Immobilization of heavy metals, selenate, and sulfate from a hazardous industrial side stream by using calcium sulfoaluminate-belite cement

Katri Piekkari a, Katja Ohenoja a, Visa Isteri b, Pekka Tanskanen b, Mirja Illikainen a, *

a Fibre and Particle Engineering Research Unit, University of Oulu, Pentti Kaiteran katu 1, 90014, Oulu, Finland
b Process Metallurgy Research Unit, University of Oulu, Pentti Kaiteran katu 1, 90014, Oulu, Finland

Article info

Article history:
Received 2 October 2019
Received in revised form 7 February 2020
Accepted 11 February 2020
Available online 18 February 2020
Handling editor; M.T. Moreira

Keywords:
Stabilization/solidification
Encapsulation
Immobilization
Hazardous waste
Leaching

Abstract

Release of heavy metals from different industries and industrial waste is a major global threat for as well humans as ecosystems. In this study, immobilization of an industrial filter sludge (FS) with an extremely high content of several heavy metals (24.6 wt% Pb, 21.7 wt% Hg, and 9.00 wt% Se) and sulfate via calcium sulfoaluminate-belite (CSAB) cement was tested. The ratios of 25%, 50% and 75% of CSAB addition were tested, and the target was to achieve immobilization of the hazardous components. The leaching of Pb, Hg, SeO4 2-, SO4 2-, Ni, Cd, Cu, and As was monitored, and the structure of the immobilized materials was examined via X-ray powder diffraction (XRD) and field emission scanning electron microscopy-energy dispersive spectroscopy (FESEM-EDS) analysis. It was observed that Hg, Cu, As, Cd, and Ni were immobilized completely and leaching of Pb was reduced by 69% from the theoretical release. On the other hand, the leaching of SeO4 2- and SO4 2- experienced major increase when CSAB was added. XRD indicated significant ettringite formation as the amount of added CSAB increased, and the formation of gypsum as the amount was decreased. FESEM-EDS indicated that the immobilization was largely based on encapsulation into the CSAB binder, but chemical immobilization into the ettringite binder was also observed. It was concluded that the increased release of SO4 2- and SeO4 2- might have resulted from an excess amount of sulfates (added gypsum) during hydration.

© 2020 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).

1. Introduction

Various industrial processes generate hazardous, heavy metals containing waste materials that need to be treated before their disposal. Different methods are used for this purpose, and their ability to immobilize components varies based on the chemistry and conditions of the treated material. Since heavy metals are harmful as elements, they cannot be decomposed or destroyed chemically. Therefore, the only viable solutions are to either remove the hazardous components or immobilize them into some insoluble component or structure via, for example, stabilization/solidification, adsorption, ion exchange, or encapsulation (Berardi et al., 1998). Stabilization/solidification with cement or hardening mineral phases is widely studied and is considered a promising path for immobilization of waste that contains heavy metals (Chen et al., 2009).

Stabilization/solidification methods are based on immobilizing the hazardous components into a solid matrix. Solidification refers to physically enclosing the contaminants into a solid with low permeability, while stabilization indicates a chemical reaction that binds the contaminants to the matrix (Wang et al., 2012). The main advantages of the method are relatively low cost due to widely available reagents, simplicity, being available for both in situ and ex situ applications, and wide compatibility with different types of waste (Derakhshan Nejad et al., 2018). For example, the method is suitable for immobilizing radioactive materials (Szajerski et al., 2019). Sometimes it is also possible to utilize the immobilized materials and therefore recycle the hazardous waste (Wang et al., 2019a). On the other hand, the contaminants remain in the solidified material, and the longevity of the solids still needs more research (Derakhshan Nejad et al., 2018).

OPC is a typical binder to be used in stabilization/solidification
of heavy metal containing materials (Chen et al., 2009), but due to the high carbon footprint of OPC there is an urge to develop more sustainable cement mixtures (Chen et al., 2019; Wang et al., 2018). Also methods for OPC-free stabilization/solidification are developed, for instance using alkali-activated binders (Ji and Pei, 2019; Wang et al., 2019b), and preparing inert ceramic materials from hazardous waste (Karayannis et al., 2017). The immobilization of the heavy metals in stabilization/solidification is typically based on several concurrent processes, such as physical encapsulation, adsorption, chemical bonding and ion substitution into the chemical structure of the binder (Chen et al., 2009; Guo et al., 2017; Ji and Pei, 2019), and it is therefore common for the immobilization to be based on more than one method (e.g. (Xia et al., 2019)).

One of the mineral phases that is able to immobilize hazardous cations and anions is ettringite. Ettringite ($\text{Ca}_6\text{Al}_2\text{(SO}_4)_3\text{(OH)}_2\text{H}_2\text{O}$) is a natural mineral that also appears in ordinary Portland cement (OPC) concrete as a common hydration product and is known to immobilize some metal cations and oxyanions inside its molecular structure (Chen et al., 2009). Ettringite consists of pillars of Al and Ca bridged by O and OH units, coated in a layer of bound OH and H2O and connected by SO4 and H2O molecules between the pillars, binding the columns together with hydrogen bonds into needle shaped crystals (Guo et al., 2017). Ettringite formation and stability require high pH conditions (Chrysochoou and Dermatas, 2006).

The ability of ettringite to immobilize ions is based on the mineral being an effective ion exchanger (Chen et al., 2009). Calcium and aluminum cations ($\text{Ca}^{2+}$ and $\text{Al}^{3+}$, respectively) and sulfate anions ($\text{SO}_4^{2-}$) can be substituted in the matrix with a wide variety of cations and oxyanions of similar ionic charge (Fig. 1) (Chen et al., 2009). Several studies have tested the immobilization of hazardous components, for example, heavy metal cations, such as $\text{Cr}^{3+}$, $\text{Pb}^{2+}$, $\text{Cu}^{2+}$, and $\text{Zn}^{2+}$ (Niu et al., 2019, 2018; Wu et al., 2012), and various oxyanions, such as $\text{SeO}_4^{2-}$, $\text{CrO}_4^{2-}$, $\text{AsO}_4^{3-}$, and $\text{MoO}_4^{2-}$ (Guo et al., 2017; Kiventera et al., 2019; Zhang and Reardon, 2003) into the ettringite structure with encouraging results. Two methods are used to incorporate heavy metals and sulfate into ettringite: encapsulating a solid material with an ettringite binder (e.g., (Albino et al., 1996; Peysson et al., 2005)), and precipitating ettringite in contaminated water (e.g., (Tolonen et al., 2016; Zhang and Reardon, 2003)).

Oxyanions are usually at their most soluble in a high pH, and therefore ettringite, which forms in high pH, is especially suitable for oxyanion immobilization (Chrysochoou and Dermatas, 2006). On the other hand, the immobilization mechanism of the anions is based on hydrogen bonds, while the metal cations are covalently bound to the solid crystalline matrix; therefore, the immobilization of oxyanions into the ettringite structure is not as strong as the immobilization of cationic components (Chrysochoou and Dermatas, 2006).

One source of solid ettringite is calcium sulfoaluminate-belite (CSAB) cement, which is widely studied as an alternative to OPC, and has ettringite as its main hydration product (Jüenger et al., 2011). CSAB production causes approximately 25–35% lower CO2 emissions compared to OPC (Hanein et al., 2018; Scrivener et al., 2018). The main components of CSAB cement are commonly ye’elimite (calcium sulfoaluminate), belite, ferrite, and anhydrite or gypsum which is added before hydration (Glasser and Zhang, 2001). The research related to waste encapsulation with CSAB and calcium sulfoaluminate (CSA) binders has focused on municipal solid waste incineration ashes rich in Pb (1.326 ppm, 0.42 wt%, 1.42 wt% PbO) and Zn (3.841 ppm, 1.17 wt%, 2.19 wt% ZnO) (Qian et al., 2008; Sun et al., 2012; Wei et al., 2011) and galvanic sludge containing a high content of Pb (112 ppm) (Luz et al., 2006) or $\text{Cr}_2\text{O}_3$ (10.05%), $\text{Ni}_0$ (1.50%), and $\text{Cd}_0$ (0.06%) (Cioffi et al., 2002). Research has also been made with arsenic rich sulfate mine tailings (Kiventera et al., 2019). In the studies presented above, the waste materials were effectively stabilized. However, the content of hazardous components was relatively low. This is the first time a solid material with extremely high content of multiple hazardous components (more than 60%) was stabilized with CSAB cement, and the heavy metal immobilization capacity of the CSAB solidification was studied.

This study targets the immobilization of a highly hazardous filter sludge from a sulfuric acid factory at a nickel and copper smelter that contains extremely high amounts of $\text{Pb}$, $\text{Hg}$, $\text{Se}$, and $\text{SO}_4$. Currently, the studied residue goes through chemical stabilization via precipitation and is ultimately stored in a pond. In this study, an alternative immobilization method via ettringite stabilization was investigated in order to develop an improved immobilization method for the residue. The residue was mixed with CSAB clinker and gypsum, and the resulting hydrated material was studied with leaching tests and structural analysis: X-ray powder diffraction (XRD) and field emission scanning electron microscopy-energy dispersive spectroscopy (FESEM-EDS). In order to get a reference for the level of hazard of the leaching components, the measured leaching rates were compared to the Finnish environmental regulations for landfilled materials (FINLEX ® 331, 2013).

2. Materials and methods

2.1. Material to be immobilized

The material that was studied was an industrial filter sludge (FS) from sulfuric acid production by a nickel and copper smelter. The FS sludge was collected before the chemical stabilization process, so it contained very high ratios of heavy metals (Table 1). The main components were detected with XRF for pressed pellets (Omnian Panalytical AXIOS, Malvern Panalytical, Malvern, UK), and inductively coupled plasma optical emission spectrometry (ICP-OES) (Thermo Electron IRIS Intrepid II XDL Duo; Thermo Scientific, Waltham, MA, USA) was used to analyze the numerous trace components. Table 1 presents only the main components, measured by XRF, and the minor components, measured by ICP, with leaching rates exceeding the Finnish environmental regulations for landfilled materials (FINLEX ® 331, 2013).

The FS sample had fine particle size distribution: 99.6% of FS particles were below 20 μm, and median particle size $d_{50}$ was 1.17 μm. The main crystalline phases detected with XRD were anglesite ($\text{PbSO}_4$), mercury selenide bromide ($\text{Hg}_2\text{Se}_2\text{Br}_3$), and nickel iron oxide ($\text{Fe}_1\text{Ni}_{1.25}\text{O}_4$).

FS was tested with a leaching test following the Finnish Standard Association’s European Standard SFS-EN 12457-2, and the results were compared to the Finnish environmental regulations for landfilled materials (Table 1). An end-over-end tumbler (Retsch, Haan, Germany) was used with 10 rpm rotation speed. It was observed that the leaching of many hazardous components exceeded the legal limits. The most hazardous components were As, Cd, Cu, Ni, Pb, and Se, which showed leaching rates above the

![Fig. 1. Examples of possible substituting ions in the ettringite structure (Chen et al., 2009; Guo et al., 2017).](image-url)
maximum value allowed for landfilled hazardous waste.

2.2. CSAB clinker preparation

The CSAB clinker was synthesized from reagent grade chemicals; aluminum oxide (Al₂O₃), silicon oxide (SiO₂), iron(III) oxide (Fe₂O₃), calcium sulfate (CaSO₄) and calcium oxide (CaO). All the chemicals were provided by Alfa Aesar (Haverhill, MA, USA). The amounts of the different oxide phases used in the synthesis and the resulting composition of the target phases, namely, ye’elimite (Ca₄Al₆O₁₂(SO₄)), belite (Ca₂SiO₄), brownmillerite or srebrodolskite (Ca₂(Al,Fe₂)₂O₅), anhydrite (CaSO₄), and calcium oxide (CaO) are listed in Table 2.

Before measuring the components, CaO was calcined at 800 °C for 4 h to ensure it did not contain any remnant moisture. The components were mixed and ground together with a mortar and pestle, and the fine mixture was placed in cylindrical corundum crucibles. The material was compressed in the crucible by hand before placing the crucible in a Nabertherm GmbH (Lilienthal, Germany) chamber furnace at 800 °C. The furnace was then heated to 1300 °C at a rate of 10 °C/min, and held at that temperature for 4 h. Then, the crucible was taken out of the furnace and cooled down rapidly by placing it on a copper table with water circulation. The cooled clinker was stored in a desiccator. More details about CSAB cement preparation can be found from (Isteri et al., 2020).

Finally, the clinker was crushed with a hammer and ground into fine powder with a TPR-D jar mill (Germatec, Ransbach-Baumbach, Germany). A stainless steel jar with a 10 L volume and 250 mm diameter was used with 180 stainless steel balls (d = 30 mm), and 2-propanol was added to prevent agglomeration. The grinding time for the clinker was 60 min on average. The XRD graph for the completed clinker is presented in Fig. 2 and a FESEM image in Fig. 3.

2.3. pH dependence of leaching of different components from FS

Table 1
Component contents, initial leaching rates, and waste ratings for each component based on the Finnish regulation for landfilled waste (FINLEX ® 331, 2013). The main components of FS, and the minor components with excess leaching are listed.

| Component | Component content in FS (wt%) | Analysis method | Leaching rate (mg/kg) | Legislative limit values (mg/kg) | Waste rating for component |
|-----------|-------------------------------|-----------------|----------------------|----------------------------------|---------------------------|
|           |                               |                 | Sw⁰                | Rw⁰                             | Hw⁰                       |
| Pb        | 24.6                          | XRF             | 51.52              | 0.5                             | 10                        | 50                        | > hazardous               |
| Hg        | 21.7                          | XRF             | 0.45               | 0.01                            | 0.2                       | 2                         | hazardous                 |
| O         | 21.3                          | XRF             | 23.56              | 1,000 (SO₄)                     | 0.5                       | 7                         | > hazardous               |
| Se        | 9.00                          | XRF             | 4,293.23 (SO₄)     | 20,000 (SO₄)                    | 50,000 (SO₄)              | regular                   |
| S         | 6.84                          | XRF             | 449.29             | 0.4                             | 40                        | > hazardous               |
| Br        | 3.25                          | XRF             | 148.77             | 2                               | 50                        | 100                       | > hazardous               |
| Ni        | 0.153                         | ICP             | 224.65             | 0.5                             | 2                         | 25                        | > hazardous               |
| Cd        | 0.017                         | ICP             | 14.28              | 0.04                            | 1                         | 5                         | > hazardous               |

Table 2
The oxide phase composition of the synthesized material and the crystalline composition of the CSAB product. The other phases contain mayenite, calcio-olivine and silicon oxide.

| Oxide phase composition |
|-------------------------|
| Phase [wt%]             | CaO | Al₂O₃ | SiO₂ | Fe₂O₃ | SO₄ |
|                         | 48.0 | 19.6  | 12.2 | 10.5  | 8.4 |

| Crystalline phase composition |
|-----------------------------|
| Phase [wt%]                 | Ye’elimite | Belite | Brownmillerite | Anhydrite | Other |
|                            | 36.5       | 34.8   | 19.8           | 6.8       | 2.1   |
to gain an understanding about the behavior of the different components in varying conditions, further leaching tests were executed in different pH values.

The standard SFS-EN 12457-2 was modified for solutions of different pH, namely, 2, 4, 10, and 13. The test was conducted with 10 g of solid and the L/S ratio of 10, and a shaker mixer (KS 260 basic, IKA, Staufen, Germany) was used. The pH of the solutions was set with HNO₃ and NaOH before introducing FS into the solution. The solution pH was not adjusted after adding FS or during the leaching. After 24 h of leaching, the solution was filtered with 0.45 μm filter paper, and the pH of the collected filtrate solution was measured with a pH meter (Model 50; Denver Instruments Co., Arvada, CO, USA) and electrode (Blueline 11 pH; SI Analytics, Mainz, Germany). The leached components were measured with ICP-OES with the exception of Hg and SO₄²⁻, which were determined via cold vapor atomic absorption spectroscopy (CVAAS) and ion chromatography (IC) respectively.

2.4. Immobilization of samples with CSAB

Three samples were prepared by mixing FS with CSAB clinker containing 15 wt% of added reagent grade gypsum (VWR, Radnor, PA, USA). The used mixing ratios were 25% (C25), 50% (C50), and 75% (C75) of clinker from the total mass of the solids. The liquid to solid (L/S) ratio of all mixtures was 0.4. The solids were first mixed thoroughly together for 3 min with a high speed stirrer (Eurostar 20 high speed digital; IKA, Staufen, Germany), water was then added, and the paste was stirred for another 3 min. A speed of 500 rpm was used for both mixings. The mixing was monitored to ensure that none of the solid stuck to the mixing equipment. The paste was molded and kept inside plastic bags at room temperature for 24 h before unmolding. The unmolded samples were then stored inside plastic bags at room temperature.

2.5. Leaching tests and applied analysis methods for the hardened samples

Leaching tests conducted in accordance with modified standard SFS-EN 12457-2 were applied to define the stability of the hazardous components in the immobilized samples, and the results were compared to the leaching of untreated FS. For the leaching test, the prisms were crushed and sieved to <2 mm size. The ICP-OES analysis method was used for the leached components. The microstructure of the hardened samples was analyzed via XRD and FESEM-EDS analysis. The XRD was executed with a SmartLab analyzer (Rigaku, Tokyo, Japan), the Cu K-β filter, and the following parameters: scan speed of 4°/min, step width of 0.02°, and scan range of 5°–120°. Internal standard was used by adding 20 wt% of rutile (TiO₂) and the quantitative amounts of the detected phases were calculated by using Rietveld refinement. The crystalline structures were identified by comparing the diffraction patterns to the International Center for Diffraction Data (ICDD) database.

The FESEM-EDS was prepared by casting crushed samples in epoxy and polishing the sample surface with ethanol, without exposing the samples to water in any part of the process. By avoiding water contact, it was ensured that the wanted components would not leach out from the surface. The imaging device was the ZEISS Ultra Plus (Oberkochen, Germany).

3. Results and discussion

3.1. Leaching of harmful components from FS in different pH conditions

Leaching of the different components was highly dependent on the solution pH, and this was also seen for the FS. Most components lost their solubility in high pH, but Pb, Se, and SO₄ reached their maximum values there (see Table 3). It is typical that oxyanions, such as sulfate and selenate, have a high solubility in high pH conditions (Chrysochoou and Dermatas, 2006). The leaching of lead could be a result of it appearing as anglesite (see 2.1.), which is known to have low solubility acidic conditions, but to be soluble at high pH (Keim and Markl, 2015; Rumble, 2019). It was also found that the introduction of FS drastically reduced the pH of the analyzed solutions. The pH was most probably decreased by the high sulfate content of FS, which would react with water to form sulfuric acid. Only the most alkaline solution was able to maintain its high pH. Therefore, all of the measurements, except pH 13, and the data gathered from them actually represented highly acidic conditions. This was in line with the observation that the leaching rates of most of the components differed vastly for pH 13 compared to the experiments in the lower pH conditions. The only exception was As, which had a major change in leaching rate between the pH 2 and pH 4 samples.

3.2. The effect of CSAB content on the stability of immobilized samples

After the leaching tests for stabilized samples C25, C50, and C75, it was observed that the pH of the solutions had again changed during the leaching test (FS: pH 2.38; C25: pH 6.87; C50: pH 9.3; C75: pH 10.0). Due to the acidic nature of FS and the alkaline nature of the CSAB binder, the pH of the solution increased as more clinker was added, reaching alkaline conditions when the cement content

| pH  | Meas. pH | 2.0  | 4.0  | 10.0 | 13.0 |
|-----|----------|------|------|------|------|
| As  | mg/kg    | 128  | 57.7 | 58.9 | 38.3 |
| Cd  | mg/kg    | 16.1 | 15.3 | 17.3 | 0.03 |
| Cu  | mg/kg    | 265  | 234  | 259  | 0.15 |
| Ni  | mg/kg    | 1,440| 1,380| 1,590| 0.32 |
| Pb  | mg/kg    | 62.6 | 43.6 | 44.9 | 17,700|
| Se  | mg/kg    | 11.6 | 8.4  | 9.4  | 2,270|
| Hg  | mg/kg    | 0.037| 0.011| 0.009| <0.01|
| SO₄ | mg/kg    | 5,450| 5,030| 5,480| 106,000|
was 50% or 75%.

The stabilized samples showed a significant decrease in the leaching of the most hazardous components as CSAB binder was added, but for sulfate and selenate, the leaching was enhanced as the portion of binder increased in the mixture (Fig. 4). Fig. 4 compares the measured leaching of the most hazardous components from the immobilized samples with theoretical values that would apply in case the clinker would only dilute FS without having any effect on the immobilization of the components.

The results suggest that the cationic metals Pb, Cu, and Hg were immobilized, as well into the formed binder structure. Since their leaching rates were low for all immobilized samples with highly varying pH values, the immobilization was probably not only a matter of pH.

The increase of sulfate and selenate leaching could have been the result of the increasing pH of the material. Furthermore, since both FS and the binder mixture had high sulfate contents, it was possible that the system simply had excess oxyanions. When ettringite is formed in a system that contains both sulfate and selenate, sulfate is preferred in the reaction, leaving selenate out of the matrix (Chrysochoou and Dermatas, 2006). Since the sulfates from the added gypsum would have taken the available places in the formed ettringite phase, there would not have been room left for the sulfates and selenates from the FS.

As mentioned in section 1, oxyanions do not bind as strongly to the ettringite matrix as the metallic cations (Chrysochoou and Dermatas, 2006). This is because the oxyanions only bind to the liquid between the crystalline columns, thus binding to the matrix via weaker hydrogen bonds. Furthermore, according to previous studies, the molar amount of selenate that ettringite can immobilize is not equal to the molar amount of the replaced sulfate (Chrysochoou and Dermatas, 2006). The resulting missing negative charge is balanced by extra hydroxyls.

3.3. Microstructure of stabilized samples

The molecular structure of the samples was defined with two different methods, XRD and FESEM-EDS. The methods were used together and the results were compared in order to gain a general understanding of the crystalline phases present in the samples. FESEM-EDS was also used for observing the location of the immobilized heavy metals in the FS containing samples.

3.3.1. XRD

The XRD graphs (Fig. 5) and crystalline phase compositions defined with the internal standard (Fig. 6) clearly show the formation of ettringite as the amount of CSAB clinker was increased: ettringite did not appear in sample C25, where CSAB content was...
low, but was abundant in samples C50 and C75. Even if the ettringite content increased, the leaching of SO$_4$ and SeO$_4$ increased (Fig. 4). This indicates that these anionic contaminants did not incorporate into the ettringite structure.

Another clear trend was that the amount of gypsum increased with the amount of FS, even though the FS contained no gypsum. Therefore, it can be concluded that the gypsum must be formed during the hydration process. After all, the ideal pH for ettringite formation is highly alkaline, and therefore the presence of the highly acidic FS might cause the reaction conditions to become unsuitable for efficient ettringite formation when the amount of FS is high. As a result, the observed immobilization mechanism of the hazardous components was not only immobilization into the ettringite structure, but also another mechanism, such as encapsulation, was involved.

3.3.2. FESEM-EDS

FESEM-EDS analysis revealed that the heavy metals had mainly not integrated into the ettringite structure; they remained as separate granules inside the binder matrix (Fig. 7). The granules contained, however, higher amounts of elements of CSAB components than the FS composition would imply. Therefore, there might also have been some kind of hydrated binder phases inside the FS granules. The observation is in line with the general reduction of leaching of the cationic contaminants (Fig. 4). Furthermore, the granules were

---

Fig. 4. (continued)

Fig. 5. XRD graphs and identified phases for all samples. Notice that the immobilized samples were analyzed with internal standard (20% rutile), while FS was not. Abbreviations for the phases: R – rutile, G – gypsum, E – ettringite, S – srebrodolskite, A – anglesite, N – Fe$_{1.85}$Ni$_{1.25}$O$_4$, M – Hg$_3$Se$_2$Br$_2$. 

---

K. Piekkari et al. / Journal of Cleaner Production 258 (2020) 120560
significantly larger than the medium FS particle size before immobilization, which might indicate that the granules formed clusters together. It was also observed that belite and srebrodolskite were left partially unreacted inside the hydrated sample.

The images also clearly show the increasing amount of FS and gypsum, and the decrease of binder phases in the sample structure as the proportion of FS is increased. In sample C75, areas can be seen where the CSAB and FS components are mixed together in one phase of unknown structure. This mixed phase is most probably partially substituted ettringite that contains immobilized components of FS. The main contaminant that was observed in the binder phase is Pb, which together with the reducing leaching of the component (Fig. 4.) shows that Pb was partially immobilized into the binder matrix.

4. Conclusions

The tested method appeared to be promising for immobilization of cationic heavy metals from the studied FS, and it was able to reduce their observed leaching drastically, even with the lowest contents of added CSAB. On the other hand, immobilization of sulfate and selenate was not successful due to the high sulfate content of FS and the added gypsum preventing integration into ettringite. Therefore, in further development of this method, the amount of sulfates in the mixture should be reduced. The most obvious way to do this is to decrease the amount of gypsum in the hydrating mixture.

It was observed that, when the proportion of FS was high, the binder could not form a uniform ettringite structure. Therefore, the proportion of FS should be kept low, maybe even lower than the 25% that was used in this experiment, in order to ensure favorable conditions for ettringite formation.

The FESEM results suggest that the heavy metals primarily remain concentrated in granules instead of incorporating into the binder matrix. Therefore, the good immobilization results of cationic heavy metals may be explained with the components also encapsulating inside the binder when the ettringite content of the binding matrix is low.

Research significance

Calcium sulfoaluminate-belite (CSAB) cement is a promising and interesting low CO₂ alternative for Ordinary Portland cement. The main hydration phase of CSAB cement is ettringite which has shown good hazardous element immobilization capacity. This is the first time when CSAB cement was used for immobilizing waste material with extremely high content of heavy metals (24.6 wt% Pb, 21.7 wt% Hg, and 9.00 wt% Se) and sulfate.
the application in heavy metal immobilization: a review. J. Environ. Manag. 231, 256–267. https://doi.org/10.1016/j.jenvman.2018.10.041.

Junger, M.C., Winnefeld, F., Provis, J.L., Decker, J.H., 2011. Advances in alternative cementitious binders. Cement Conc. Res. 41, 1232–1243. https://doi.org/10.1016/j.cemconres.2010.11.012.

Karayannis, V.G., Karapanagioti, H.K., Domopoulou, A.E., Komilis, D.P., 2017. Stabilization/solidification of hazardous materials from solid wastes into ceramics. Waste Biomass Valorization 8, 1863–1874. https://doi.org/10.1007/s12649-016-9713-z.

Kein, M.F., Markl, G., 2015. Weathering of galena: mineralogical processes, hydrochemical fluid path modeling, and assessment of the growth rate of pyromorphite. Am. Mineral. 100, 1584–1594. https://doi.org/10.2138/am-2015-5183.

Kiventera, J., Piekari, K., Isteri, V., Ohenoja, K., Tanskanen, P., Ililainen, M., 2019. Solidification/stabilization of gold mine tailings using calcium sulfoaluminate– belite cement. J. Clean. Prod. 239, 118008. https://doi.org/10.1016/j.jclepro.2019.118008.

Luz, C., Rocha, J., Cheriaf, M., Pera, J., 2006. Use of sulfoaluminate cement and bottom ash in the solidification/stabilization of galvanic sludge. J. Hazard Mater. 136, 837–845. https://doi.org/10.1016/j.jhazmat.2006.01.020.

Niu, M., Li, G., Wang, Y., Cao, L., Han, L., Li, Q., Song, Z., 2019. Immobilization of Pb2⁺ and Cd³⁺ using bentonite–sulfoaluminate cement composites. Construct. Build. Mater. 225, 868–878. https://doi.org/10.1016/j.conbuildmat.2019.06.184.

Niu, M., Li, G., Wang, Y., Li, Q., Han, L., Song, Z., 2018. Comparative study of immobilization and mechanical properties of sulfoaluminate cement and ordinary Portland cement with different heavy metals. Construct. Build. Mater. 193, 322–332. https://doi.org/10.1016/j.conbuildmat.2018.10.206.

Peyssson, S., Péra, J., Chabanne, M., 2005. Immobilization of heavy metals by calcium sulfoaluminate cement. Cement Conc. Res. 35, 2261–2270. https://doi.org/10.1016/j.cemconres.2005.03.015.

Qian, G.R., Shi, J., Cao, Y.L., Xu, Y.F., Chui, P.C., 2008. Properties of MSW fly ash–calcium sulfoaluminate cement matrix and stabilization/solidification on heavy metals. J. Hazard Mater. 152, 196–203. https://doi.org/10.1016/j.jhazmat.2007.06.118.

Rumble,J.R., 2019. Physical constants of inorganic compounds. In: CRC Handbook of Chemistry and Physics. CRC Press/Taylor & Francis, Boca Raton, FL.

Scriveren, K.L., John, V.M., Gartner, E.M., 2018. Eco-efficient cements: potential economically viable solutions for a low-CO2 cement-based materials industry. Cement Conc. Res. 114, 2–26. https://doi.org/10.1016/j.cemconres.2018.03.015.

Sun, Q.N., Li, J.M., Huo, B.Q., Wang, J.R., 2012. Application of sulfoaluminate cement for solidification/stabilization of fly ash from municipal solid waste incinerators. Appl. Mech. Mater. 178–181, 793–798. https://doi.org/10.4028/www.sciencedirect.net.

Szajerski, P., Bobogowicz, A., Bern, H., Gasiorowski, A., 2019. Quantitative evaluation and leaching behavior of cobalt immobilized in sulfur polymer concrete composites based on lignite fly ash, slag and phosphogypsum. J. Clean. Prod. 222, 90–102. https://doi.org/10.1016/j.jclepro.2019.03.010.

Tolonen, E.T., Hu, T., Ramo, J., Lassi, U., 2016. The removal of sulphate from mine water by precipitation as ettringite and the utilisation of the precipitate as a sorbent for arsenate removal. J. Environ. Manag. 181, 856–862. https://doi.org/10.1016/j.jenvman.2016.06.053.

Wang, J., Feng, X., Anderson, C.W.N., Xing, Y., Shang, L., 2012. Remediation of mercury contaminated sites—a review. J. Hazard Mater. 221–222, 1–18. https://doi.org/10.1016/j.jhazmat.2012.03.035.

Wang, L., Chen, L., Tsaing, D.C.W., Kwa, H.W., Yang, J., Ok, Y.S., Ding, S., Hou, D., Poon, C.S., 2015a. The roles of biochar as green admixture for sediment-based construction products. Cement Conc. Compos. 104, 103348. https://doi.org/10.1016/j.cemconcomp.2018.10.034.

Wang, L., Cho, D.-W., Tsaing, D.C.W., Cao, X., Hou, D., Shen, Z., Alesis, D.S., Ok, Y.S., Poon, C.S., 2019b. Green remediation of as and Pb contaminated soil using cement-free clay-based stabilization/solidification. Environ. Int. 126, 336–345. https://doi.org/10.1016/j.envint.2019.02.057.

Wang, L., Yu, K., Li, J.-S., Tsaing, D.C.W., Poon, C.S., Yoo, J.-C., Baek, K., Ding, S., Hou, D., Dai, J.-G., 2018. Low-carbon and low-alkalinity stabilization/solidification of Pb-contaminated soil. Chem. Eng. J. 351, 418–427. https://doi.org/10.1016/j.cej.2018.06.118.

Wei, G.X., Liu, H.Q., Zhang, S.G., 2011. Using of different type cement in solidification/stabilization of MSWI fly ash. Adv. Mater. Res. 291–294, 1870–1874. https://doi.org/10.4028/www.scientific.net/AMR.291-294.1870.

Wu, B., Li, X., Ma, B., Zhang, M., 2012. Solidification of heavy metals in ettringite and its stability research. In: Presented at the Second International Conference on Microstructural-Related Durability of Cementitious Composites, Amsterdam, The Netherlands, p. 9.

Xia, M., Muhammad, F., Zeng, L., Li, S., Huang, X., Jiao, B., Shuai, Y., Li, D., 2019. Solidification/stabilization of lead-zinc smelting slag in composite based geopolymer. J. Clean. Prod. 209, 1206–1215. https://doi.org/10.1016/j.jclepro.2018.10.265.

Zhang, M., Reardon, E.J., 2003. Removal of B, Cr, Mo, and Se from wastewater by incorporation into hydroaluminole and ettringite. Environ. Sci. Technol. 37, 2947–2952. https://doi.org/10.1021/es0206969.