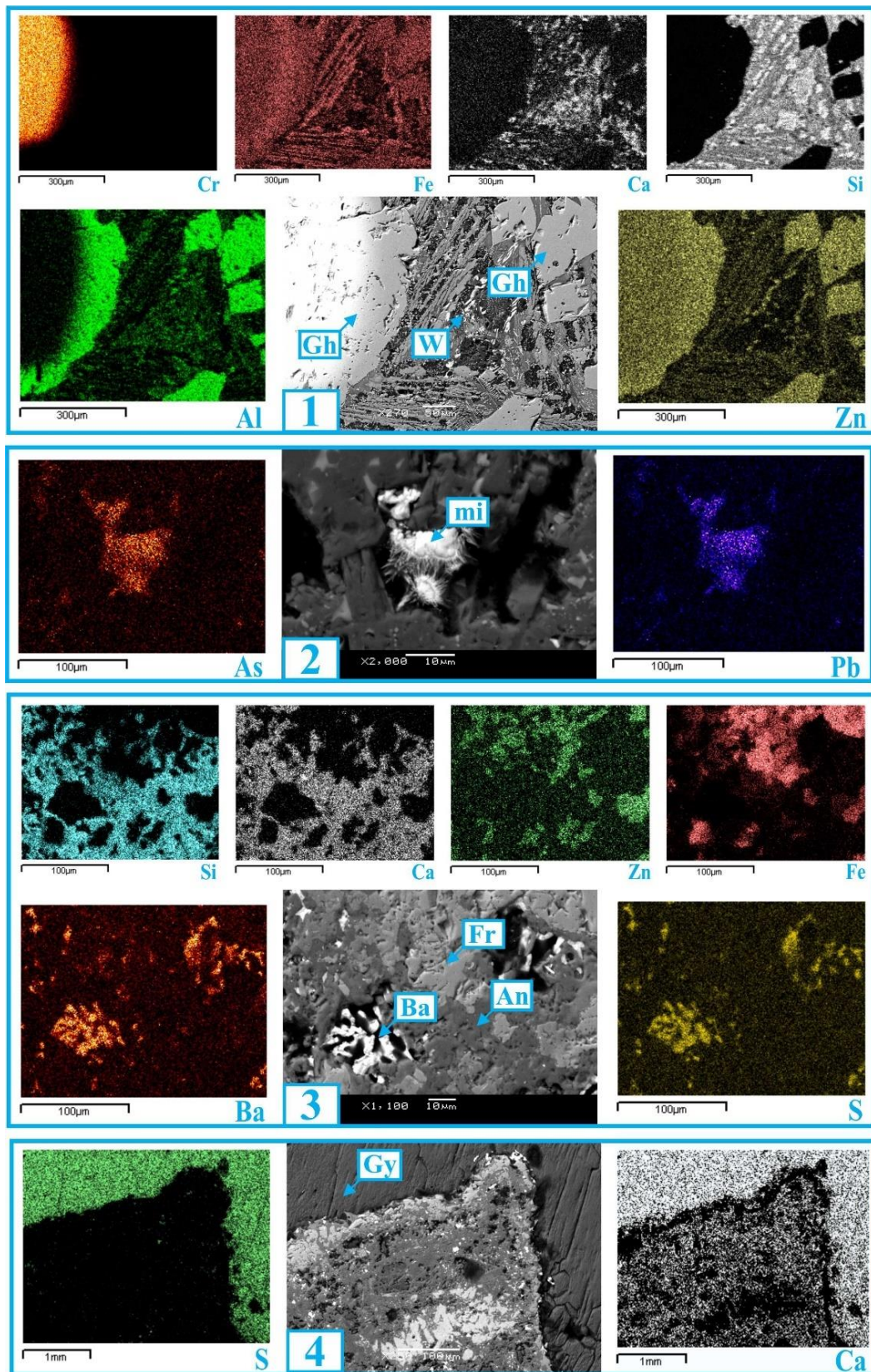


Figure 5.6: Microimages of polished sections of slag from CS, and with the results of the EDS mapping analysis of the selected elements. Markings in microimages represent anorthite (An), barite (Ba), franklinite (Fr), gahnite (Gh), gypsum (Gy), mimetite (mi), willemite (W).

Secondary minerals were formed after alteration or weathering of primary minerals of slags and metallurgical residues. Cerussite, mimetite, gypsum, goslarite and zincite were identified in slag from CS both by SEM/EDS and by XRD. These minerals are very susceptible to dissolution according to literature data [170], [342]. Thus, they were the most probable source of water-soluble Zn and Pb in leaching tests, beside their exchangeable fractions, bound to the surface of the aluminosilicate minerals of soil. On the contrary, minerals franklinite and gahnite are considered to be very stable phases of Zn as they are formed at high temperatures (1300 °C) and are classified within the group of spinel type minerals [343].

The physical characteristics of the CS from sampling area 3, which was used for remediation experiments, are given hereinafter. The BET specific surface area and the density of the CS were measured to be 10.00 m²/g and 2.71 Mg/m³, respectively. The particle size distribution of CS showed that 0.085 mm, 3.27 mm and 12.2 mm correspond to d₁₀, d₅₀, and d₉₀ (Fig. 5.7). The content of grain size fraction < 0.002 mm of CS accounted for 9.23 wt.%. Due to a very low clay fraction the potential impact of clay minerals on retention of PTE in soil remediation experiments was not considered. Based on granulometric data and according to SIST EN ISO 14688-2:2004 [137], soil can be classified as non-plastic sandy silty gravel.

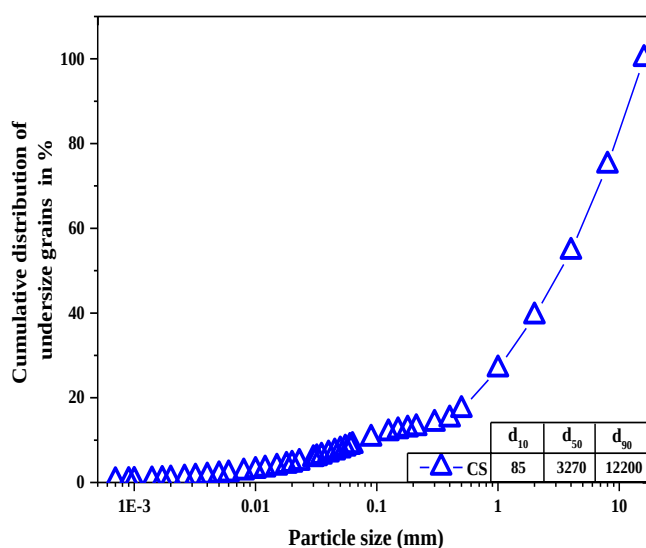


Figure 5.7: Cumulative particle size distribution for CS.

5.2 Characterization of Immobilization Additives

The basic characterization of materials, which were used as immobilization additives in remediation experiments, included chemical analyses (Table 5.3), basic physical and chemical characteristics (Table 5.4), mineralogical and microstructural analyses (given in sections, where materials are described in detail). From the results of chemical analyses of eluates (Table 5.3), it is evident that all materials can be classified as non-hazardous wastes according to landfilling policy (Official Gazette of RS, No. 36/16 [152]), except CAT. However, the latter still contains a relatively high concentration of water-soluble SO₄²⁻. All materials were alkaline and produced eluates with a higher conductivity than the CS from sampling area 3. This indicates that all contain a relatively high content of water soluble minerals and alkalis. The only exception, which is explained further in text, was RM.

Table 5.3: Total concentrations of selected elements additives and concentrations of selected elements, sulphate and chloride in eluates ("/" indicates that there is no data).

Parameter (mg/kg d. m.)	PA		CAV		CAT		LSA		LSH		RM	
	Total	Eluate ¹	Total	Eluate ¹	Total	Eluate ¹	Total	Eluate ¹	Total	Eluate ¹	Total	Eluate ¹
SO ₄ ²⁻	/	20	/	900	/	5000	/	10	/	10	/	100
Cl ⁻	/	120	/	22.5	/	269	/	200	/	270	/	280
As	2.8	0.002	26.08	0.026	36.67	0.0058	19.32	0.003	<1	0.001	98.14	0.492
Ba	408.18	34.9	1304.37	1.32	1855.6	0.72	457.95	4.9	808.63	6.21	370.47	0.007
Cd	6.15	0.0001	<1	0.002	<1	0.002	<1	0.001	<1	0.0007	10.4	0.0006
Cr	31	0.022	339.94	3	108.09	0.14	1850.06	0.022	382	1.13	394.6	0.039
Cu	274.94	0.15	122.11	0.0035	51.88	0.0038	196.27	0.001	211.36	0.013	100.05	2.2
Hg	<0.1	0.0029	<0.1	0.016	<0.1	0.013	<0.1	0.0002	<0.1	0.0021	13.01	0.0021
Mo	7.58	0.065	8.63	1.39	<1	0.18	85.34	0.99	219.4	4.39	3.53	0.314
Ni	108.48	0.001	699.97	0.003	199.13	0.002	437.28	0.0004	984.75	0.001	236.28	0.069
Pb	69.21	0.094	116.6	0.048	<1	0.01	76.78	0.086	159.29	0.001	112.27	0.012
Sb	1.59	0.0001	<0.001	0.001	<1	0.0032	<1	0.0002	<1	0.002	42.01	0.0033
Se	0.73	0.004	9.22	0.55	9.25	0.037	5.29	0.005	8.75	0.023	4.49	0.02
Zn	152.99	0.634	1055.39	0.061	142.58	0.065	719.77	0.69	920.78	0.038	269.2	0.102
Major elements (wt.%) and in oxide form (%)												
Al (Al ₂ O ₃)	5.2 (9.83)		8.33 (15.74)		5.02 (9.49)		9.07 (17.14)		5.9 (11.15)		9.44 (17.84)	
Fe (Fe ₂ O ₃)	0.29 (0.41)		6.6 (9.44)		12.9 (18.44)		6.14 (8.78)		7.23 (10.34)		13.64 (19.5)	
Si (SiO ₂)	5.83 (12.47)		16.63 (35.57)		10.87 (23.25)		3.65 (7.8)		7.53 (16.1)		3.79 (8.11)	
K (K ₂ O)	0.26 (0.31)		1.4 (1.69)		0.68 (0.82)		<100 (<0.01)		<100 (<0.01)		0.27 (0.33)	
Ca (CaO)	38.77 (54.25)		10.01 (14.01)		11.89 (16.64)		24.33 (34.04)		21.4 (29.94)		14.9 (20.85)	
Mg (MgO)	2.11 (3.5)		3.52 (5.84)		5.4 (8.95)		17.73 (19.45)		9.1 (15.09)		0.51 (0.85)	
P (P ₂ O ₅)	0.08 (0.18)		0.21 (0.48)		<100 (<0.01)		<100 (<0.01)		0.0600 (0.14)		0.1400 (0.32)	
S (SO ₃)	0.28 (0.7)		1.15 (2.87)		1.38 (3.45)		1.17 (2.92)		0.4300 (1.07)		0.33 (0.82)	

¹Mean value of 3 measurements is given.

Table 5.4: pH, conductivity, specific surface area and density of investigated additives.

Parameter	PA	CAV	CAT	LSA	LSH	RM
pH	12.7	13.32	12.49	12.64	12.13	9.0
Conductivity (mS/cm)	9.7	9.63	1.27	7.14	2	0.3
BET Specific surface area (m ² /g)	8.13	10.0	39.29	2.91	5.42	20.1
Density (Mg/m ³)	2.58	2.58	2.7	2.8	2.8	3.07

5.2.1 Paper ash

Leaching test of PA showed that the water-soluble concentration of Ba was 1.7 times higher than the limit value for inert materials (Official Gazette of RS, No. 36/16). None of the other PTE exceeded the values for inertness. Comparable results were reported by Pavšič et al. (2014). The elevated total content of PTE Ba and Cu compared to other PTE in PA had also been reported by Mladenovič et al. [232]. However, they determined approximately 1.5 higher concentration of Ba and 1.2 times higher concentration of Cu as the mean values determined in the present research. These differences were attributed to the variety of factors, such as heterogeneity in composition of incinerated paper sludge and biomass material [232].

The small elevated background in the XRD pattern (region 10 - 35 ° 2θ) reflected the presence of amorphous phase, which was further confirmed also by SEM/EDS analysis. It occurs in the form of irregularly shaped groundmass with small rounded pores, which constitute a large fraction of the PA as can be seen in Fig. 5.9(1) and magnified in Fig. 5.9 (2), marked as gli. EDS analysis revealed that the glassy phase was composed primarily of Si, Al and Ca, associated with minor elements K, Na, and Mg were in different proportions.

The most abundant element in PA was Ca (Table 5.3), which was mostly partitioned between calcite, lime, and portlandite, while some also originating from small amounts of calcium aluminium silicates (Fig. 5.8). Calcite represented the major crystalline phase (Fig. 5.8 and in Fig. 5.9(3) marked by a C). Larger grains of calcite (in Fig. 5.9(3) marked by a C), which were not calcined to lime during combustion or were a result of carbonatization of lime from PA, were noted. The presence of high concentrations of water soluble calcium oxide and hydroxide resulted in alkalinity of PA eluate and high buffer capacity of PA, due to chemical equilibria at the dissolution of portlandite [344].

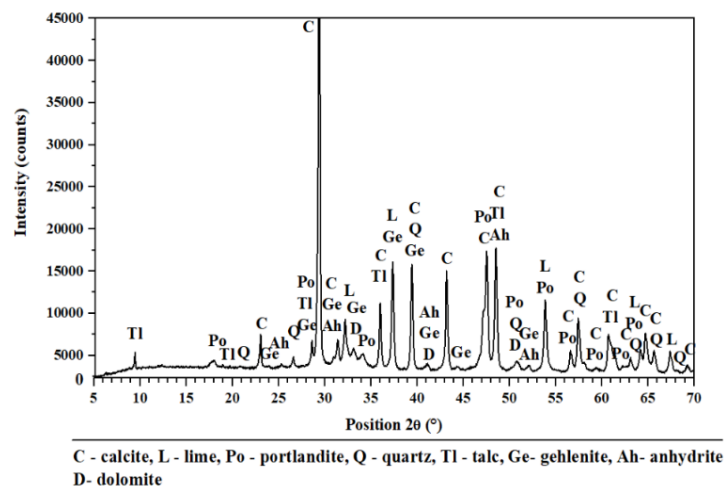


Figure 5.8: XRD pattern of the PA.

The identification of barite as the major Ba bearing phase was accomplished by SEM/EDS (in Fig. 5.9(4) marked by a Ba).

Quartz was identified as a minor phase along with talc, gehlenite, anhydrite, and dolomite (Fig. 5.8). In Fig. 5.9(5) (marked by Q) quartz grain with inclusions of TiO_2 can be seen.

Similar mineralogical composition of PA as in this study was also reported by multiple scientific sources [232] [237], [238], [239].

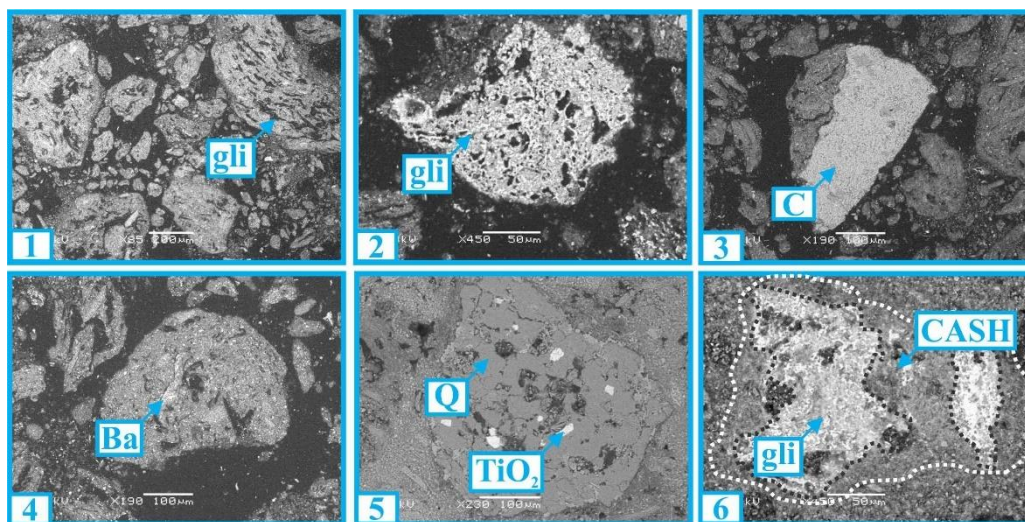


Figure 5.9: SEM microimages of PA polished sections, representing a general structure with glassy phase (gli) (1), glassy phase (gli) (2), calcite grain (C) (3), barite mineral phase (Ba) (4), quartz (Q) grain with TiO_2 inclusions (5), and glassy phase (gli) after reaction with water, where relicts of glassy grains are marked with black and the reaction product (CASH) with a white dotted line (6).

In order to define the potential hydraulic reactivity of PA, XRD analysis of PA paste with water / solid (w / s) 1 / 1, was performed at different time intervals as shown in Fig. 5.10. Results have revealed that after 7 days, different calcium aluminate hydrates phases have formed, namely hemicarboaluminate, hydrocalumite and monocarboaluminate. At longer curing times no new hydration product was identified, only the change in ratios between the phases was detected. A clear transition of hemicarboaluminate to monocarboaluminate can be observed with the time of hydration as the quantity of hemicarboaluminate was decreasing, and the quantity of monocarboaluminate was increasing. The mechanism of carboaluminate conversion was in accordance with the reported investigations: firstly, at room temperature, hemicarboaluminate is not stable in the presence of excess calcite [345] which represents the major phase of PA, and secondly, monocarboaluminate is the energetically favoured carboaluminate phase [346]. The results pointed out that PA was a hydraulic active material as it forms different hydration products when mixed with water. The SEM/EDS analysis further confirmed the products of hydraulic activity of the PA, since the reaction rims around the relicts of PA were observed and relicts of amorphous (glassy) phase after its dissolution were identified in groundmass of the PA paste, as it is presented in Fig. 5.9(6). The reaction rims were thus formed of microcrystalline calcium aluminium silicate hydrate (CASH) phase, which was confirmed by EDS analyses and was also reported by Mladenović et al. [232].

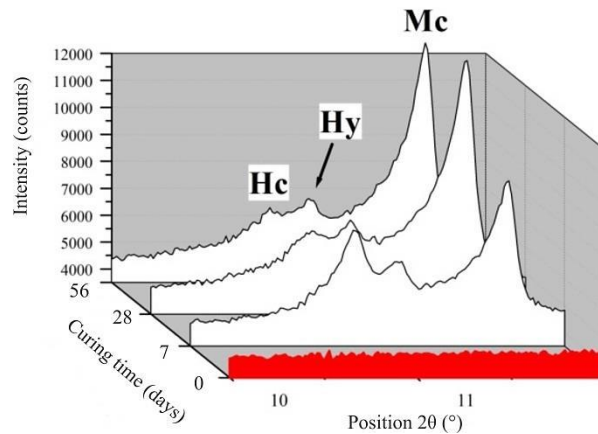


Figure 5.10: Section of the XRD patterns of the PA pastes at 7, 28 and 56 days of hydration. The most intense (I_{100}) peaks of newly formed mineral phases hemicarboaluminate (Hc), hydrocalumite (Hy) and monocarboaluminate (Mc) are indicated.

The BET specific surface area of PA amounted to be $8.13 \text{ m}^2/\text{g}$ and the density to be $2.63 \text{ Mg}/\text{m}^3$ (Table 5.4). PA was a fine graded material with d_{10} , d_{50} and d_{90} of 0.0034 mm , 0.071 mm and 1.288 mm , respectively (Fig. 5.11). PA contains finer particles than both coal fly ashes, which were included in this study. Some authors reported even lower size grains for their PA samples [238] and more than 30% lower density [237], which could imply on physical and chemical variability of PA in different studies due to variable composition of burned material, conditions during incineration, and storing.

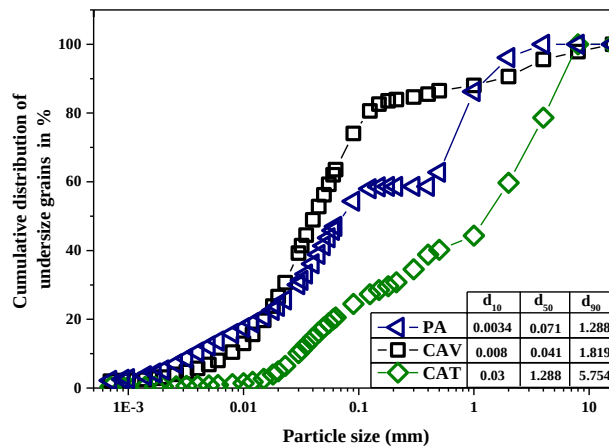


Figure 5.11: Cumulative particle size distribution for ashes PA, CAV, and CAT.

5.2.2 Coal combustion fly ashes

A minor difference in total concentrations of the major elements was observed between coal fly ashes. The CAV contained approximately 5 wt.% more Si and 3 wt.% more Al, while CAT contained approximately 6 wt.% higher total concentration of Fe. Otherwise, both coal fly ashes have a chemical composition, which is similar to the composition of fly ashes classified as calcareous according to SIST EN 14227-4:2013 [226], [223], [224]. Both, CAV and CAT have a very similar content of Ba and As. However, relatively high total content of Zn, Ni and Cr was determined in CAV.

The pH of eluates from CAV and CAT was 13.32 and 12.49, respectively (Table 5.4). The former has the highest pH among immobilization additives, which might be

connected to its high content of K and dissolution of its oxides rather than dissolution of portlandite, which sustains pH 12.3 at its chemical equilibria [344]. The eluate from CAV also has 7.5 times higher conductivity than from CAT, and was similar to eluate from PA. Leaching test of CAV showed that the water-soluble concentration of Cr(total) for 2.5 mg/kg d. m. exceeded the limit value for inert materials according to the Official Gazette of RS, No. 36/16 [152], Mo for 0.89 mg/kg d. m. and Se for 0.05 mg/kg d. m. On the other hand, no elements exceeded the limits for inertness in eluate from CAT, if we consider SO_4^{2-} limit value of 1000 mg/kg d. m. (Official Gazette of RS, No. 36/16 [152]). However, the concentration of the latter was the highest among all additives. Determined values of water-soluble PTE and sulphate were indicative only for the samples of ashes used in this study. Namely, content of PTE in coal fly ashes is very variable [228] and therefore, before practical use, it is necessary to test leachability of metals from the batch of ash, which is going to be used for remediation purposes.

Quartz and calcite represented the major crystalline phases along with magnetite, gehlenite, and anhydrite. Meanwhile, lime and portlandite were present as minor phases (Fig. 5.12).

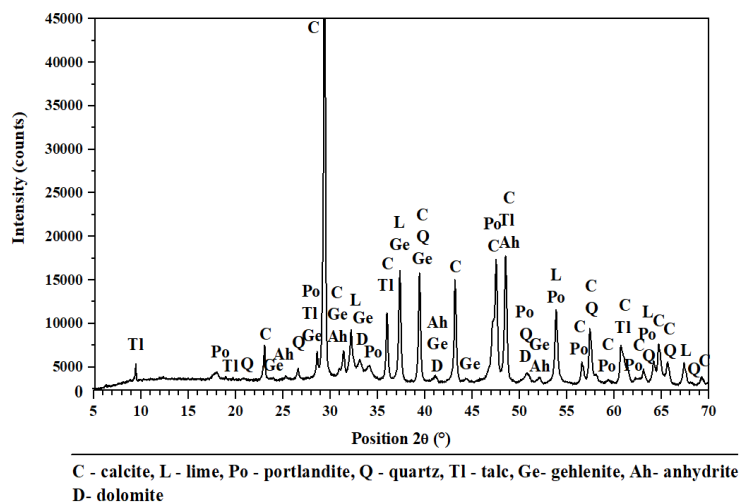


Figure 5.12: XRD pattern of the CAV.

The elevated background of the CAV XRD spectrum in the range of 7 – 38 ° 2θ with the maxima at approximately 27 ° 2θ (Fig. 5.12) resembles the presence of glassy phase in the ash, which was further confirmed also by SEM/EDS analysis (Figs. 5.13 (1 and 2)).

The physical appearance of CAV was substantially different than PA (Fig. 5.13(1)), as it was formed of a glassy phase in the shape of rounded porous and dense particles (glr) and irregularly shaped porous grains (gli) (Fig. 5.13 (2)). Glassy phase represents the reactive pozzolanic phase of the coal ash [347]. Porous spherules tend to contain equal or more Al than Si, while dense spherules were predominantly formed of Si, as determined by EDS analyses. The iron oxide grains were also abundantly present (Fig. 5.13(3)), thus confirming the XRD analyses. Particles of charcoal, quartz, and calcite (Fig. 5.13(1)) were also identified.

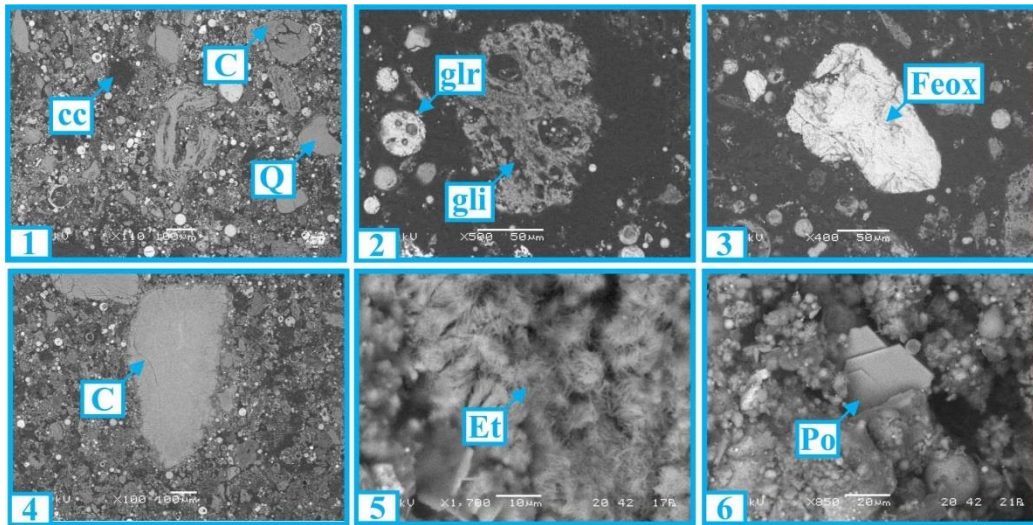


Figure 5.13: SEM microimages of CAV polished sections, representing a general structure with charcoal (cc), calcite (C), quartz (Q) (1), glassy particles in the form of spherules (glr) and irregularly shaped groundmass (gli) (2), iron oxide (Feox) (3), calcite (C) grain (4), needle shaped ettringite (Et) (5) and hexagonal plates of portlandite (Po) (6).

The potential hydraulic activity of CAV was analysed with determination of newly formed mineral phases in the CAV paste ($w / s = 1 / 1$) by XRD at different time intervals (Fig. 5.14(1)). Results have shown that after 7 days, two phases were formed, namely, ettringite, and hemicarboaluminate. At longer curing times, 56 days, monocarboaluminate phase was also identified, and the change in relative content of hemicarboaluminate. Namely, the intensity of its peak has lowered, indicating its possible transformation into the monocarboaluminate phase. Decreasing of hemicarboaluminate on the account of monocarboaluminate increase was in accordance with the reported investigations and mechanisms already described at PA hydration mechanisms [345], [346]. The results pointed out that CAV was hydraulic active material as different hydration products were formed, when it was mixed with water. The calcite grains were being disintegrating in grain borders (Fig. 5.13(4)), due to a formation of hydration products. The SEM/EDS analysis further confirmed the hydraulic activity of the CAV, since ettringite (Fig. 5.13(5)) was clearly observed along with portlandite crystals (Fig. 5.13(6)), and CASH.

PA acted as an activator for the latent hydraulic reaction of CAV, due to the lime and portlandite content. During the hydration of CAV/PA paste slightly different mineral phases (Fig. 5.14(2)) were formed as in the case of CAV paste (Fig. 5.14(1)). The relative abundance of ettringite was lower than in the CAV paste. The intensity of its characteristic peak was lower during all curing times. This can be related to the 45 times lower water soluble SO_4^{2-} content in PA than in CAV that has also lowered the overall available sulphate content in CAV/PA paste in comparison to the CAV paste. Formation of hemicarboaluminate and monocarboaluminate also showed similar trends as in the CAV paste. However, the formation of hydrocalumite, which was also observed in PA paste hydration, was also observed in combination with CAV, with a time-dependent trend of increasing.

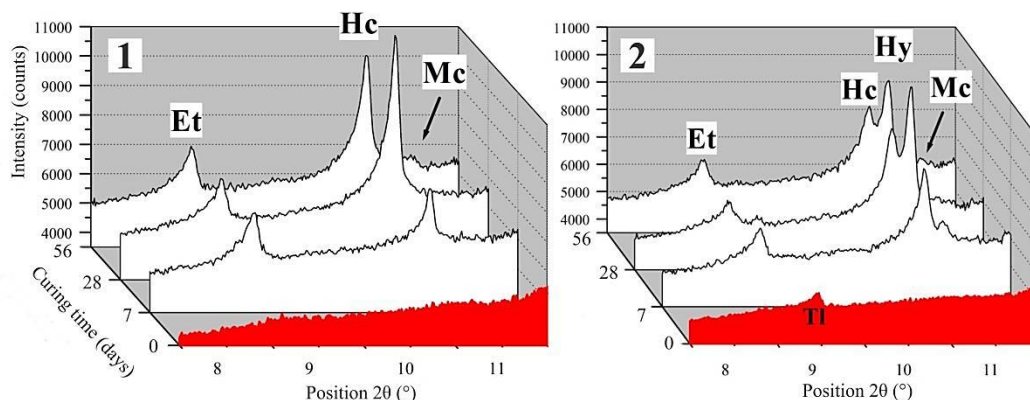


Figure 5.14: Section of the XRD patterns of the CAV (1) and CAV in combination with PA (CAV/PA) (2) pastes at 7, 28 and 56 days of hydration. The most intense (I_{100}) peaks of talc (Tl) and newly formed mineral phases ettringite (Et), hemicarboaluminate (Hc), hydrocalumite (Hy), and monocarboaluminate (Mc) are indicated.

Quartz, magnetite, hematite (also visible on the microimage in Fig. 5.16(2)), and ettringite were the major mineral phases of CAT (Fig. 5.15). Portlandite, lime, calcite, and other mineral phases were in minority. The presence of ettringite (Figs. 5.15 and 5.16(5)) in CAT indicated that it has at least partly reacted with water to produce hydration phases before it was used for experiments.

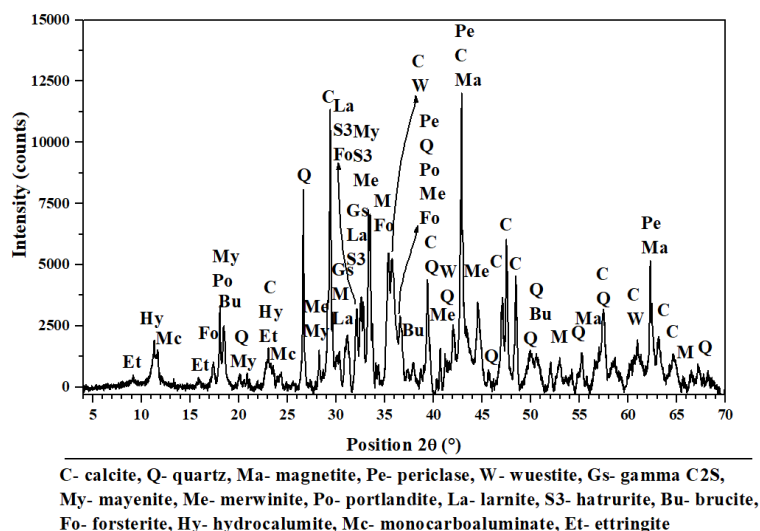


Figure 5.15: XRD pattern of the CAT.

The glassy phase in CAT was detected and visualised with SEM/EDS analyses. The spherical and irregularly shaped glassy particles – pozzolanic phase (Fig. 5.16 (1) [347], and charcoal particles are visible on the general microimage of the CAT (Fig. 5.16(1)). Similar as in the case of CAV, glassy phase was present both in porous (Fig. 16(3)) and dense (Fig. 5.16(4)) spherules, which differ between each other by their elemental composition. Namely, in the former Al predominates over Si, while the latter was mostly formed of Si (defined by EDS analyses). Mineral phases ettringite (Fig. 5.16(5)) and hemicarboaluminate, which were the result of hydration reactions, were already present in ash (Fig. 5.15) before experiments and therefore in its pastes (prepared with $w/s = 1/1$) they remained in unchanged quantities through all intervals of curing in CAT paste

their quantity remains constant which indicates that CAT did not react further with water (Fig. 5.17(1)).

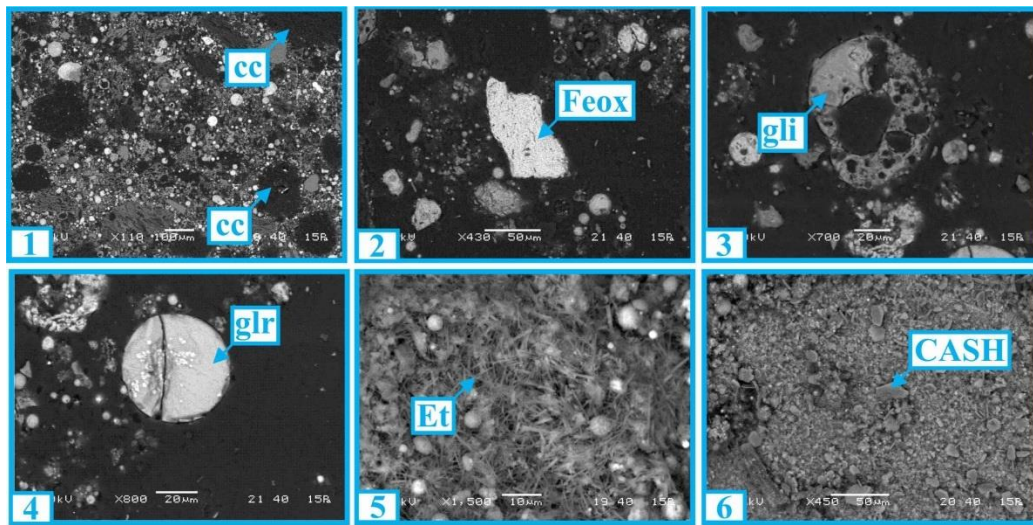


Figure 5.16: SEM microimages of CAT polished sections, representing a general structure with charcoal (cc) (1), iron oxide (Feox) (2), hollow irregularly shaped glassy particle (gli) (3), and round dense glassy particle (glr) (4), needle shaped ettringite (Et) (5), and microstructure of CASH (6).

The PA was used to test if it can act as an activator for the potential latent hydraulic reaction of CAT. In paste CAT/PA the intensity of ettringite peak in fresh paste was approximately half lower, which was due to the addition of PA. However, after 7 days of curing the content of ettringite has increased due to the consumption of SO_4^{2-} from CAT and hydration of Ca and Al containing phases from both ashes (Fig. 5.17(2)). The formation of ettringite was favoured over hemicarboaluminate, hydrocalumite, and monocarboaluminate, due to a high available content of soluble SO_4^{2-} from CAT, which was 5.5 times higher than in CAV.

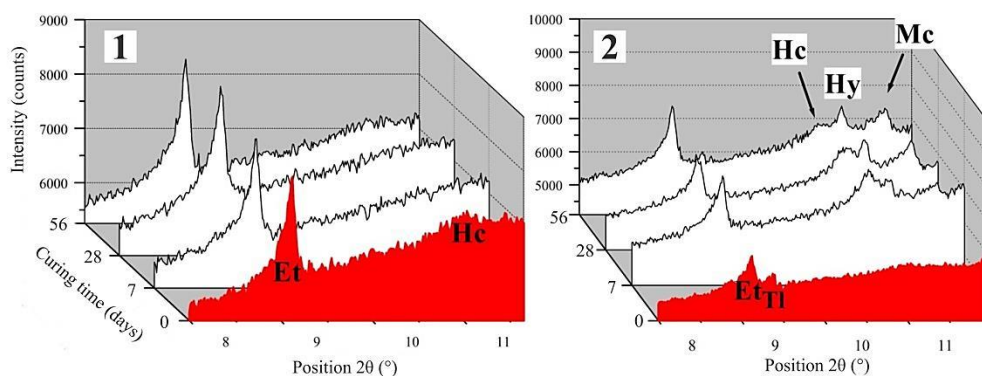


Figure 5.17: Section of the XRD patterns of the CAT (1) and CAT in combination with PA (CAT/PA) (2) pastes at 7, 28 and 56 days of hydration. The most intense (I_{100}) peaks of talc (Tl), ettringite (Et), hemicarboaluminate (Hc), with hydrocalumite (Hy), and monocarboaluminate (Mc) are indicated.

Therefore, the amount of newly formed ettringite was higher in CAT/PA than in CAV/PA, and on the other had lower amounts of hemicarboaluminate, hydrocalumite, and monocarboaluminate were formed. The microstructural analyses of CAT/PA paste

have also confirmed the formation of CASH (Fig. 5.16(6)). The relative comparison of the newly formed minerals after hydration of CAV and CAT showed substantially higher hydraulic reactivity of CAV. Namely, higher quantities of products were detected in CAV and CAV/PA pastes compared to CAT and CAT/PA pastes.

The BET specific surface area of CAV and CAT was determined to be 10 and 39.29 m²/g, respectively. Both coal ashes have a higher specific surface area compared to other additives, which can be related to the presence of charcoal particles [348], which were according to the microstructural analyses present in different amounts in both coal ashes. The density of coal ashes was 2.58 Mg/m³ for CAV and 2.7 Mg/m³ for CAT (Table 5.4). CAV was a finer graded material, with d₁₀, d₅₀ and d₉₀ of 0.008 mm, 0.041 mm and 1.82 mm, respectively, compared to CAT, which had d₁₀, d₅₀ and d₉₀ of 0.03 mm, 1.29 mm, and 5.75 mm, respectively (Fig. 5.11). CAV was finer than PA, while CAT was much coarser, which was also related to its lower hydraulic (pozzolanic) reactivity [349].

5.2.3 Ladle slags from steelmaking process

The ladle slag was delivered from ABS in dry powdered form, after extraction of valuable metals. Meanwhile, ladle slag from Harsco was delivered slightly wet due to the use of water during the extraction of valuable metals from ladle slag from the Acroni steel plant. Ladle slag from ABS steel plant originated from the production of different types of steel alloys as at Acroni. This resulted in the substantially different content of major elements (except Ca, which was 24.3 wt.% in LSA and 21.4 wt.% in LSH) and PTE (Table 5.3). Higher total concentrations of Ca and lower concentrations of Fe were reported for ladle slag from the same source as LSH [247]. Similar concentrations of major elements for ladle slag from ABS were reported by Zalar Serjun et al. [243]. Loncnar et al. [247] reported similar total concentration of Mo, and approximately 4 times lower concentration of Ba in the same ladle slag as LSH from this study. LSA contained 4.8 times higher total concentration of Cr compared to LSH.

In the eluate from LSA, only Mo exceeded the limit value for inertness according to the landfilling policy (Official Gazette of RS, No. 36/16 [152]), namely, its concentration was determined to be 0.99 mg/kg d. m. Meanwhile, in eluate from LSH, 8.78 times higher values of Mo and 2.26 times higher value of Cr were determined, than the limit values for inertness. Very similar concentrations of water-soluble PTE in eluates from ladle slag as in LSH were also reported in literature [350], and much lower concentrations of Mo and Cr in eluates were reported by Loncnar et al. [247]. Also, Zalar Serjun et al. [243] reported that ladle slag from ABS is an inert material. However, numerous parameters during the steelmaking process can cause differences in geochemical properties between different batches of ladle slag from the same source steelmaking plant [247]. The pH of eluates from both ladle slags was very similar as reported by scientific literature [243], [247], namely 12.64 and 12.13 (Table 5.4), for LSA and LSH, respectively, and was controlled by the solubility of portlandite [243], [344]. The presence of the latter in both slags was also confirmed with XRD. However, the conductivity of eluates was substantially different, with 3.6 times higher value for LSA compared to LSH.

The microimage of LSA was showing the mixture of metal (mostly iron) oxides (Feox) (Fig. 5.19(1)), grains of lime (L) (Fig. 5.19(2)) calcium aluminates (cA) (Fig. 5.19(3)) and calcium silicates (cS) (Fig. 5.19(4)). The mineral composition of LSA was shown in Fig. 5.18. The forms of cA phases were tricalcium aluminate, mayenite, gehlenite, and as minor phases monocarboaluminate, monosulphoaluminate, hydrocalumite, and brownmillerite. Less abundantly present were cS phases present in the form of γ -C₂S, larnite, hatrurite, and merwinite, which were also identified with SEM (Fig. 5.19(4)). Grains of reactive minerals, which were exposed to air moisture, were

commonly covered by a few tens of μm thick layers of hydration products. Hematite, magnetite, and wustite, were iron oxide minerals of LSA. Periclase and brucite, the Mg oxide and hydroxide, were less abundant. Similar mineral composition of ladle slag from ABS was reported by Zalar Serjun et al. [243].

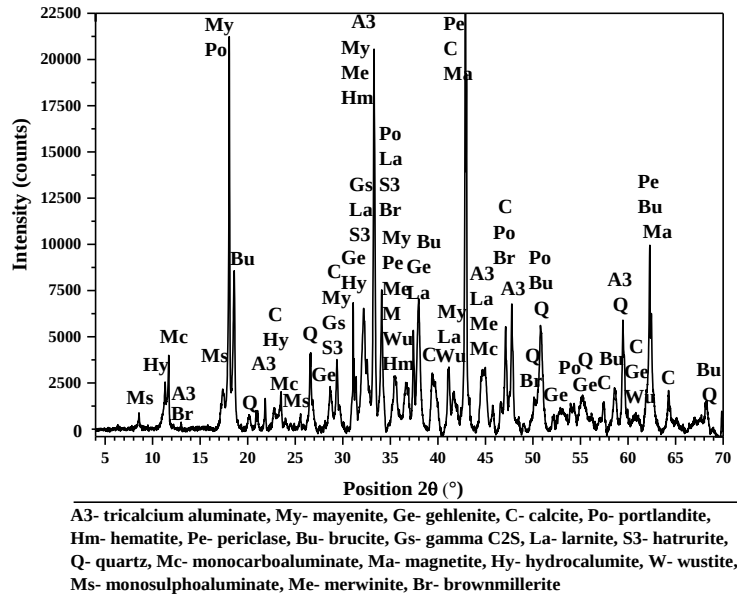


Figure 5.18: XRD pattern of the LSA.

The hydraulic activity of LSA was further investigated with analyses of mineral composition of LSA pastes (water / solid ratio 1 / 1) by XRD (Fig. 5.20(1)). It was observed that the hydrocalumite phase did not change with time after the addition of water to the ladle slag. On the other hand, time-dependent increase of CAH phases (Fig. 5.19(5)), specifically monocarboaluminate, was observed until 28 days of curing, and no change was observed until 56 days.

The content of monosulphoaluminate was constant until 28 days, and slightly dropped until 56 days of curing. The mineralogical analyses of LSA/PA pastes, where activation potential of PA was tested, have showed different trends (Fig. 5.20(2)).

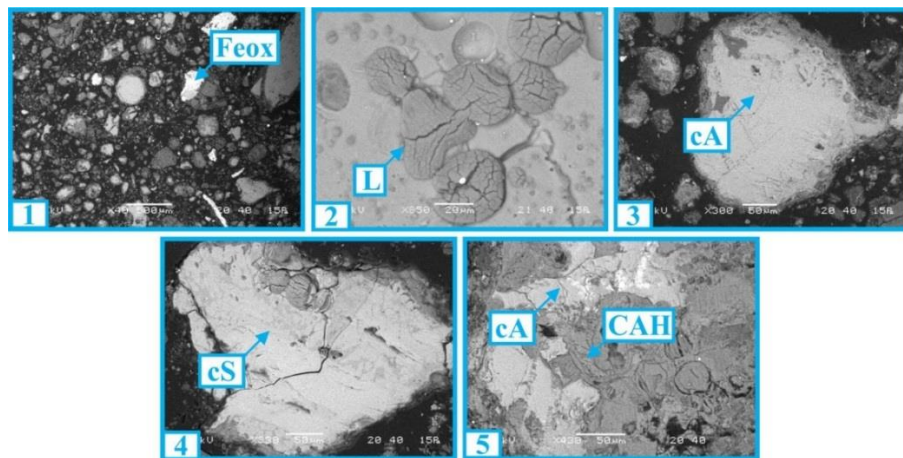


Figure 5.19: SEM microimages of LSA polished sections, representing general structure, with marked iron oxide (Feox) (1), lime (L) (2), calcium aluminate grain (cA) (3), calcium silicate grain (cS) (4), and cA transitioning into CAH (5).

Small time-dependent increase of monosulphoaluminate was observed until 28 days of curing, followed by a decrease until 56 days. This indicated that after 28 days of curing the content of carbonate in the system was increasing compared to the sulphate. The latter could also be confirmed by a time-dependent increase in content of hydrocalumite and monocarboaluminate that was observed until 56 days of curing. After 7 days, hemicarboaluminate was also formed and its content did not further change significantly. Formation of hemicarboaluminate, hydrocalumite, and monocarboaluminate in LSA/PA paste was similar as observed in other pastes, where PA was used in combination with CAV, CAT and LSH.

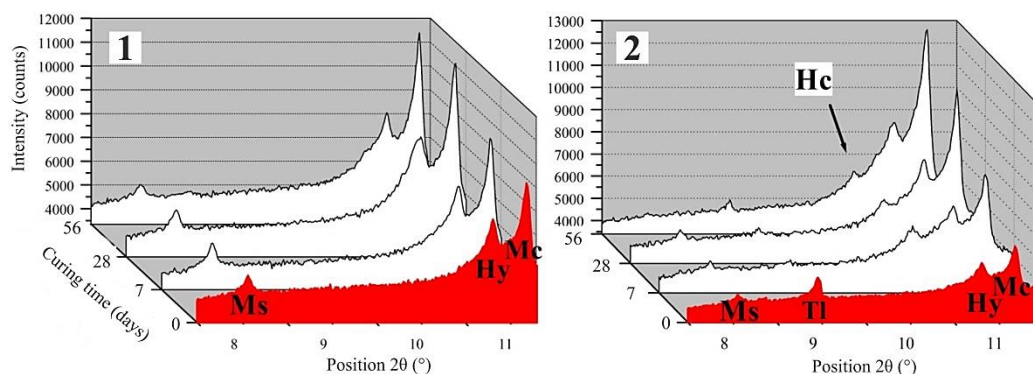


Figure 5.20: Section of the XRD patterns of the LSA (1) and LSA in combination with PA (LSA/PA) (2) pastes at 7, 28 and 56 days of hydration. The most intense (I_{100}) peaks of mineral phases talc (Tl), monosulphoaluminate (Ms), hydrocalumite (Hy), hemicarboaluminate (Hc), and monocarboaluminate (Mc) are indicated.

Ladle slag from Harsco (Acroni steel plant) compared to ABS had a different microstructural appearance (Fig. 5.22(1)) and in a different mineral composition (Figs. 5.18 and 5.21). Calcite, quartz, magnetite, periclase, and wustite were the major phases. Periclase was transitioning in brucite, as it can be seen in Fig. 5.22(4), due to a contact with water. Less abundant in LSH than in LSA were calcium aluminate phases-mayenite, gehlenite, monocarboaluminate, hydrocalumite, and ettringite. In Fig. 5.22(2) a grain composed of calcium aluminate phase interstition with iron oxide phase is visible. Meanwhile, abundance and the types of calcium silicate phases in LSH were comparable to that in LSA as the following phases were identified: γ -C₂S, larnite, hatrurite, and merwinite. The grain of calcium silicate phase with iron oxides is visible in SEM microimage in Fig. 5.22(3). Hydration of grains of calcium aluminate, resulting in the formation of CASH (Fig. 5.22(5)), and the hydration of calcium silicate, resulting in the formation of CSH (reaction rim in Fig. 5.22(6)), was observed.

Meanwhile, it was reported that at the water cooling process of ladle slag from Acroni steel plant, secondary mineral phases have formed, like for example ettringite, similarly as determined in LSH in this study [247].

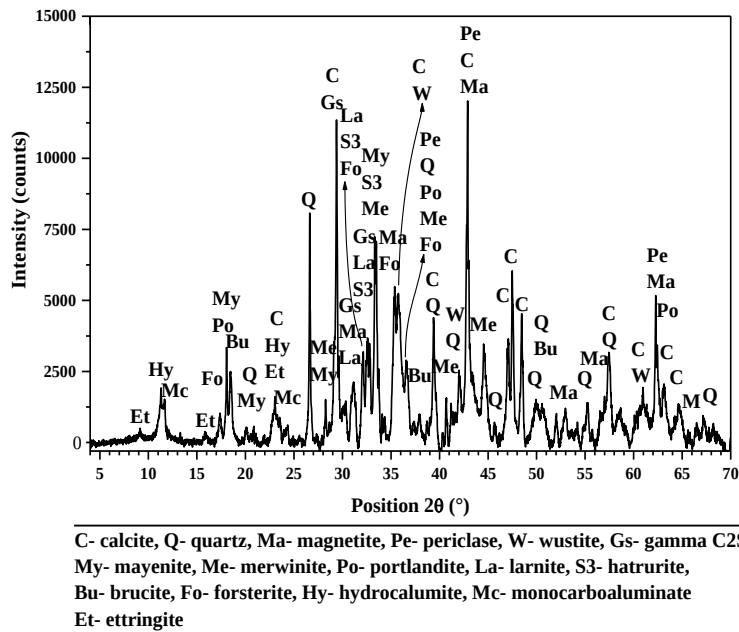


Figure 5.21: XRD pattern of the LSH.

The hydraulic activity of LSH was assessed according to analyses of mineralogical composition of LSH paste after 7, 28 and 56 days of curing (Fig. 5.23(1)). Different trends have been observed when a comparison to LSA paste was performed. Ettringite, hydrocalumite, and monocarboaluminate were already present in LSH sample as it was received from the producer. Time-dependent increase in monocarboaluminate abundance and no changes of hydrocalumite were observed. The trend was similar as in the case of LSA paste. The formation of different calcium aluminate hydrate mineral phases during the hydration of LSH was in line with the reports of scientific literature [247], [244]. Interestingly, after 7 days of curing the presence of ettringite in LSH paste could not be detected.

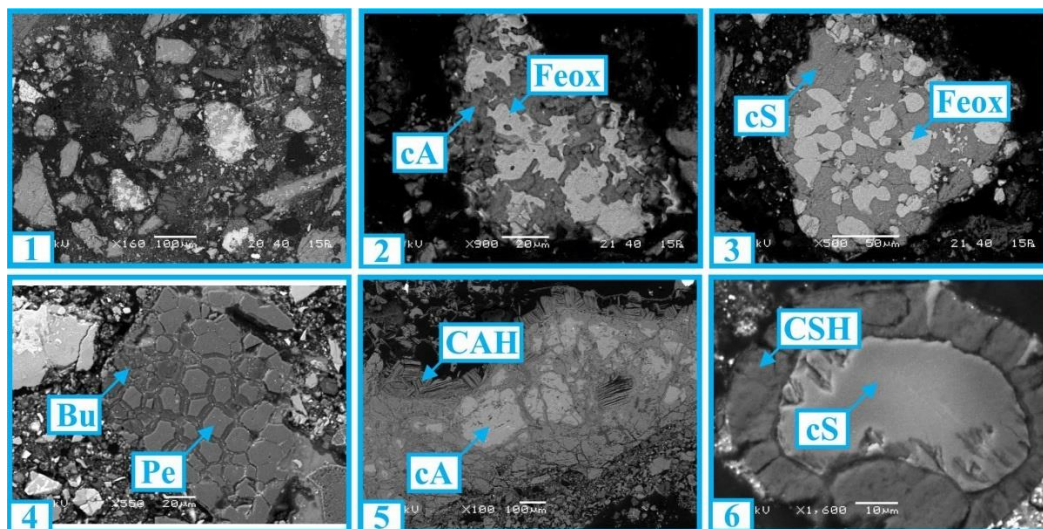


Figure 5.22: SEM microimages of LSH polished sections, representing general structure (1), calcium aluminate (cA) and iron oxides (Feox) (2), calcium silicate (cS) and iron oxides (Feox) (3), periclase (Pe) and brucite (Bu) (4), cA transitioning into CAH phase (5), cS with reaction rim of CSH (6).

The addition of PA to the paste to test the possible activation of LSH by the ash has resulted in the same effect for ettringite, which could not be detected after 7 days of curing. The initial content of hydrocalumite, monocarboaluminate, and ettringite was relatively half lower in LSH/PA paste compared to LSH paste due to the addition of PA. Similarly, in the case of LSA/PA paste, a trend of increase in hydrocalumite and monocarboaluminate abundance was observed as well as the formation of hemicarboaluminate. However, despite the fact that the addition of PA was equal in both cases, considerably smaller quantity of monocarboaluminate was formed in LSH/PA paste compared to the LSA/PA paste. The same trend was also observed if we compared the LSH and LSA paste.

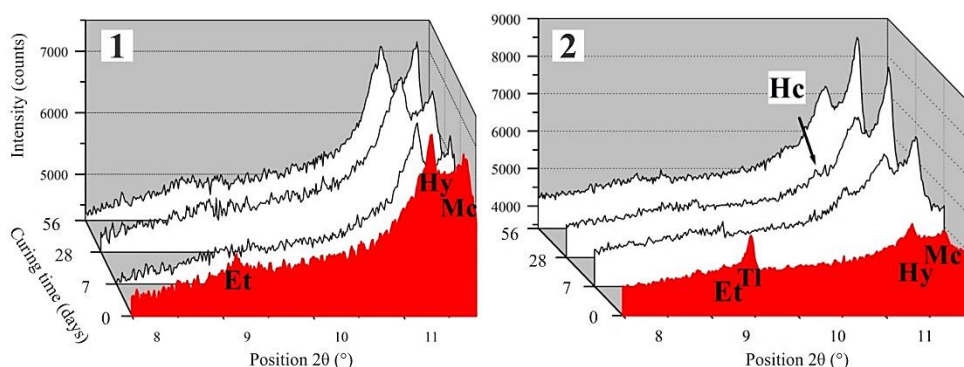


Figure 5.23: Section of the XRD patterns of the LSH (1) and LSH in combination with PA (LSH/PA) (2) pastes at 7, 28 and 56 days of hydration. The most intense (I_{100}) peaks of talc (Tl), ettringite (Et), hydrocalumite (Hy), hemicarboaluminate (Hc), and monocarboaluminate (Mc) are indicated.

This can lead to the conclusion that, in relative comparison, LSH has a lower hydraulic activity than LSA. Namely, a lower amount of newly formed hydration products was formed in LSH and LSH/PA pastes compared to LSA and LSA/PA pastes.

The density of both ladle slags was the same, 2.8 Mg/m^3 , which was higher than for three investigated ashes. The specific surface areas of LSA and LSH were 2.91 and $5.42 \text{ m}^2/\text{g}$, respectively, which are the lower values among all additives. The LSH has a higher specific surface area despite its coarser grain size distribution. Namely, LSA has 10% (d_{10}) of the grains smaller than 0.025 mm , median distribution (d_{50}) of 0.3 mm , and 90% of grains smaller than 1.4 mm (Fig. 5.25). On the other hand, LSH constituted of larger grains, 0.044 of d_{10} , 1.3 of d_{50} , and 4.36 of d_{90} . This indicates that LSH formed larger grains due to agglomeration and cementation after the extraction procedure at Harsco, when it came in contact with water.

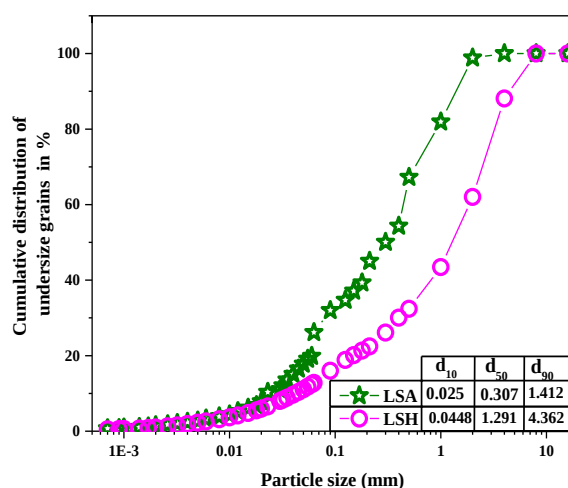


Figure 5.24: Cumulative particle size distribution for ladle slags LSA and LSH.

5.2.4 Red mud

The pH and the conductivity of the investigated RM eluate were measured to be 9 and 0.3 mS/cm, respectively (Table 5.4). The results indicate that the alkalinity of investigated RM was partly neutralised due to aging and exposure to natural conditions in an open depot [351], [352]. Chemical analysis of eluate (Table 5.3) indicated that RM cannot be declared as inert but rather as a non-hazardous waste if we follow the limit values set by the landfill policy (Official Gazette of RS, No. 36/16 [152]). Concentration of Cu in the eluate exceeded the limit value for inert materials as its concentration 2.2 mg/kg d. m. (Table 5.3) was determined. Further, the concentration of As was only slightly lower (for 0.01 mg/kg d. m.) while all others elements were far below their limit values. Based on leaching test results, we can conclude that metals, which have high total concentrations (Cr, Ba, Zn, Ni), were strongly bound in RM constituents as they were present in low water-soluble concentrations. According to the XRF total elemental analysis (Table 5.3) the most abundant constituent in the RM was calcium, which makes up almost 15% of the RM. This is in line with XRD analyses, where calcite was determined as the most abundant phase (Fig. 5.25). Other major phases were hematite, gibbsite, followed by boehmite and phase of the feldspathoid group of minerals. Goethite, quartz, ilmenite, illite/ muscovite, perovskite and rutile were present as minor constituents (Fig. 5.25).

The composition of the RM resembled those reported by different authors such as [248]. Some other studies showed that RM may contain Ca from 25 wt.% to up to 50 wt.% [351]. Concentration of chromium, which is a common contaminant found in red mud [248], was less than 400 mg/kg in RM from this study (Table 5.3).

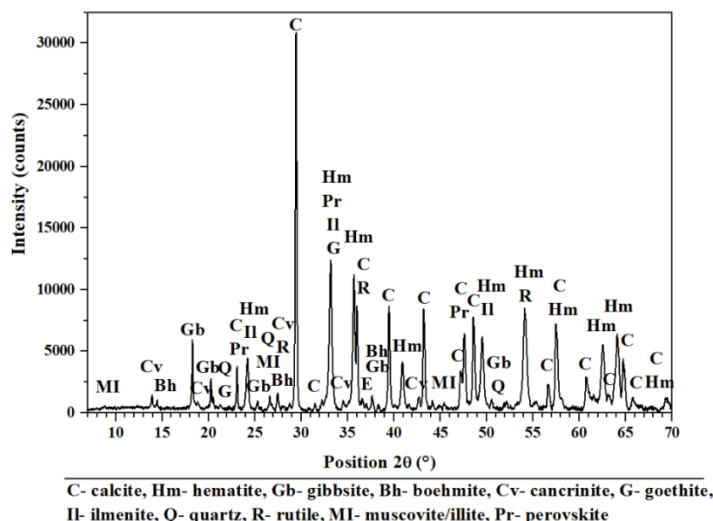


Figure 5.25: XRD pattern of the RM.

SEM/EDS analysis showed that dolomite was also present as a minor phase of RM. The presence of feldspathoid mineral cancrinite was further observed with SEM/EDS (Fig. 5.26 (2)). The results of the phase analysis of the RM were in good corroboration with the chemical analysis and comparable to those found in the literature [248].

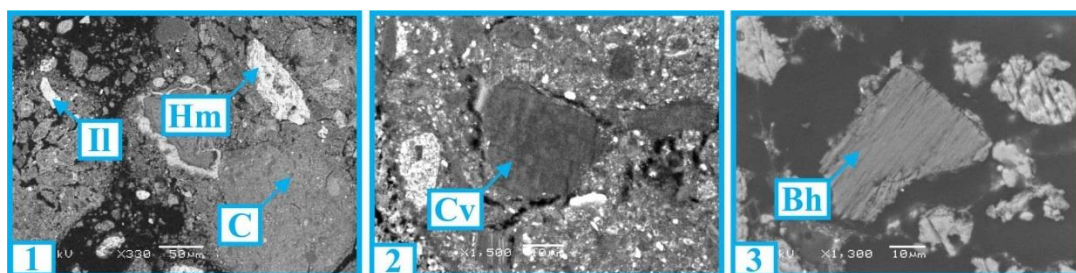


Figure 5.26: SEM microimages of RM polished sections, representing general structure with marked ilmenite (Il), calcite (C), and hematite (Hm) (1), cancrinite (Cv) (2), and boehmite (Bh) (3).

The results of the XRD and the SEM/EDS analysis of the RM paste indicate that RM was not a hydraulic active material as no new mineral phases were formed during the different curing time intervals (Fig. 5.27(1)). XRD analyses of the RM/PA paste were performed at 7, 28 and 56 days of curing to investigate if PA could, due to the portlandite content, act as an activator for the potential latent hydraulic reaction of RM (Fig. 5.27 (2)).

After 7 days of curing two different CAH phases were formed, hemicarcoaluminate and monocarboaluminate. At longer curing time intervals, a slight depletion of hemicarboaluminate could be defined but the transformation into monocarboaluminate was not considerable, notwithstanding the fact that in the system with the hydraulic active material (PA) the excess of calcite was present. This points to the fact that the activity of the RM/PA paste was low. In comparison to the PA paste, the quantity of CAH formed in RM/PA paste was more than a half smaller, which can be correlated to the fact that 50 wt.% lower amounts of PA were present in the RM/PA paste. This leads to the conclusion that RM did not attribute to the formation of hydraulic products and could not be activated by the presence of portlandite. RM was therefore considered to be

a non-hydraulic material. SEM/EDS analysis of RM/PA paste showed partially reacted grains of PA while on the fragments of RM, no traces of reaction could be defined.

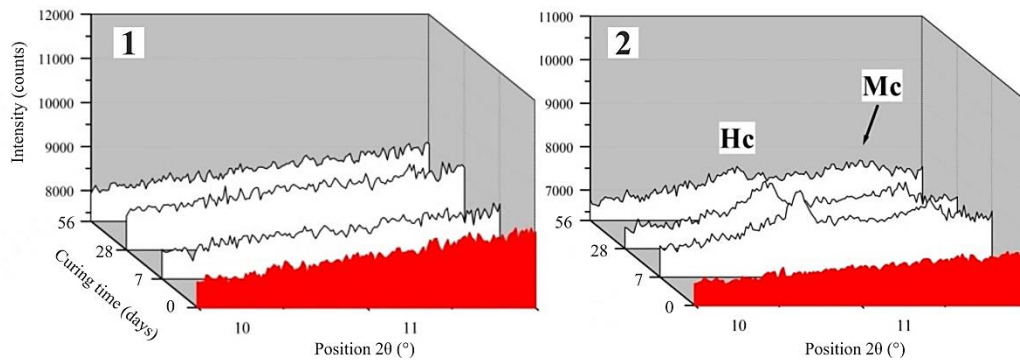


Figure 5.27: Section of the XRD patterns of RM (1) and RM/PA (2) pastes at 7, 28 and 56 days of hydration. The most intense (I_{100}) peaks of newly formed mineral phases hemicarboaluminate (Hc), and monocarboaluminate (Mc) are indicated.

As shown in Table 5.4, a large specific surface area and density were measured for RM, which is in line with literature data [353]. The density of RM was the highest among all used additives. From the particle size distribution data of the RM presented in Fig. 5.28 it is apparent that particle size at d_{10} was 0.025 mm, which was smaller than LSA, LSH, and CAT. However, median distribution of the particles (d_{50}) was < 2.805 mm, and 90% of the particles (d_{90}) was < 8.2 mm, which was coarser than for all other additives.

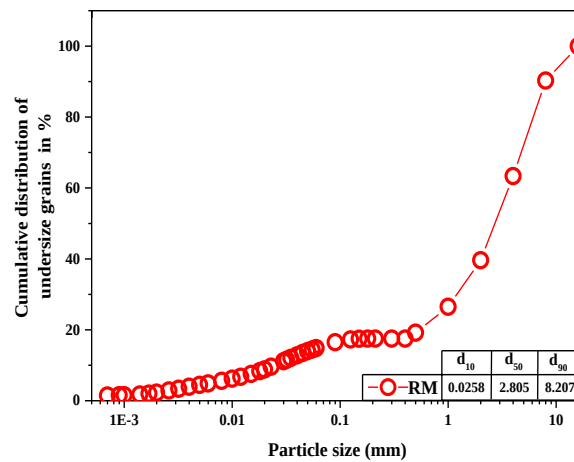


Figure 5.28: Cumulative particle size distribution for RM.

5.3 Remediation of Contaminated Soil

5.3.1 Mineralogical and microstructural analyses

The analyses of pastes prepared from PA have shown that newly formed minerals were different calcium aluminate hydrate phases (CAH), namely, hemicarboaluminate, hydrocalumite, and monocarboaluminate. In CAV paste and LSA paste sulphates containing CAH phases were identified, which were monosulphoaluminate and ettringite, respectively. On the other hand, ettringite was already present in CAT and LSH in a

form as received from the producers, which points to the fact that they were in contact with moisture even before they were used in experiments. When the potential of PA for activation of CAV, CAT, LSA, LSH, and RM was tested, the analyses of mineral composition have shown a time-dependent increase in the formation of CAH phases. In CAV/PA and CAT/PA pastes ettringite was formed, due to higher concentrations of soluble SO_4^{2-} , available in both coal ashes, compared to other additives. Meanwhile, the source of Al for the formation of CAH originated from PA or/and from pozzolanic glassy phases of CAV and CAT [347]. The formation of ettringite was preferential over other CAH phases due to a sufficient content of sulphate [354], [355].

Analyses of hydration products in pastes made of additives served as an indirect indicator of the formation of CAH phases responsible for immobilization of PTE in composites. Other hydration products (for example CSH or CASH) were nevertheless identified in pastes by SEM/EDS. Due to their gel to microcrystalline structure and indefinite composition they could not be confirmed by XRD analyses.

Determinations of mineral composition of composites from remediation experiments have shown a very heterogenic composition. As it is evident from Figs. 5.29 and 5.30, composites were formed of mineral phases that constitute CS, additives and crystalline hydration products. The results of XRD and SEM/EDS analyses have confirmed that CAH were present in composites, as it was previously confirmed for pastes from additives (except for pure RM paste) and was also reported by scientific literature [232], [220], [221], [243]. The exception, where no newly formed minerals of hydration and pozzolanic reactions were determined, was composite CS/RM. Ettringite was the only hydration product, which was semi-quantified by XRD due its abundancy in composite and well defined crystalline structure. Ettringite was preferentially formed over other CAH phases, because a relatively high quantity of sulphate from CS was available for its formation. This was important because the potential of ettringite for immobilization of PTE is high [213], [220], [356].

The use of additives PA, CAV, and LSA for the preparation of composites with CS, resulted in a similar time-dependent increase of ettringite formation in composites CS/PA, CS/CAV, and CS/LSA (Fig. 5.29) as in pastes from PA, CAV and LSA. High alkalinity of these additives in contact with water initiated hydrolysis of reactive phases from additives that released aluminate, portlandite provided soluble Ca, while gypsum from CS was a source of sulphate, for the formation of ettringite [344], [357]. Only a small amount of ettringite was detected in CS/LSH which accounts mostly to the quantity of this phase present in the LSH sample as it was delivered. Ettringite was not formed in CS/RM (Fig. 5.29).

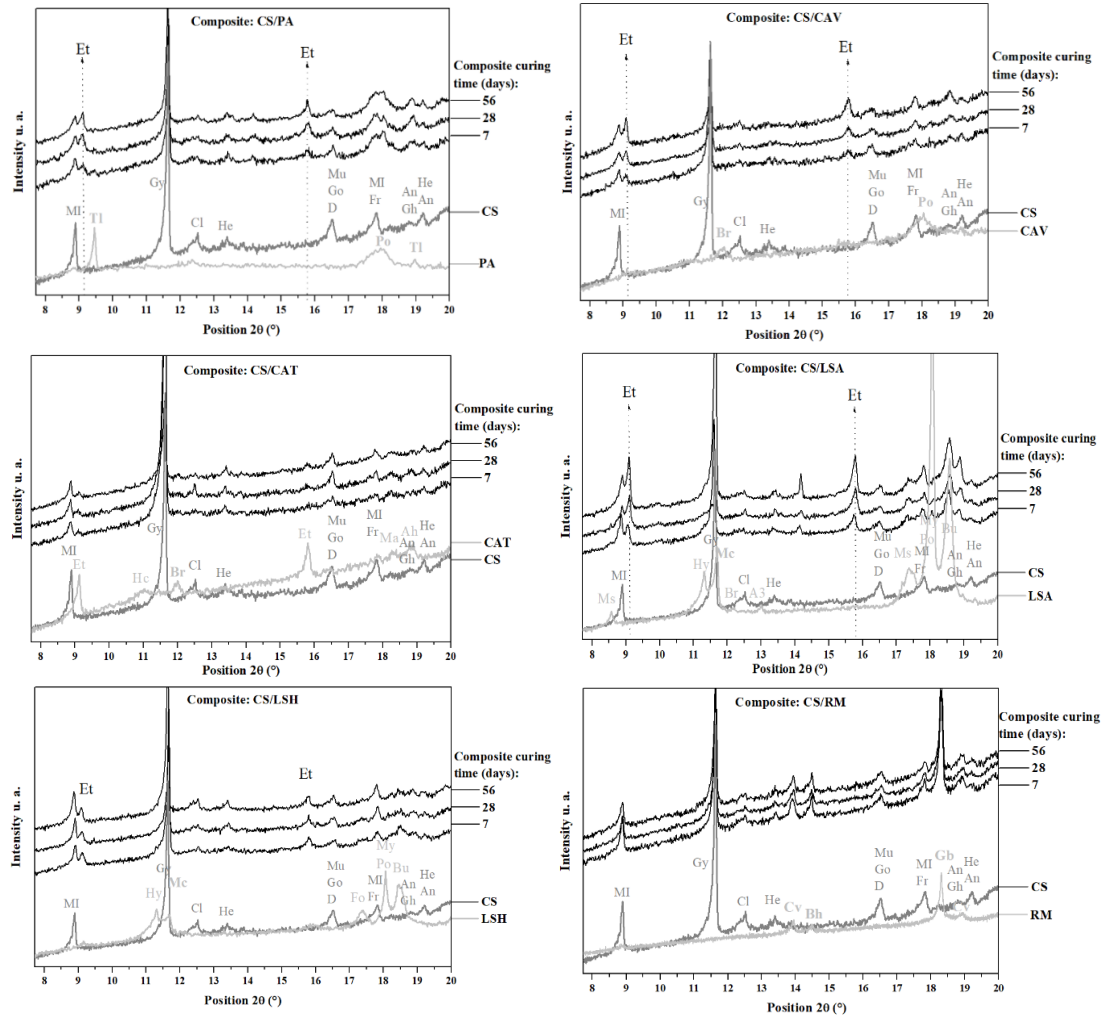
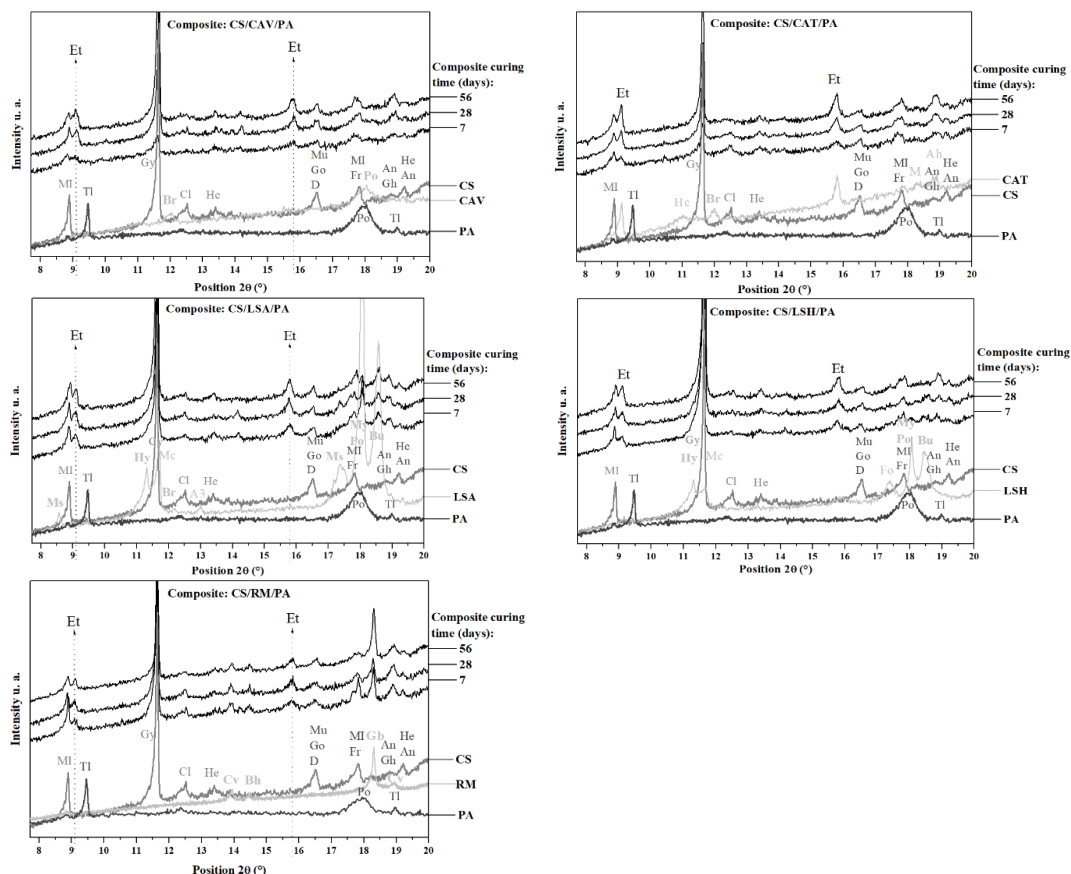


Figure 5.29: XRD patterns of investigated composites and their individual components (CS/PA, CS/CAV, CS/CAT, CS/LSA, CS/LSH, CS/RM).

Increasing time-dependent trend of ettringite formation was observed in all ternary composites (Fig. 5.30). It was observed that the trend was more pronounced for ternary composites CS/CAT/PA, CS/LSH/PA and CS/RM/PA compared to binary composites CS/CAT, CS/LSH and CS/RM, in which PA was not used.



CS phases: An – anorthite, D – dolomite, Fo – forsterite, Fr – franklinite, Gh – gahnite, Go – goslarite, Gy – gypsum, He – hemimorphite, Mi – muscovite/illite, Mu – mullite
Additive phases: Bh – boehmite, Br – brownmillerite, Bu – brucite, Cl – chlorite, Cv – cancrinite, Gb – gibbsite, Ma – magnetite, My – mayenite, Po – portlandite, A3 – tricalcium aluminate
Hydration products: Et – ettringite, Hc – hemicarboaluminate, Hy – hydrocalumite, Mc – monocarboaluminate, Ms – monosulphoaluminate

Figure 5.30: XRD patterns of investigated composites with the patterns of their individual components (CS/CAV/PA, CS/CAT/PA, CS/LSA/PA, CS/LSH/PA, CS/RM/PA).

Following the qualitative results of XRD analyses, the relative quantity of ettringite according to RIR semi-quantitative method was defined in binary and ternary composites (Figs. 5.31 and 5.32). As can be seen from Fig. 5.31, the highest relative quantity of ettringite, among binary composites (with one additive), was formed in CS/PA during 7 and 28 days of curing. This is in line with the scientific literature that PA is a hydraulic material. The results are also in line with findings that in composites, which contain gypsum and PA, ettringite was formed relatively fast [240]. After 56 days of curing the highest quantity of ettringite was determined in CS/CAV followed by CS/PA. This can be related to 38% higher total Al content in CAV comparing to PA. The Al in CAV is evidently in a form available for the formation of CAH phases. The CAV contained pozzolanic glassy phase, which formed higher quantities of hydration products at longer periods of curing time [358]. On the other hand, very low relative amount of sulphate bearing CAH phase was formed in CS/CAT, CS/LSA, and CS/LSH despite the fact that CAT, LSA and LSH have comparable total content of Al as PA and CAV. However, most of Al in CAT, LSA, and LSH was not in a form that could be activated. No newly formed hydration products were detected in CS/RM.

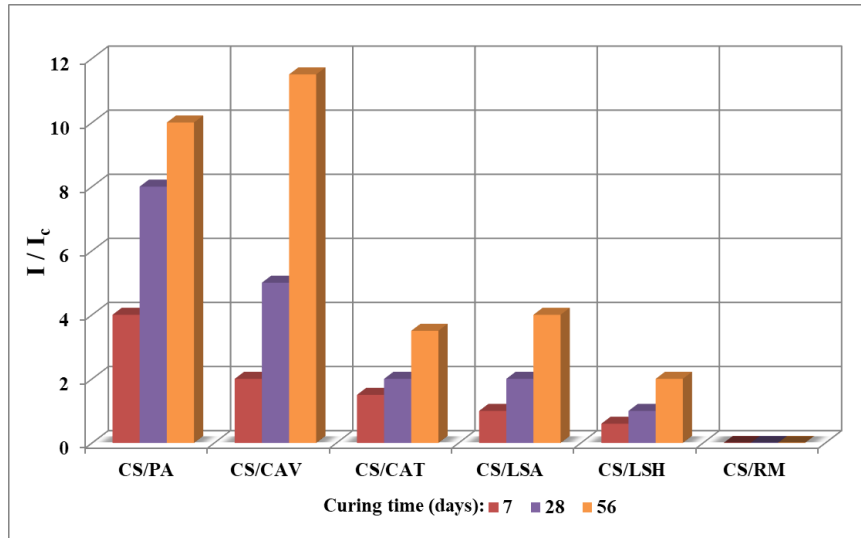


Figure 5.31: Relative mass fraction of ettringite formed in the composites CS/PA, CS/CAV, CS/CAT, CS/LSA, CS/LSH, and CR/RM, after 7, 28 and 56 days of curing.

The results of RIR analyses for ettringite in ternary composites compared to binary composites show that the formation of ettringite at 7 and 28 days of curing was in ternary composites controlled by a relatively fast hydration of PA. The highest relative quantity of ettringite after 7 and 28 days of curing time was among ternary composites defined for CS/CAV/PA (Fig. 5.32), which also formed the highest relative quantity of ettringite among all investigated composites after 56 days of curing. Again, it was evident that the activation of glassy phases in CAV was slower, even when it was combined with PA. This phenomenon was similar as observed in a retarded setting of Portland cements due to delayed activation of reactive glassy phase [358]. Also, due to delayed activation of pozzolanic phases of CAT, 56 days of curing was needed for the formation of a comparable relative amount of ettringite in CS/CAT/PA as in CS/PA. However, less ettringite was formed in CS/CAT/PA compared to CS/CAV/PA due to a coarser grain size distribution of CAT [349], and because it was partly pre-hydrated when delivered by the producer.

The positive effect of combining the PA with LSA and LSH in ternary composites (Fig. 5.32) reflected in the formation of higher relative quantity of ettringite compared to CS/LSA and CS/LSH (Fig. 5.31). The result was also slightly better for CS/LSA/PA than for CS/LSH/PA, and less pronounced in comparison to CS/CAT/PA. Results show that relative quantity of newly formed ettringite was comparable for CS/LSH/PA and CS/RM/PA. Differences in hydraulic activity between LSA and LSH were attributed to two factors. Hydraulically active mineral grains in LSA were encapsulated by a thin layer of hydration products due to the slight pre-hydration of LSA (Fig. 5.19(3)). Grains of LSH were encapsulated by thicker layers of hydration products (Fig. 5.22(6)) due to a direct contact with water during processing with the use of water at the producer (Harsco). In LSA thinner protection layers were formed, which less inhibited the contact of grains of hydraulically active mineral phases with water than in composites with LSA. Also, much coarser grain size distribution of LSH compared to LSA could have an effect on lesser hydraulic activity of the former [359].

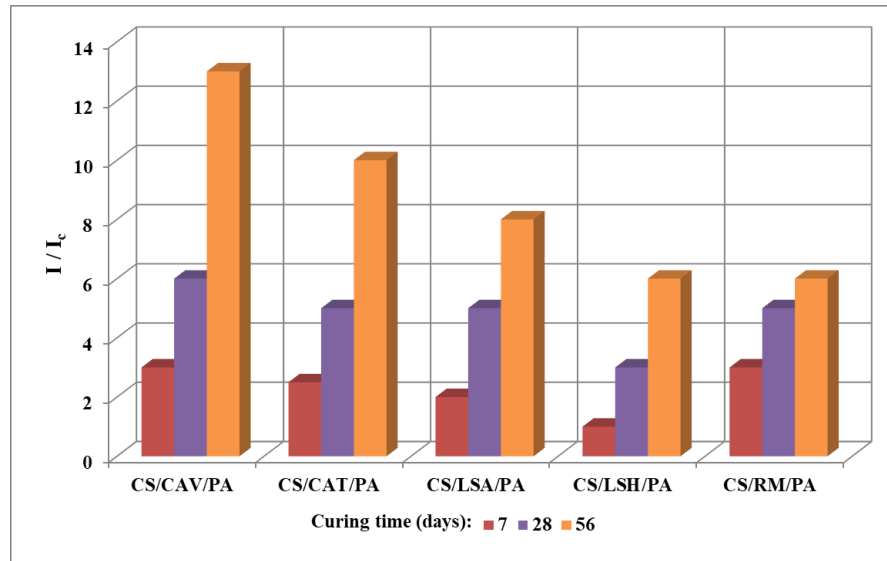


Figure 5.32: Relative mass fraction of ettringite formed in the composites CS/CAV/PA, CS/CAT/PA, CS/LSA/PA, CS/LSH/PA, and CR/RM/PA, after 7, 28 and 56 days of curing.

Microstructural analyses of composites have revealed that similar phases have formed as in pastes made of additives, which were described in previous sections. Grains of slag, which are the most hazardous material in CS, contaminated with PTE, were physically encapsulated in a compacted matrix of composites (Fig. 5.33(1)).

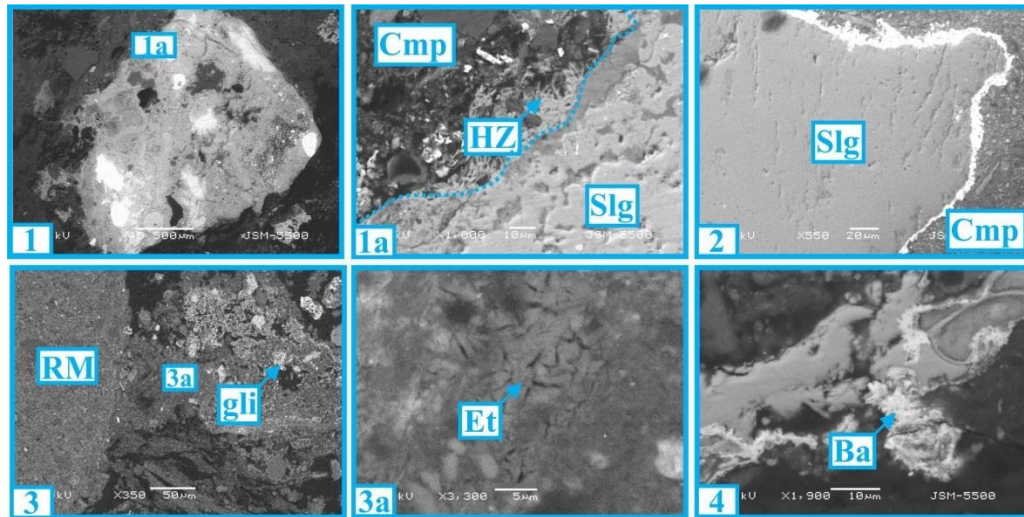


Figure 5.33: SEM microimages of a random slag particle in CS/PA (1), with magnified spot with indicated slag (Slg), composite matrix (Cmp) and newly formed mineral (HZ) at the border (marked with dotted line) (1a), intimate contact of slag (Slg) and composite matrix (Cmp) (2), CS/RM/PA composite with a grain of agglomerated RM, glassy phase (gli) from PA (3), with magnified spot representing ettringite (Et) (3a), formation of barite (Ba) in CS/PA (4).

In composites where PA was utilised, rarely, in pores on the border between slag and composite matrix, newly formed crystals of a mineral containing Ca and Zn were observed (Fig. 5.33(1a)) which could represent the calcium hydrozincite phase. The

formation of the latter from saturated solution of $\text{Ca}(\text{OH})_2$ in the presence of Zn^{2+} , which was similar as in the composites with the use of PA, was described in literature [360]. In most cases an intimate contact between slag and composite matrix was observed (Fig. 5.33(2)). However, the occurrence of Zn-rich reaction rim, on the border between composite matrix and slag particle, could not be confirmed to be the result of formation of newly formed minerals incorporating Zn.

The formation of ettringite was regularly observed in ternary composites. For example, in CS/RM/PA (Fig. 5.33(3)), we can distinguish a larger grain of agglomerated RM and partly dissolved glassy particle from PA, and in between a mixed composite matrix (magnified in Fig. 5.33(3a)). In the matrix the cross section of massive ettringite was observed (Fig. 5.33(3a)), which filled the pores. Ettringite displayed a characteristic shrinkage-induced pattern of curved cracks, described as 'tiger stripe' morphology [361] (Fig. 5.33(3a)).

Formation of barite crystals in the pores, especially at the borders between slag grains and composite matrix were observed (an example from CS/PA is presented in Fig. 5.33(4)).

No other mineral phases, which included selected PTE, could be directly determined by SEM/EDS. Namely, beside very heterogenic mineral composition also concentrations of water-soluble or available PTE for the formation of newly formed mineral phases were relatively low. Due to efficient compaction of composites there was only a small amount of pore spaces, which were filled with hydration products in which incorporation of PTE could not be confirmed by SEM/EDS analyses.

Therefore, chemical immobilization mechanisms were rather indirectly interpreted from the knowledge of chemical behaviour of individual PTE, known information about chemical mechanisms of immobilization from simple artificial experimental matrices, and from time-dependent trends in results of mineralogical, chemical and physical analyses of composites.

5.3.2 Environmental assessment and chemical immobilization efficiency of geotechnical composites

The preliminary soil remediation experiments were performed in order to evaluate the potential of immobilization additives for remediation at relatively low (from 1 to 5 wt.%) addition. Additives were mixed with the most contaminated CS and water to simulate the simplest way of application, as it is described in soil remediation studies [207]. After 28 days of curing leaching tests according to SIST EN 12457-2:2004 [151] were performed, and the most relevant PTE from CS (Cd, Pb, and Zn) along with Mo were determined in eluates by ICP-MS. Although Mo concentration in eluates from CS was never problematic, it was additionally investigated in eluates due to its different chemical properties as oxyanion, compared to the cationic metals Cd, Pb, and Zn [213], [163]. None of the investigated experimental mixtures were inert, according to the landfilling policy limits (Official Gazette of RS, No. 36/16 [152]), as at least one of four parameters were exceeding limits. However, the synthesis of results has shown distinctive pH-dependent leaching of four PTE (Fig. 5.34), which is very similar as described by geochemical models (for example [213], [362]). Cationic metals Cd, Pb, Zn, are generally less soluble in alkaline environment [163]. However, their behaviour is amphoteric, which means that they have minimal solubility at a certain range of alkaline pH, followed by an increase in leachability beyond that range and at lower neutral or acidic pH [363]. The behaviour of Cd is, according to the results of this study and geochemical models, determined by a drop of leachability at pH of approximately 8 with a slight increase in leachability towards alkaline pH values. The range of minimal leachability is from 10 to

12.5 as reported in models and in this study from pH 9.5 to 12. It is governed by precipitation of low soluble hydroxide ($\text{Cd}(\text{OH})_2$) as shown in the scientific literature [362], [363]. The leachability of Pb according to geochemical models is the lowest in range between pH 9.5 to 11.5. The increase in leachability above pH 11 is evident, and caused by formation of soluble hydroxyl complexes. However, results of this study show that also at pH below 10 (to 7) an increase in leachability, due to amphoteric chemical behaviour of Pb, was less pronounced as in models. Similar effect was observed in immobilization experiments from scientific studies, where authors correlated the effect with the formation of low soluble Pb minerals [362]. The lowest leachability of Zn, as predicted by models, is between pH 10 and 11.5, which is roughly in line with experimental results of this study. Increase in leachability beyond pH 11.5 is caused by a formation of soluble hydroxyl complexes [362], [363].

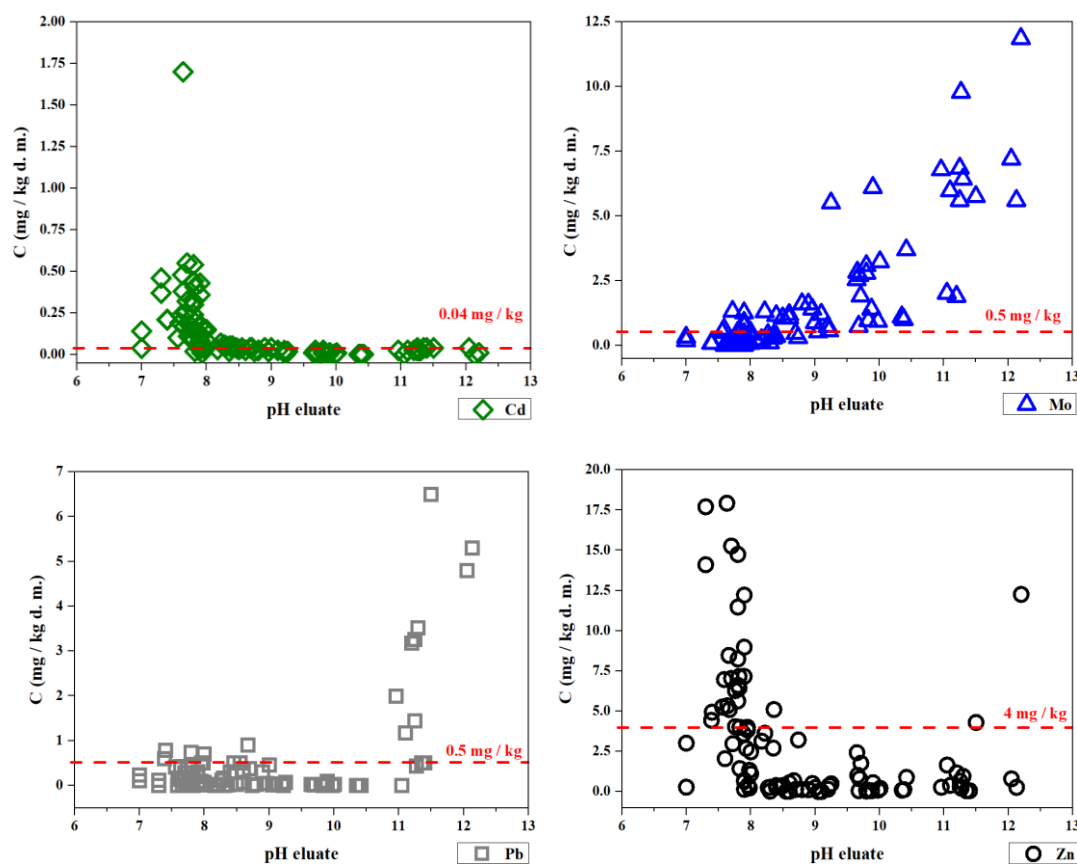


Figure 5.34: Leaching of Cd, Mo, Pb, and Zn from mixtures of CS from sampling area 3 and immobilization additives from preliminary experiments. Limit value for inertness, according to the landfilling policy limits (Official Gazette of RS, No. 36/16), is presented with a red number and dashed line.

The complete opposite was behaviour of Mo, which is an oxyanionic element. Geochemical models show a rapid drop of adsorption and immobilization efficiency of Mo and all oxyanion PTE in transition from neutral to alkaline pH [213]. Leachability of Mo in this study is showing similar trends. However, scattering of results at alkaline values might not only be due to a heterogeneity of CS samples used in preliminary experiments, but also due to chemical mechanisms of immobilization by incorporation of Mo into newly formed mineral phases, when hydraulically active additives were used [213], [356].

Described pH dependent leaching behaviour of Cd, Mo, Pb, and Zn was important for understanding the immobilization in experimental geotechnical composites, which is going to be further discussed.

Tank leaching test was performed on monoliths of samples of composites from remediation experiment, according to the modified leaching procedure SIST EN 1744-2:2002, after 7, 28, and 56 days of curing to evaluate time-dependent immobilization efficiency.

As can be seen from Fig. 5.35, the pH values of eluates varied between different composites, depending on their buffering capacity and content of alkalis. For most of the composites time-dependent changes of pH can also be seen, which are related to the formation of new mineral phases during the hydration reactions. On the other hand, conductivity of the eluates was a relatively stable parameter (with exceptions CS/PA and CS/RM), which was substantially lower for eluates from composites compared to eluates from CS.

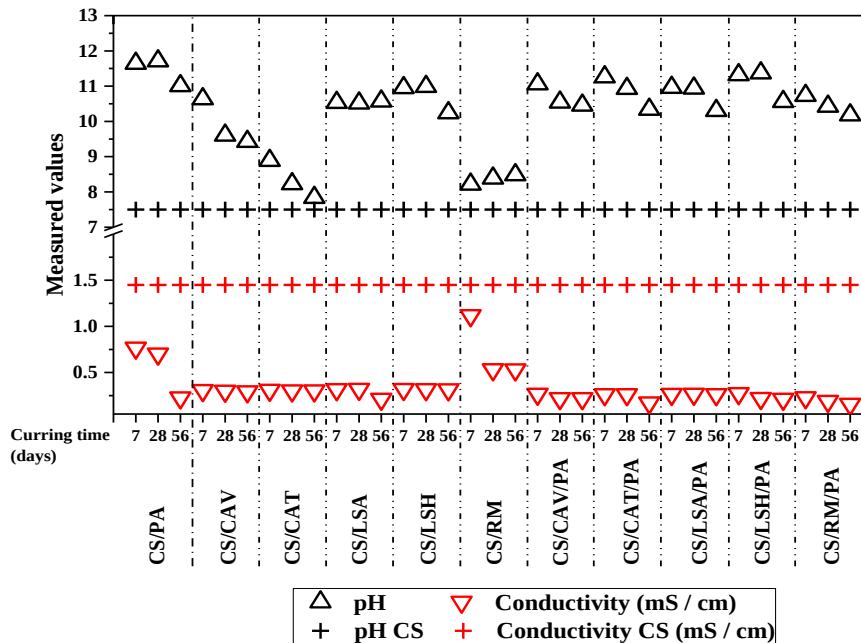


Figure 5.35: pH and conductivity of the eluates from CS from sampling area 3 and composites after 7, 28 and 56 days of curing. The data represent the mean value from two replications.

The eluates from composite CS/PA were the most alkaline among the tested composites, when we compared them after leaching at individual curing periods (Fig. 5.35). Also, conductivity of the eluates was relatively high, which was also observed in the eluates from CS/RM that had the highest conductivity. There was a time-dependent trend in lowering of pH and conductivity of CS/PA eluates, which indicates gradual formation of hydration mineral products, consumption of dissolved ions, and neutralization of alkalinity [364], [209]. There was a very efficient, more than 99%, immobilization of Cd in CS/PA composite after 7 days of curing. High pH, which is in a range of low leachability for this element [363], favours formation of low soluble $\text{Cd}(\text{OH})_2$ and $\text{CaCd}(\text{OH})_4$, and its immobilization in new hydration phases [217], [365]. Time-dependent increase in immobilization efficiency was also observed for Zn and Pb (Fig. 5.36). The Pb immobilization was highly governed by alkalinity of composite. Namely, immobilization efficiency was lower, when pH was beyond 11.5 at 7 and 28 days of

curing, and was higher at 56 days of curing when a drop to pH 11 occurred (Figs. 5.35 and 5.36). The scientific studies reported the formation of low soluble $\text{CaPb}(\text{OH})_4$, $\text{Pb}(\text{OH})_2$ and surface sorption of Pb, as the main immobilization mechanisms, while the formation of soluble hydroxy complexes governs leachability of Pb at highly alkaline values [366], [362]. However, the incorporation of Pb into newly formed minerals of hydration reactions, for example CSH, has also been reported for immobilization of Pb at pH higher than 11.5 [367]. This effect can be seen after 7 and 28 days of curing of CS/PA composite, which produced eluates with pH higher than 11.5 (Fig. 5.35). Such an alkaline would otherwise cause an increase in leachability of Pb (similarly as seen in Fig. 5.34). On the contrary, Pb immobilization efficiency was increasing at 28 days (Fig. 5.36) due to the incorporation into newly formed minerals of hydration and pozzolanic reactions. Possible chemical immobilization mechanism of Zn is the formation of low soluble calcium hydrozincite ($\text{CaZn}_2(\text{OH})_6 \cdot 2\text{H}_2\text{O}$), zinc hydroxide, or other hydration products [368]. The formation of calcium hydrozincite was also confirmed with microstructural analyses by SEM/EDS (Fig. 5.33(2)). The time dependent immobilization efficiency pattern is similar for Zn as for Pb. Therefore, similar chemical mechanisms governed immobilization of both cationic metals. Due to much lower water-soluble concentrations of Pb compared to Zn, no newly formed mineral phases with Pb could be found by SEM/EDS analyses.

Interestingly, immobilization of As was observed in eluates, despite high pH that otherwise favours mobilization of As(V) and As(III) oxyanions. This can be attributed to formation of sparingly soluble calcium arsenates (for example $\text{CaHAsO}_4 \cdot \text{H}_2\text{O}$, or $\text{Ca}_5(\text{AsO}_4)_3(\text{OH})$). Namely, the concentration of Ca^{2+} ions in pore solution of composite CS/PA was high due to a high content of portlandite and lime in PA, which favoured their precipitation [366]. Incorporation of As in calcium aluminate hydrate phases was also possible, but could not be correlated with RIR analyses [213], [212].

Concentrations of Ba were the highest in eluates from CS/PA compared to other composites. This can be attributed the chemical composition of PA, which contains 27 times higher water-soluble concentrations of Ba than CS. However, the concentrations of Ba in eluates from CS/PA were approximately 100 times lower as from PA. Namely, solubility of Ba in composite was controlled by a precipitation of low soluble BaSO_4 , which also consumed soluble sulphate from CS [220]. Newly formed BaSO_4 in composites with PA was further observed by SEM/EDS (Fig. 5.33(4)). After 28 days of CS/PA curing, all PTE were below limit values for inertness (Official Gazette of RS, No. 36/16).

The alkaline pH caused increase in leachability of Cr and Mo oxyanions, and Cu cationic metal [213], [210]. The increased leachability of Cr is related to its pH and redox depending behaviour, since Cr tends to be oxidised to highly mobile and toxic Cr(VI) species under alkaline oxidative conditions. The adsorption efficiency of chromate is similar as for molybdate oxyanion, which is increasing below the pH of 9 [213], [205]. The leachability of Cu is highly pH dependent and shows similar amphoteric behaviour as Pb and Zn, with minimum at pH 8. Increase in leachability of Cu in composites is caused by a formation of soluble hydroxyl complexes [205]. However, leachability of Cu compared to Cr was lower despite the fact that total concentration of Cu was 70 times lower than Cr in CS from sampling area 3. This can be attributed to better immobilization of Cu in composites, which extends immobilization maxima for Cu into highly alkaline area [210]. Nonetheless, concentrations of Cr and Cu were well below limit values for inert materials. On the other hand, leachability of Mo was the highest at 7 days of curing, which was followed by an evident time-dependent trend in lowering of Mo leachability after 28 days of curing. Immobilization of Mo can be attributed to the formation of CaMoO_4 and to incorporation in calcium aluminate hydrate phases, which were more abundantly formed after 28 and 56 days of curing as indicated by RIR analyses (Fig. 5.31) [213], [369].

The eluates from CS/CAV and CS/CAT were less alkaline than that from CS/PA, and a time-dependent trend in lowering of pH was observed (Fig. 5.35), which can be correlated to the formation of newly formed mineral phases that uptake alkalis at longer curing times [344]. The CAV had the highest pH of eluate among additives, and pH of eluate from CAT was also alkaline (Table 5.4). However, their buffering capacity is lower than for PA, which is evident if we compare pH of eluates from CS/PA, with CS/CAV and CS/CAT. Namely, PA contained a relatively higher amount of lime and portlandite than CAV and also CAT (Figs. 5.8, 5.12, 5.15). The time-dependent trends of immobilization efficiency were not evident for CS/CAV and CS/CAT (Fig. 5.36). The leachability of Cd, Pb, and Zn was effectively lowered below limit values for inertness in both composites (Official Gazette of RS, No. 36/16). However, this can be both due to a chemical mechanism of incorporation into newly formed mineral phases [220], [223], [221], surface adsorption due to a high specific surface area [229] or due to physical mechanisms (low water permeability, micro-encapsulation) [210]. Lower was also the water-soluble concentration of Ba, which can be due to the formation of BaSO_4 that consumed water soluble SO_4^{2-} from ashes [220]. Observed was an increase in leachability of Mo from CS/CAV and CS/CAT in eluates after 7 days of curing, followed by a drop below limit values for inertness after 28 and 56 days of curing. This effect might be related to a substantial increase in the formation of newly formed mineral phases in CS/CAV at longer curing times, as confirmed by RIR analyses (Fig. 5.31), and incorporation of Mo in ettringite. However, in CS/CAT the immobilization effect of Mo can also be due to a substantial drop of pH (Fig. 5.35) within a range of lower leachability of Mo [213]. Leachability of Cr from CS/CAV was also increased but stayed below inertness limits. The use of CAV and CAT for immobilization of PTE in geotechnical composites from CS is comparable to that where PA was used. However, due to their lower buffering capacity, and low hydraulic reactivity of CAT (which was due to the formation of hydration products before its use), their use is limited.

The pH and conductivity of eluates from CS/LSA and CS/LSH was relatively stable through all curing periods (Fig. 5.35). Problematic PTE, Cd, Pb, and Zn were in both composites effectively immobilized below limit values for inertness (Official Gazette of RS, No. 36/16), without distinctive time-dependent trends (Fig. 5.36). The efficiency of aluminate phases, which are abundantly present in LSA and LSH, for adsorption of Zn was proved to be very efficient and fast [370]. Gradual reduction in leachability of As and Cr (the latter was in eluate after the initial curing period of 7 days mobilized) was observed from CS/LSA, which can also be related to its incorporation in newly formed calcium aluminate hydrate phases [371]. Constant increased leachability of Mo from CS/LSA was observed, which exceeded limits for inertness after all curing periods. On the other hand, increase in leachability of As, Cr, Cu, Sb, and Se was also observed in CS/LSH. The concentration of Mo in eluates from CS/LSH was the highest of all investigated composites. Increased leachability of oxyanions and Cu from CS/LSH can be a result of the low hydraulic activity of ladle slags, relatively low amount of newly formed mineral phases (Fig. 5.31), and the combination of alkaline pH (the same effects were already described in the case of CS/PA). Nevertheless, water-soluble concentrations of Cr and Mo in LSH, and Mo in LSA, were already exceeding limits for inertness in eluates from ladle slags (Table 5.3). Due to the increased leachability of oxyanions, for example Mo, from the ladle slags at alkaline pH (as for example observed by Lončar et al. [247]), the use of ladle slags for remediation of CS is limited. Also, if we compare LSH, which was subjected to quenching with water, to LSA, which was prior to its use not in contact with water, the former is less appropriate for use as immobilization additive. Namely, relatively less new mineral phases were formed in CS/LSH, which lowers its immobilization efficiency.

Different studies report that PTE immobilization mechanisms by RM are governed by surface sorption and precipitation processes [372]. Iron and aluminium hydroxide mineral phases, goethite, hematite, feldspathoid group of minerals (cancrinite), and gibbsite, provide a large number of adsorption sites and have high PTE adsorption capacity [373]. Neutralization of high alkalinity of fresh RM is usually needed for its beneficial use, as pH highly affects the PTE sorption processes [373], [374]. Higher adsorption capacity of RM after neutralization is reported by Liu et al. [372]. Mildly alkaline pH of RM investigated in this study, which was neutralised by exposure to natural conditions, was favourable for immobilization of multiple PTE, as their adsorption maxima is close to neutral pH [374].

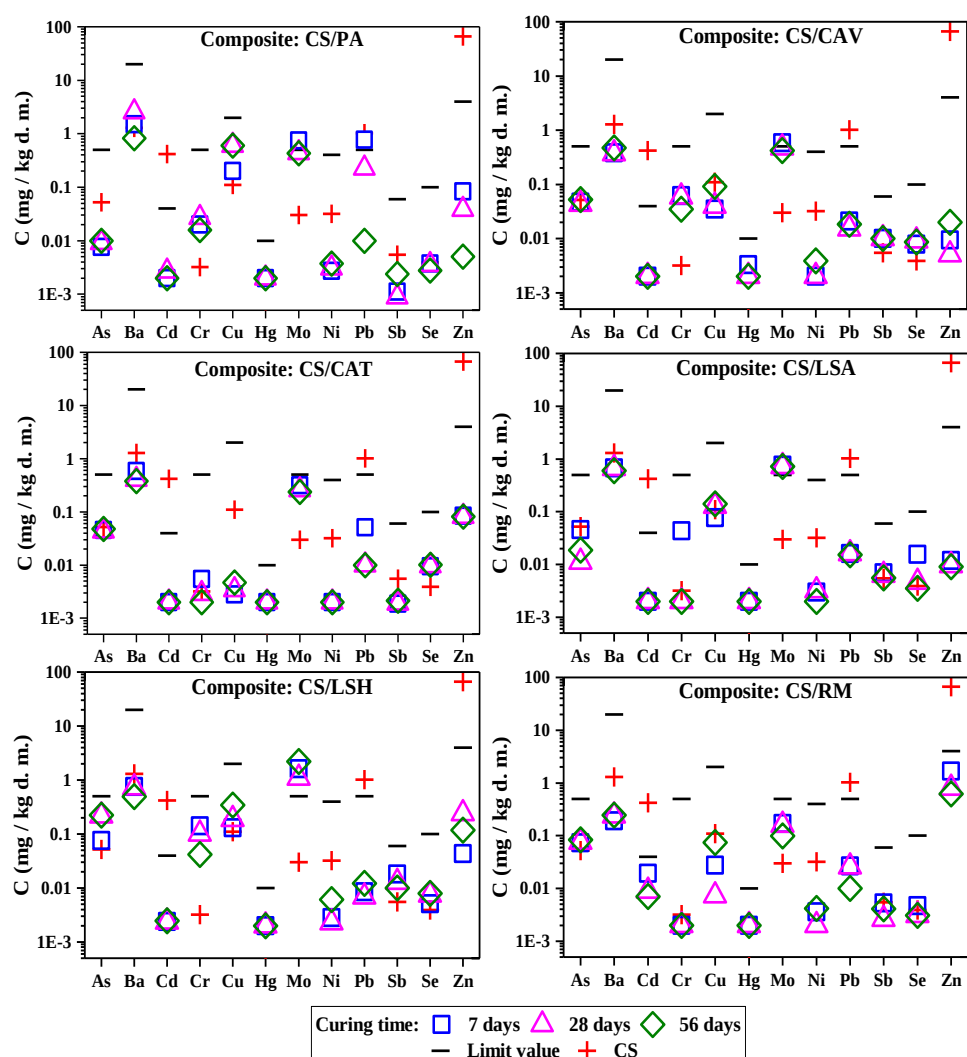


Figure 5.36: Leaching of PTE from the CS and composites with single immobilization additive after 7, 28 and 56 days of curing. Limit values are indicating the regulation for inert materials (Official Gazette of RS, No. 36/16).

No apparent time-dependent immobilization efficiency trend for most of the PTE could be defined, which is consistent with the literature data (Fig. 5.36). This could have resulted from the relatively fast process of RM adsorption immobilization mechanism [294]. However, in the immobilization of Cd, Pb, and Zn, a minor time dependent increase is demonstrated by the results, and could be attributed to slow diffusion of these PTE in composite to reach adsorption sites. The highest concentration of sulphate was

measured in the eluates from CS/RM, as shown in Fig. 5.38. The absence of cations which could form low soluble complexes with sulphate in CS/RM may explain this phenomenon. Also, sulphate anion cannot be adsorbed to the surface adsorption sites, as they are mostly negatively charged at moderately alkaline pH of CS/RM. According to the surface complexation model negatively charged ligands form surface complexes at moderately acidic pH values [191]. On the other hand, concentration of chloride was in eluate from CS/RM the lowest among the three composites. CS has 7.5 times lower leachable concentration of chlorides than RM. Therefore, the lowest chloride concentration in CS/RM can be accounted to physical immobilization and to dilution factor in composite. On the other hand, pH of eluates from CS/RM is the lowest, which still enables partial adsorption of anions. There was a slight increase in concentrations of As, Cu in eluates from CS/RM compared to eluates from CS, which can be attributed to the release of those elements from RM, as it was already reported in the literature [248]. Also, As oxyanion is mobile and less efficiently adsorbed at alkaline pH, which is present in CS/RM [213].

The purpose of experiments with the use of combinations of PA with individual immobilization additives (CAV, CAT, LSH, LSA, and RM) for the preparation of ternary geotechnical composites was to investigate the ability of the former to enhance immobilization efficiency due to activation of pozzolanic phases in additives by portlandite and lime from PA [220], [375], [376]. Thus, more hydration products were formed as confirmed by RIR analysis in Fig. 5.32. The results of chemical analyses of eluates from composites with binary immobilization additives were showing characteristics of remediation with PA and each individual additive. Effective immobilization of Cd, Pb, and Zn was achieved in all composites (Fig. 5.37). While decreasing time dependent trend of immobilization efficiency for Zn can be seen in eluates from CS/CAV/PA, CS/LSA/PA, CS/LSH/PA, and CS/RM/PA. The same effect was observed for Pb in eluates from CS/CAT/PA, CS/LSH/PA, and CS/RM/PA, while in CS/CAV/PA and CSLSA/PA immobilization efficiency was unchanged at all curing periods. In eluates from all composites with binary additive increased leachability of Cr and Mo was observed similarly as for CS/PA (Fig. 5.37). Due to the same mechanisms as described for CS/PA, water-soluble As concentration was decreased in all composites. Since lower addition of PA was used in composites with binary additive, the concentration of Ba in eluates was lower compared to CS/PA and similar for all composites as the same concentration of PA was added.

Comparison of CAV and CAT in combination with PA has shown that composite CS/CAV/PA has better immobilization efficiency for Mo, Pb, and Zn compared to CS/CAT/PA (Fig. 5.37). This can be correlated with the formation of relatively more new hydration products in the latter as indicated by RIR analyses (Fig. 5.32). The overall immobilization efficiency of CS/CAV/PA was higher than for CS/CAV, CS/CAT/PA, and CS/CAT.

There was a difference in the results of chemical analyses of eluates between composites CS/LSA/PA and CS/LSH/PA (Fig. 5.37). The former has shown higher immobilization efficiency for As, Mo, Pb, and Zn after 56 days of curing, and much less leached Cr compared to CS/LSH/PA. The immobilization efficiency of CS/LSA/PA was higher for Pb, Zn, and Mo compared to CS/LSA (Fig. 5.36). Namely, the CS/LSA/PA was an inert material if we consider chemical analyses of eluates after 56 days of curing. The same trend was observed for CS/LSH/PA compared to CS/LSH, where higher immobilization of former was observed for As, Mo, and Zn. However, leachability of Mo was still higher than the limit for inert materials (Official Gazette of RS, No. 36/16), even after 56 days of curing. Due to higher alkalinity of the ternary composites, increase

in Mo leachability of the Mo was higher compared to binary composites (Figs. 5.36 and 5.37).

A time dependent-trend in increase of immobilization efficiency was observed in CS/RM/PA for Pb and Zn that can be correlated with the formation of new minerals as confirmed by RIR (Fig. 5.32). In comparison to CS/RM a significant increase in Mo leachability was also observed, which turned below limit value for inert materials, after 56 days of curing (Figs. 5.36 and 5.37). Although, both composites CS/RM and CS/RM/PA were inert after 56 days of curing, the latter has higher immobilization efficiency for Cd, Zn, and SO_4^{2-} (Figs. 5.36, 5.37, and 5.38).

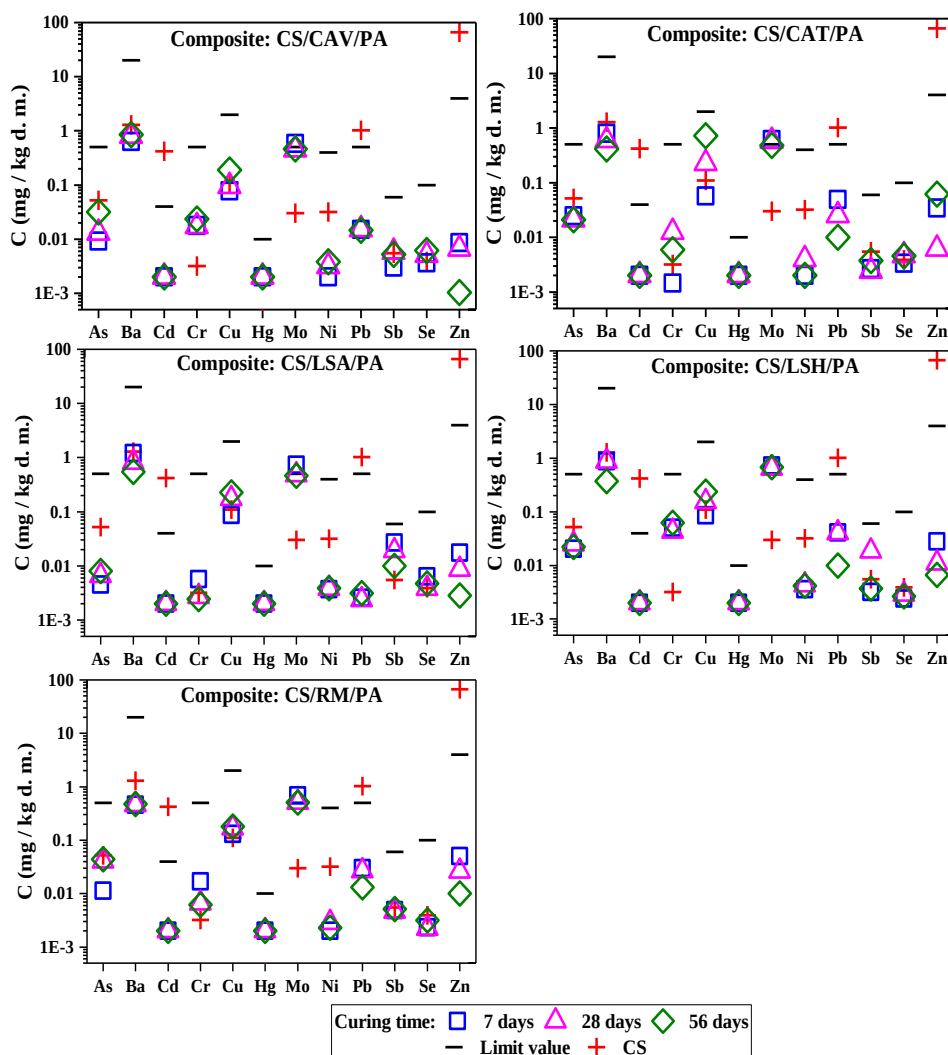


Figure 5.37: Leaching of PTE from the CS and composites with immobilization additives in combination with PA after 7, 28 and 56 days of curing. Limit values are indicating the regulation for inert materials (Official Gazette of RS, No. 36/16).

Generally, all ternary composites had less leachable Ba and more efficient immobilization of Pb and Zn compared to CS/PA, which had a slightly more efficient immobilization efficiency for As and SO_4^{2-} . The composites with binary additives also had higher immobilization efficiency of SO_4^{2-} compared to binary composites without PA (Fig. 5.38), which might be correlated with the formation of a higher quantity of ettringite (Figs. 5.31 and 5.32) [344], and consumption of soluble Ba from PA for the formation of low soluble BaSO_4 [220].

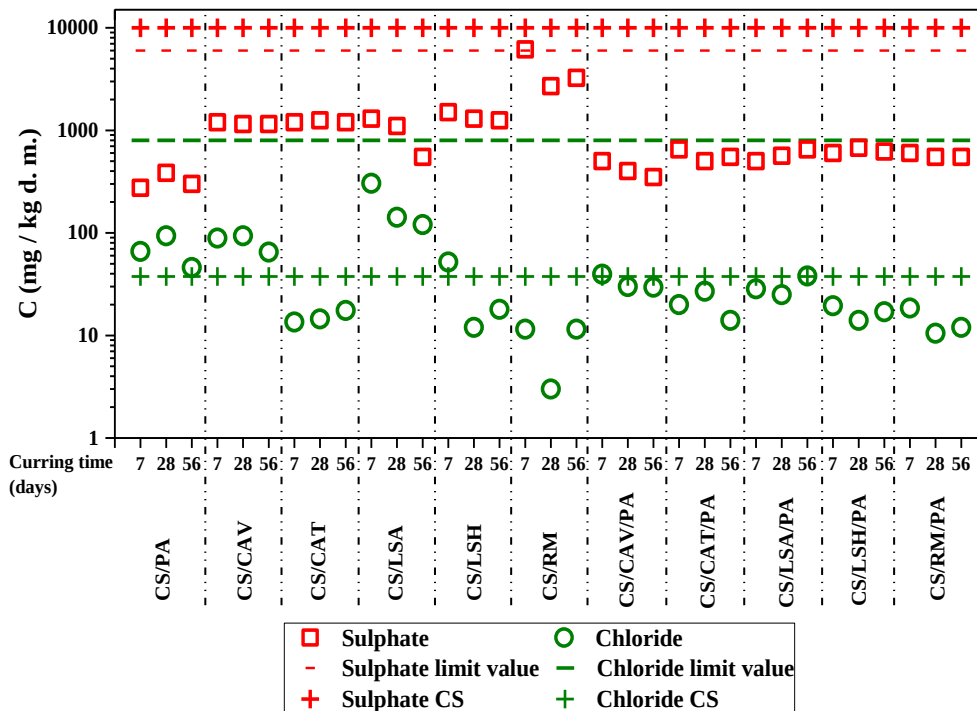


Figure 5.38: Leaching of sulphate and chloride from the CS and composites after 7, 28 and 56 days of curing and from CS. Limit values are indicating the regulation for inert materials (Official Gazette of RS, No. 36/16).

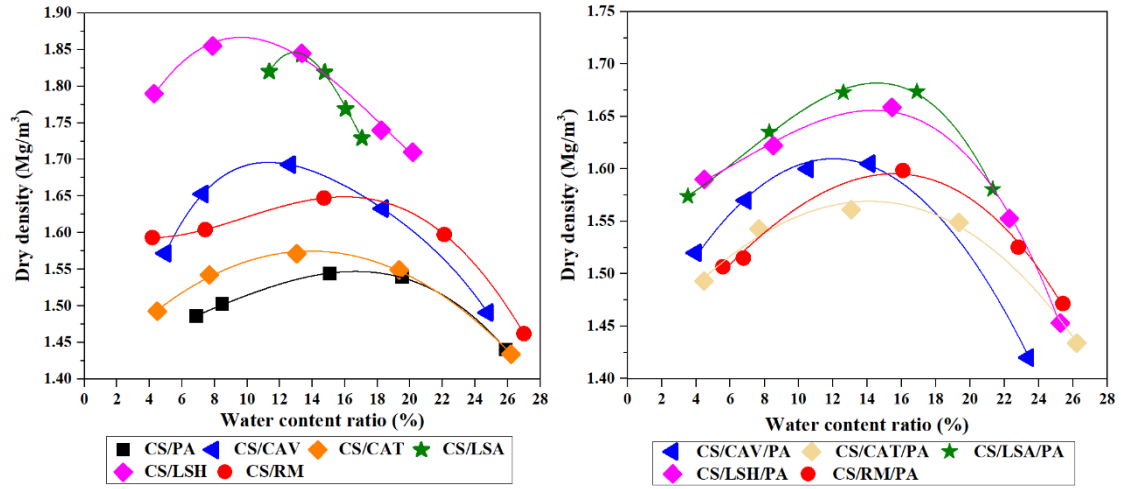
The immobilization of chloride in binary composites was the most efficient for CS/CAT, CS/LSH, and CS/RM. In these composites additives, which contained the highest amounts of water soluble Cl^- were used (Table 5.3) and were proved to be least hydraulically active. Therefore, rather than chemical immobilization of Cl^- , lower concentrations can be attributed to the dilution factor and physical mechanisms of immobilization in composites. On the other hand, in composites CS/PA, CS/CAV, and CS/LSA leachability of Cl^- was increased during 7 and 28 days curing periods, and was gradually decreasing upon 56 days of curing. This might be related to the initial release of Cl^- due to the dissolution of alkali chlorides, followed by immobilization in new mineral products of hydration reactions. Namely, calcium aluminium hydrate phase Friedel's salt ($\text{Ca}_2\text{Al}(\text{OH})_6(\text{Cl}) \cdot 2\text{H}_2\text{O}$) can incorporate chloride from pore solutions [243], [377]. However, its presence in composites was not confirmed by XRD or SEM analyses due to relatively low concentrations of Cl^- .

Among ternary composites, in which PA was combined with other additives, the lowest concentrations of Cl^- were measured in CS/CAT/PA, CS/LSH/PA, and CS/RM/PA (Fig. 5.38). However, due to the addition of PA, concentrations were higher compared to CS/CAT, CS/LSH, and CS/RM. On the other hand, lower concentrations of Cl^- were measured in eluates from CS/CAV/PA, CS/LSA/PA, compared to CS/PA, CS/CAV, and CS/LSA. This indicates that immobilization of Cl^- was more efficient due to a higher content of newly formed calcium aluminate hydrates in CS/CAV/PA and CS/LSA/PA compared to CS/CAT, and CS/LSA, as also confirmed by RIR analyses (Figs. 5.31 and 5.32).

5.3.3 Basic geotechnical properties

Physical mechanisms of immobilization of contaminants within a composite are important for successful utilization of the described remediation procedure. The optimal

water content and maximal dry density of composites were determined by the Proctor compaction procedure. The Proctor compaction curves for binary and ternary composites



are given in Fig. 5.39.

Figure 5.39: Proctor compaction curves for binary composites (left) and ternary composites (right) from soil remediation experiments.

The difference between parameters optimal water content and maximal dry density (Table 5.5), which were determined according to the modified Proctor procedure, were observed between composites. However, these were apparently not due to the grain size distribution of composites, which was very similar for all investigated composites as can be seen from the grain size distribution curves for composites, which are given in Fig. 5.40.

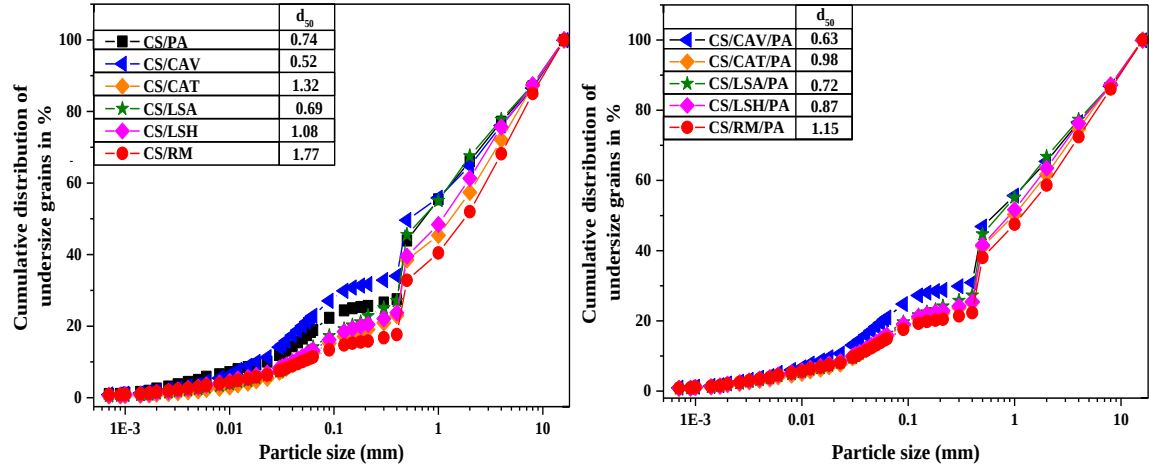


Figure 5.40: Cumulative particle size distribution curves for binary composites (left) and ternary composites (right).

The highest optimum water contents, among binary composites, were determined for CS/PA and CS/RM while among ternary composites for CS/RM/PA (Table 5.5). The relatively higher optimum water content determined for CS/PA was probably caused due to absorption of water by porous glassy grains in PA and due to the exothermic reaction between lime from the ash and water, which was also reported by literature [238]. The relatively higher consumption of water in composite SC/RM to achieve the desired

maximum compaction was governed by a rehydration of RM grains with a high specific surface area (Table 5.4), which lost free water during drying at 105 °C before it was delivered in the laboratory. Also, it was reported [378] that drying at such temperatures causes loss in plasticity of rehydrated RM due to the reduction of content of clay and silt grain fraction. These were bonded during drying [378] and were only partly disintegrated at rehydration as larger agglomerated grains were still observed by SEM analysis (Fig. 5.33(3)). The optimum water content was the lowest for CS/CAV, despite high specific surface area and smallest d_{10} and median (d_{50}) grain size distribution of CAV comparing to other additives. However, similar values of optimal water content were reported for geotechnical stabilization of silty/sandy materials with the use of siliceous fly ashes [379]. The higher optimum water content of ternary composite CS/CAV/PA, compared to CS/CAV, was observed due to the use of PA. Composites with CAT, compared to those with CAV, generally had higher optimum water content, despite much coarser grain size distribution of the CAT comparing to CAV. As seen in Fig. 5.40, the difference between grain size distribution of composites was not substantial. Thus, the difference is more probably related to the fact that grains of CAT were partly bonded into agglomerates due to the hydration of ash as it was wetted directly before dispensing from TE-TOL fly ash silo. Therefore, higher addition of water during compaction (compared to the case of CS/CAV) could cause better disintegration, redistribution and packing of ash grains in the composite.

Table 5.5: Grain density, optimum water content, maximal dry density and water permeability coefficient measured for geotechnical composites from remediation experiments.

Composite	Grain density (Mg/m ³)	Optimum water content (%)	Maximal dry density (Mg/m ³)	Degree of saturation at optimum	Water permeability coefficient (m/s)
CS/PA	2.68	16.69	1.55	0.63	$3.95 \cdot 10^{-9}$
CS/CAV	2.68	11.97	1.7	0.57	$8.73 \cdot 10^{-8}$
CS/CAT	2.71	14.21	1.57	0.54	$8.82 \cdot 10^{-8}$
CS/LSA	2.73	13.0	1.85	0.76	$6.18 \cdot 10^{-8}$
CS/LSH	2.73	13.2	1.87	0.799	$6.51 \cdot 10^{-8}$
CS/RM	2.8	16.1	1.65	0.66	$8.76 \cdot 10^{-8}$
CS/CAV/PA	2.68	13.73	1.62	0.57	$2.87 \cdot 10^{-8}$
CS/CAT/PA	2.69	14.95	1.56	0.57	$2.95 \cdot 10^{-8}$
CS/LSA/PA	2.71	14.53	1.68	0.66	$2.45 \cdot 10^{-8}$
CS/LSH/PA	2.71	15.43	1.66	0.67	$1.9 \cdot 10^{-8}$
CS/RM/PA	2.74	16.0	1.59	0.62	$5.19 \cdot 10^{-8}$

Binary composites with the addition of ladle slag had comparable optimum water content, with a slightly higher value for CS/LSH than for CS/LSA. The trend of higher optimum water content value for CS/LSH/PA compared to CS/LSA/PA was observed for ternary composites, where 0.9% difference was determined. Interestingly, a similar effect was observed in the case of coal ashes. Namely, composites with LSH, which was pre-hydrated before it was used in experiments, had higher values for optimal water content, comparing to composites with LSA. Again, at points of compaction with the use of higher addition of water this could cause better disintegration of bonded grains, and thus denser packing was achieved. Generally, determined values for optimum moisture content of composites were in line with scientific models for non-plastic sandy soils (for example [380]).

Although the parameter maximal dry density can vary substantially (according to SIST EN 13286-2:2005 [296] variation in range of $\pm 0.1 \text{ Mg/m}^3$ are allowed) due to the heterogeneity of the CS in composites some general observations could be discussed. The lowest maximal dry density was determined for CS/PA (Table 5.5), due to a low grain density of PA (Table 5.4). Higher maximal dry density was determined for CS/CAV than for CS/PA although CAV had the same density as PA (Table 5.4) and the grain size distribution of both composites was similar (Fig. 5.40). Therefore, it can be considered that at the same compaction energy the densification of CS/CAV was more efficient. On the other hand, CS/CAT and CS/RM had insignificantly 0.02 and 0.1 Mg/m^3 higher maximal dry density in comparison to CS/PA. Nevertheless, this can also be on account of higher grain density of CAT and RM (Table 5.4). The highest maximal dry density was determined for binary CS/LSA and CS/LSH. Both ladle slags had lower grain density than RM. This points out that densification of CS/LSA and CS/LSH could be higher than for CS/RM at the same compaction energy. This can be related to finer median and d_{90} grain size distribution of ladle slags compared to RM. The composites CS/CAV/PA, CS/LSA/PA, CS/LSH/PA, and CS/RM/PA had lower maximal dry density than binary composites, where no PA was combined (CS/CAV, CS/LSA, CS/LSH, and CS/RM). This can be attributed to the use of PA, which had a lower grain density (Table 5.4), except for CAV, which had the same grain density.

The water permeability is a parameter which determines a rate at which water can flow through the treated material. It also determines the potential for transport of contaminants from the composite [215]. The lowest water permeability was determined for CS/PA that was in the range of clays. Similar findings were reported by Kogbara et al. [210], which stated that at the addition of more than 20 wt.% of hydraulic binder (Portland cement, or PA in case of this study) in stabilisation of clayey silty sandy gravel, water permeability of $< 10^{-9} \text{ m/s}$ can be achieved. The water permeability of CS/CAV, CS/CAT, and CS/RM was very comparable, while the permeability of CS/LSA and CS/LSH was lower due to apparently higher densification. The ternary composites with the use of combinations of additives with PA had higher permeability than CS/PA. On the other hand, 3 times lower permeability was determined for CS/CAV/PA and CS/CAT/PA compared to binary composites CS/CAV and CS/CAT. The CS/LSA/PA had 2.5 and CS/LSH/PA had 4.1 times lower water permeability than CS/LSA and CS/LSH. Although, approximately 10 times lower water permeability was reported in geotechnical composites from ladle slag [381], in the case of this study, coarse grain size distribution of soil is causing higher permeability of composites. Highest permeability among ternary composites was determined for CS/RM/PA, and was 1.7 times lower compared to CS/RM. Lower, permeability of ternary composites can be related to the formation of a higher quantity of new hydration products (Figs. 5.31 and 5.32) that caused the pore filling effect, and due to a better packing of grains because of the use of fine grained PA. Again, the composite with the use of LSH (CS/LSH/PA) had apparently better compaction efficiency than the composite with the use of RM (CS/RM/PA). Namely the former had almost 5 times lower permeability despite the fact that both additives had similarly coarse grain size distribution and in both composites relatively the same amount of hydration products was formed as confirmed by RIR analyses (Fig. 5.32). The water permeability of ternary composites was in a range reported for similarly stabilized contaminated clayey silty sandy gravel by ordinary Portland cement [215]. Generally, lower permeability values in the range of 10^{-9} m/s were reported for composites with RM after compaction (for example [378]). However, the content of clay and fine silt grain fractions was much higher compared to RM from this study, which had the most coarse-grained d_{50} and d_{90} distribution among utilized additives.

Higher leachability of SO_4^{2-} from CS/RM, or Mo from CS/LSH (Figs. 5.36 and 5.38) can be correlated with the higher water permeability. On the other hand, higher immobilization efficiency or lower leachability from ternary composites can be attributed to generally lower water permeability of the latter compared to binary composites. Similarly, Kogbara [215] (also [210]) correlated lower leachability of contaminants from remediated soil with lower water permeability. However, the trend could not be undoubtedly confirmed as lowering of water permeability and leachability also followed the trend of higher addition of hydraulic binders. On the other hand, low water permeability of CS/PA did not increase immobilization efficiency for all PTE although the differences are small. This suggests that leaching from CS/PA was also driven by the diffusion mechanism. The latter depends on the concentration gradient between demineralized water, as a leaching solution, and concentrated pore solution with dissolved PTE species that were not chemically immobilized by sorption or incorporation in newly formed mineral phases [209].

Unconfined compressive strength (UCS) was tested after 3, 7, 28, and 56 days of curing as shown in Fig. 5.41 and 5.42 for binary and ternary composites, respectively.

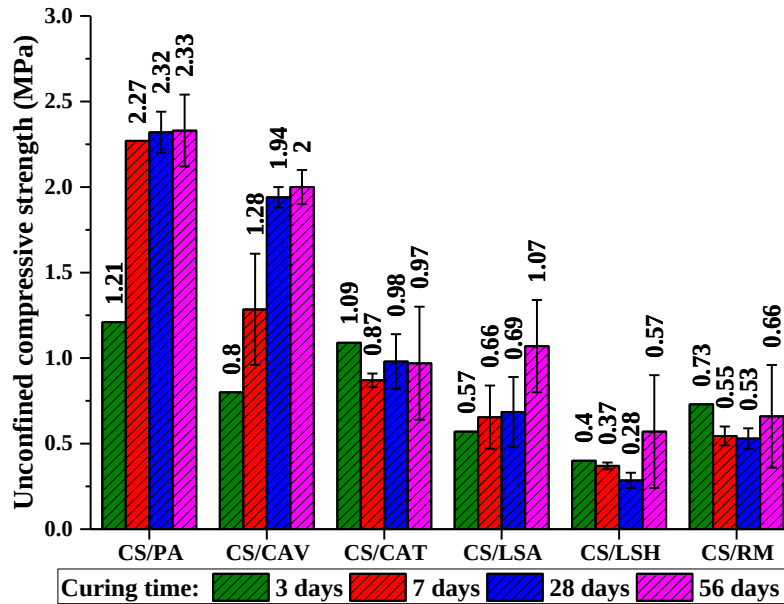


Figure 5.41: Development of the unconfined compressive strengths (UCS) of the binary composites after 3, 7, 28 and 56 days of curing.

The highest UCS after each curing interval was determined for CS/PA. The most pronounced increase in USC of CS/PA was observed at early ages of curing, between 3 and 7 days. Similar results were obtained by Segui et al. [238], who utilized PA for geotechnical stabilization, and the similar results of RIR analysis were observed (Fig. 5.31), which indicated the highest yield in the formation of new hydration products during early curing periods. Although the highest relative amount of hydration products was formed in CS/CAV until 56 days of curing, compared to other composites with the use of one additive, the CS/PA revealed approximately 1.17 times higher UCS. New hydration products evidently contributed less to the UCS in CS/CAV and contributed more to the effect of filling the pores. The time-dependent increase in UCS was also observed for CS/LSA. However, approximately 2 times lower UCS was determined after 56 days of curing compared to CS/PA and CS/CAV that can be correlated with a substantially lower relative amount of newly formed hydration products (Fig. 5.31).

Interestingly, the highest yield of UCS was for CS/LSA observed between 28 and 56 days of curing. On the other hand, no time dependent trends in changes of UCS were observed for CS/CAT, CS/LSH, and CS/RM (Fig. 5.41), as these additives were confirmed to be the least hydraulically active. For example, RM acted in composite only as inert filler.

Time-dependent trends in the increase of UCS were observed for all ternary composites (Fig. 5.42), with the use of PA and its combinations with CAV, CAT, LSA, LSH, and RM. This can be correlated with RIR analyses (Fig. 5.32), which further confirmed that higher UCS of composites with the addition of PA are a result of formation of new mineral phases, and not only of more efficient packing due to the use of fine grained PA. The highest yield in UCS, which can be attributed to a relatively fast hydration of PA, was for these composites observed in curing period from 3 to 7 days. Composites CS/CAV/PA and CS/CAT/PA also had a pronounced yield of UCS between 28 and 56 days of curing. This indicates the activation of pozzolanic phases from siliceous fly ashes at longer time intervals [358]. Composites CS/LSA/PA and CS/LSH/PA had the highest yield of UCS between 3 and 7 days of curing, which could be attributed to the hydration of PA phases, and between 28 and 56 days of curing. High yield of UCS for composites CS/LSA, CS/LSA/PA and CS/LSH/PA at longer curing times can be attributed to (s)lower reactivity of both ladle slags due to the encapsulation of grains of hydraulic mineral phases by layers of hydration products. Scientific literature on the other hand also reported that ladle slag may contain pozzolanic phases, which can be activated at curing times longer than 28 days [359]. Although more hydration products were formed in CS/PA compared to CS/RM/PA, the latter produced approximately 1.2 times higher UCS. This was attributed to the physical properties of RM used, which can act as filler that enables a more efficient support of grains.

The high benefit of combining coaly fly ash with lime material for the preparation of geotechnical composites from CS with a similar grain size distribution as in this study was described by [220]. However, similar results were obtained in this study with the use of PA as alternative "lime contributing" material, which not only increased the immobilization efficiency, but also enhanced UCS of composites.

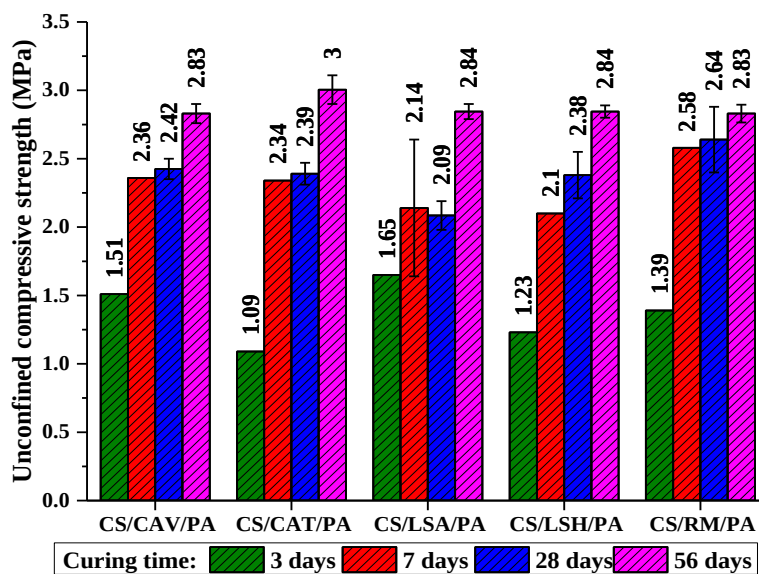


Figure 5.42: Development of the unconfined compressive strengths (UCS) of the ternary composites after 3, 7, 28 and 56 days of curing.

If we take into consideration the Slovenian Technical Specifications [382] for road construction, the composite CS/PA (56 days of curing) comply with the lower UCS limit value (> 2.5 MPa), for the use as base course for road foundations. All other composites with a single additive did not comply with this value. On the other hand, all composites with a combination of PA and other individual additives achieved the lower limit value until 56 days of curing. However, none of the investigated composites achieved the UCS limit value given as the average of multiple measurements (3.5 MPa).

The water permeability coefficient and unconfined compressive strength, which are the most commonly used performance tests for composites from remediation procedures in immobilization [215], are very dependent of compaction energy and degree of saturation as for example as reported by Daniel & Benson, [383]. Therefore, it must be emphasized that lower water permeability coefficients and higher compressive strengths can be obtained after compaction of composites, which are wetter than at optimum water content determined by Proctor test. Optimally, at least 80 % degree of pore saturation should be achieved after compaction. As can be seen in Table 5.5., only binary composites CS/LSA and CS/LSH were prepared near that degree of saturation, while other composites were less saturated because they were prepared at optimal water content. Geotechnical characteristics and immobilization efficiency of composites from experiments in this study could thus be further improved if they would be prepared with higher water content than optimal determined according to [296]. Similar findings were also reported in literature [215], [362].

Volumetric stability of the composites is also an important issue, which can impact the parameters water permeability and compressive strength. Expansion, which can cause cracking and disintegration of the composites, was reported with the use of ladle slags [244] and paper ash [238]. However, these effects were not observed in composites with PA, LSH and LSA. This was despite the fact that periclase, which could cause expansion during transformation to brucite, was determined in LSA and LSH. Therefore lower immobilization efficiency and lower compressive strength of composites with LSA and LSH could not be related to expansive behaviour of ladle slags.

Despite the fact that the use of investigated composites in road construction is limited, their possible beneficial use could still be for less demanding structures that do not bear dynamic loadings. For example, successful use of composites from CS *in situ* for rehabilitation of degraded sites was already reported [231], [203], [384].

Chapter 6

Conclusions

Water scarcity is a global problem caused by multiple interconnected factors, among which global climate changes, overuse and contamination are the most persistent. European Union is also facing this problem, especially due to the increased occurrence of droughts. Therefore, there is interest in the European community to develop many diverse sustainable water treatment solutions, with a purpose of reusing municipal wastewater. Management of municipal wastewater, in areas with dispersed settlements, is currently based on SBWTPs, which purify water up to a quality suitable for release into nature. However, effluent water from SBWTP cannot be safely used for human needs. It still contains a relatively high and very variable concentration of pathogenic bacteria. As it was seen in this study, it can contain from a few 1000 to more than 1000,000 Coliform bacteria, or from less than 1000 to more than 300,000 *Escherichia coli*. Also, concentrations of toxic ammonia and nitrate are much higher than the limits for drinking water. Although, concentrations of PTE were usually lower than the limits for drinking water, peaks were observed, which could be caused by their release from households. A number of hazardous and persistent organic pollutants were determined in effluent water. Nanotechnology, more specifically nZVI, represents a possible solution for the development of effective and environmentally friendly water reuse. However, differences exist among available nZVIs, which originate from variations in synthesis. It was seen in this study that nZVI synthesized by reduction of Fe^{2+} with NaBH_4 have a higher reactivity, (originating from disordered microcrystalline structure and high specific surface area) compared to the commercially available nZVI. However, applicability of nZVI synthesized according to this procedure is limited due to a possible release of toxic B, which is incorporated in their structure, into water. The commercially available air stable nZVI (Nanofer STAR) were the least reactive and efficient, because they contained the smallest amount of reactive Fe^0 component. The most suitable for the water remediation were commercially available non-stabilised nZVI, Nanofer25 slurry, which were used in experiments for the optimization of dose, and operational parameters (mixing and settling time).

Thus, the first hypothesis of the water remediation study was confirmed. There is a difference between differently synthesised nZVI, which influence their potential applicability for water remediation. Therefore, the selection of the most appropriate nZVI is crucial for efficient remediation of the effluent water from the SBWTP.

Further research of remediation mechanisms and kinetics was the basis of optimization of the nanoremediation process. Rapid drop in disinfection efficiency was observed, when less than 0.25 g/L nZVI was applied. Disinfection efficiency increased with the extension of mixing time from 60 to 400 min. At longer mixing times regrowth of bacteria was observed, which was explained by gradual oxidation of nZVI to harmless

iron oxides. Mixing time also influenced adsorption/desorption of PTE at 0.1 g/L nZVI dose. Meanwhile, increased adsorption was observed for most of PTE (except for Cu, Sb and Se) at 0.5 g/L nZVI dose and mixing times longer than 240 min. The behavior of nitrogen species was very complex. Concentration of ammonia cation was slightly lowered, which was attributed to the adsorption and/or ammonia stripping effect. A small quantity of nitrate was transformed to nitrite, due to reduction at oxidation of Fe^{2+} .

The understanding of remediation mechanisms and kinetics of disinfection, PTE adsorption/desorption and changing of concentration of nitrogen species was crucial for the determination of the most optimal dose of nZVI (not less than 0.25 g/L) and mixing time (between 240 and 400 min). Therefore, the second hypothesis of the water nanoremediation study was confirmed.

The settling of iron particles after nanoremediation was less efficient in the case of nZVI dose <0.25 g/L. At higher doses agglomerates of iron particles were formed faster compared to lower nZVI doses, at which more efficient stabilization particles by organic matter occurred. The stabilization effect was also indicated by the fact that more nZVI remained unoxidised after nanoremediation, when doses 0.25 and 0.1 g/L were applied. Therefore, the third hypothesis of the water remediation study was partly rejected as oxidised iron particles can, only at doses of nZVI higher than 0.25 g/L, be efficiently removed from water by settling times longer than 600 min.

Nanoremediation was combined with the oxidation process by the use of NaDCC, due to multiple reasons. The dose of nZVI needed for efficient disinfection (>90%) was lowered from 0.5 to 0.25 g/L. Any possible nZVI remaining in suspension after nanoremediation can thus be oxidized. Oxidation was followed by filtration through zeolite column and activated carbon filter, to remove ammonia cation and organic pollutants, respectively. Optimised multistage remediation process was evidently successfully developed. Namely, it was proved that water according to drinking water quality standards can be produced from real effluent water from the SBWTP. Thus, the last hypothesis of the water remediation study was successfully confirmed.

The contamination of soil is a persistent problem in EU and worldwide. The EU has a tendency to develop a zero-land-degradation system, which includes the initiative to enhance land recycling. This means that rehabilitation of brownfields (or degraded sites) is preferred over the use of greenfields. However, the environmental problems related to management of contamination of soil, which is usually present at degraded sites, can prevent this process. This was in Slovenia most prominently seen in the case of the Old Zinc-works site (Celje), which was used as a case study in the present work. The analyses showed that metallurgical slags were the main carriers of contamination at the site. Contaminated soil, which contained high proportion of slag, was determined to be a hazardous waste according to Slovenian waste and landfilling policy. Among potentially toxic elements were the highest total and water soluble concentrations of Zn. Above inertness limits were also water-soluble concentrations of Cd, Pb and sulphate. The remediation of soil with the use of immobilization approach was selected as the most optimal based on multiple practical experiences. As a more sustainable alternative to the use of Portland cement, recycled materials (paper ash, fly ash from coal combustion, ladle slag from steelmaking processes and red mud from bauxite processing) were tested and compared as immobilization additives.

Paper ash and coal fly ash from VIPAP, ladle slag from ABS, which were delivered in a dry form, had high potential for the formation of new hydration products. On the other hand, coal fly ash from TE-TOL and ladle slag from Harsco were in contact with water before delivery and were prehydrated. Therefore they formed a substantially lower amount of new hydration products during experiments. Red mud from this study was

partly neutralised due to exposure at open depot and did not form any new mineral phases in contact with water. The first hypothesis of this study was only partly confirmed. Furtheron the results of this study showed that ashes (and partly ladle slag), which were used in a dry and not prehydrated form, also produced more hydration products in composites with contaminated soil. This was correlated with higher immobilization efficiency and better geotechnical properties. Therefore it was concluded that the hydraulic activity is a very important characteristic of the recycled materials, which are intended to be used for remediation of soil by immobilization.

The preliminary experiments, with the use of low doses of additives, have shown that pH is one of the most important parameters for PTE immobilization. Cationic metal elements Cd, Pb, Zn were far less mobile in alkaline environment, in which Mo oxyanion was mobilized. The preliminary experiments have also revealed that relatively high doses of recycled materials are needed to be used in composites for efficient immobilization. Therefore experimental composites were prepared with a mass ratio of additive 25% and compacted at optimum water content up to the maximum dry density.

The time dependent increase in immobilization efficiency for Zn and/or Pb in composites with paper ash, coal fly ashes and ladle slags was correlated with gradual time-dependent formation of new mineral phases due to pozzolanic and hydration reactions. Increased leachability of Mo was observed in all composites with the use of ashes and ladle slags, due to alkaline pH of additives. Paper ash proved to have the most beneficial characteristics from the scope of immobilization efficiency and development of basic geotechnical properties. Furtheron, the experimental data indicated that the substitution of a part of coal ashes, ladle slags and red mud with paper ash in ternary composites resulted in the formation of more reaction products of pozzolanic and hydration reactions. Consequently, immobilization efficiency was improved, as well as geotechnical characteristics in comparison to binary composites without paper ash.

In composite with the use of red mud the immobilization of PTE was driven by adsorption mechanisms. The adsorption of sulphate was limited in the composites with red mud. However, in the composite with a combination of red mud and paper ash immobilization efficiency for sulphate has increased due to the formation of low soluble sulphate incorporating minerals. Addition of paper ash has also enhanced basic geotechnical properties of the composite with the use of red mud.

Therefore, the second hypothesis of soil remediation study was confirmed. The combination of paper ash with other recycled materials can be beneficial for soil remediation by immobilization in geotechnical composites.

Investigation of immobilization efficiency in composites revealed that after 56 days of curing all composites, except those with the use of ladle slags, were inert. Nevertheless, care must be taken when using coal ashes, which showed a gradual drop in pH values. This indicated that their buffering capacity is low, which can limit their use because drop of pH can lead to a subsequent increase of leachability of PTE. On the other hand, potential increased leachability of Mo oxyanion can be problematic, due to the alkaline nature of the additives. This was especially evident in composites with the use of ladle slags. The final hypothesis of the soil remediation study was thus only partly confirmed because not all investigated composites were inert. However, limit values for inertness were only slightly exceeded. Further modification of receptures and optimization of geotechnical parameters is possible to obtain higher immobilization efficiency and better geotechnical properties of composites. Therefore all investigated composites from this study are potentially applicable, especially *in situ* for rehabilitation of degraded sites.

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Publications Related to the Thesis

Journal Articles

- Oprčkal, P., Mladenovič, A., Vidmar, J., Mauko Pranjič, A., Milačič, R., Ščančar, J. (2017). Critical evaluation of the use of different nanoscale zero-valent iron particles for the treatment of effluent water from a small biological wastewater treatment plant. *The chemical engineering journal*, 321, pp.: 20-30, doi: 10.1016/j.cej.2017.03.104.
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Conference Contributions

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Other Conference Contributions

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- Mladenovič, A., Oprčkal, P., Nadrah, P., Sever Škapin, A., Ščančar, J., Milačič, R., Vidmar, J., Mauko Pranjic, A. (2016). LIFE+ RusaLCA - an advanced water purification method with utilization of zero - valent iron nanoparticles. In: Godec, M. (Ed.), et al. Program and book of abstracts, 24th International Conference on Materials and Technology, 28th-30th September, 2016, Portorož, Slovenia, pp.: 165.
- Mladenovič, A., Oprčkal, P., Nadrah, P., Sever Škapin, A., Ščančar, J., Milačič, R., Vidmar, J., Mauko Pranjic, A. (2015). Life+ Rusalca - an innovative prototype system for the remediation of municipal waste water. In: Godec, M. (Ed.), et al. Program and book of abstracts, 23rd International Conference on Materials and Technology, 28th-30th September, 2015, Portorož, Slovenia, pp.: 175.
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- Mauko Pranjic, A., Mladenovič, A., Turk, J., Šajna, A., Zalar Serjun, V., Oprčkal, P., Bras, V. (2016). Krožno gospodarstvo in vrednotenje okoljskih odtisov ("*Circular economy and evaluation of environmental impacts*") LCA delavnica Vrednotenje procesov, novih rešitev in produktov z vidika okoljskih učinkov, Ljubljana, 27th Oktober, 2016, Ljubljana, Slovenia.
- Mladenovič, A., Milačič, R., Ščančar, J., Sever Škapin, A., Nadrah, P., Mauko Pranjic, A., Oprčkal, P. (2016). LIFE RusaLCA (LIFE 12 ENV/SI/000443) Nanoremediation of water from small waste water treatment plants and reuse of water and solid remains for local needs: LIFE water platform meeting Water works - overcoming challenges to achievin good water status in urban areas, 24th-25th May, 2016, Manchester, UK. Manchester, UK.

Invited Lectures

- Mladenovič, A., Oprčkal, P. (2017). In-situ remedian of soil contaminated by past industrial activities: Dubrovnik International ESEE Mining School - DIM ESSE 2017 "Zero waste management", EIT RawMaterials, 19th November, 2017.
- Mladenovič, A., Oprčkal, P. (2017). Nano-remediation of water from small wastewater treatment plants: Dubrovnik International ESEE Mining School - DIM ESSE 2017 "Zero waste management", EIT RawMaterials, 24th November, 2017.
- Mladenovič, A., Oprčkal, P. (2017). Remediacija onesnaženih zemljin ("*Remediation of contaminated soils*"): Okoljski dan gospodarstva - Po sledeh nevarnih snovi, Ljubljana, 1st June, 2017.
- Mladenovič, A., Oprčkal, P., Milačič, R., Ščančar, J., Vidmar, J., Sever Škapin, A., Nadrah, P., Mauko Pranjic, A., Ivanušič, M. (2016). Nanoremediacija vode iz male čistilne naprave za ponovno uporabo in izzivi z vidika mikroonesnaževal ("*Nanoremediation of water from the small wastewater treatment plant for its reuse from the scope of micropollutant issue*"). In: Zupančič Justin, M., (Ed.): Pharmacologically active substances in wastewater: optimisation of analytical methods and removal processes: proceedings of the conference, Closure conference of the project LIFE PharmDegrade, Pharmacologically active compounds in wastewater: optimization

of analytical methods and removal processes, Ljubljana, 24th-25th November, 2016. Ljubljana, Slovenia, pp.: 84-87.

Prepared or Submitted and not yet Published Works

- Oprčkal, P., Mladenovič, A., Ašler, A., Zupančič, N., Ščančar, J., Milačič, R., Nikolič, I., Zalar Serjun, V., (manuscript). Valorisation of red mud and paper ash for sustainable remediation of contaminated soil with immobilization approach. *Prepared for submission in Journal of Environmental Management (March, 2018)*.
- Vidmar, J., Oprčkal, P., Milačič, R., Mladenovič, A., Ščančar, J., (submitted article). Investigation of the behavior of zero-valent iron nanoparticles and their interactions with Cd^{2+} in wastewater by single particle ICP-MS. *Under review in The Science of the Total Environment, (March, 2018)*.
- Mauko Pranjič, A., Oprčkal, P., Mladenovič, A., Zapušek, P., Urleb, M., Turk, J., (submitted article). Comparative life cycle assessment of possible methods for the treatment of contaminated soil at an environmentally degraded site. *Under review in Journal of Environmental Management (March, 2018)*.
- Mladenovič, A., Oprčkal, P., Milačič, R., Ščančar, J., Vidmar, J., Sever, Škapin, A., Nadrah, P., Mauko Pranjič, A., Šprinzer, M., (submitted patent). A remediation device and a process for the remediation of water from small biological wastewater treatment plants. *Under review and examination at the World Intellectual Property Organization (March, 2018)*.

Biography

Education

- 2007: Matura exam
- 2007: enrolled at the Faculty of Natural Sciences and Engineering, University of Ljubljana, program Geology
- 2013: Graduated at the Faculty of Natural Sciences and Engineering, University of Ljubljana, program Geology
- 2013: Enrolment in Jožef Stefan International Postgraduate School, program Ecotechnology

Employment:

- 2011-2012: Internship and student work at Geological Survey of Slovenia
- 2013: Internship and student work at Slovenian National Building and Civil Engineering Institute, Department of Materials, Laboratory for Stone, Aggregate and Recycled materials
- 2013-2018: Young Researcher at Slovenian National Building and Civil Engineering Institute, Department of Materials, Laboratory for Stone, Aggregate and Recycled materials

Project work:

- Program P2-0273 (Andraž Legat): Bulding structures and materials
- LIFE12 ENV/SI/000443 (Ana Mladenovič): Nanoremediation of water from small waste water treatment plants and reuse of water and solid remains for local needs
- L7-6747 (Ana Mladenovič): In-situ remediation of polluted ground in the area of the Old Zinc-Works at Celje
- V1-1649 (Ana Mladenovič): In situ immobilization of contaminated soil using innovative nanotechnology, for processing and use as urban soils