Solidification/stabilization of gold mine tailings using calcium sulfoaluminate-belite cement

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

a University of Oulu, Fiber and Particle Engineering, University of Oulu, P.O. Box 4300, FIN-90014, Oulu, Finland
b University of Oulu, Process Metallurgy, University of Oulu, P.O. Box 4300, FIN-90014, Oulu, Finland

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A B S T R A C T
In this study, calcium sulfoaluminate-belite cement (CSAB) was used to stabilize gold mine tailings, which are challenging materials to effectively immobilize due to high heavy metal and sulfate content. The hydration of CSAB cement yields ettringite and monosulfate with good capability for immobilizing sulfates and oxyanions in their crystal structure, in addition to physical encapsulation/stabilization in a cementitious matrix. Different mix designs of CSAB cement and mine tailings were prepared, and the samples were cured at room temperature. Mechanical strength and heavy metal leaching were analyzed after 7 days, 28 days, and 90 days of curing, and the phase composition (XRD), thermogravimetric analysis (TGA), and microstructure (FESEM) were also studied. All harmful elements (cationic and oxyanion elements) were effectively immobilized during 7 days of curing, and the heavy metal immobilization remained constant after longer curing, according to an environmental leaching test. High mechanical strength results and good sulfate immobilization were obtained with mine tailing content up to 50 w-% of total binder material. With higher mine tailing content (75 w-% and 90 w-%), the mechanical strength and immobilization ability substantially decreased.

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1. Introduction

Sustainable management of sulfide containing waste materials such as gold mine tailings is challenging due to the complex chemical composition of the material. Gold mine tailings include high levels of sulfates and several heavy metal containing minerals. Usually, mine tailings are deposited into the tailings ponds. When tailings are in contact with oxygen and water, sulfidic minerals such as pyrite (FeS2), arsenopyrite (FeAsS), and pyrrhotite (Fe1-xS) can be oxidized, generating sulfuric acid (Park et al., 2019). The produced acid decreases the pH of the water and dissolves heavy metal containing minerals yielding harmful elements, like sulfates and oxyanions such as toxic and carcinogenic arsenic, into the environment (Ritcey, 2005; Wang et al., 2017). The phenomena is called Acid Mine Drainage (AMD). AMD can cause serious environmental problems for a long time after the closure of a mining site, and therefore, safety management methods need to be developed to achieve more sustainable mining in the future (Park et al., 2019; Ritcey, 2005).

Solidification/stabilization (S/S) of wastes using cementitious materials is one approach to the management of solid waste materials prior to landfiling. The goal of the S/S method is to mix the solid waste with the cementitious material in order to achieve good physical properties and immobilize harmful components within a solidified material (Chen et al., 2009). While production of ordinary portland cement (OPC), usually used as a reagent in the S/S method, consumes large amounts of energy and is responsible for high CO2 emissions, more sustainable cement materials such as calcium sulfoaluminate-belite (CSAB) cement have been developed (Andrew, 2018; Chen et al., 2012; Glasser and Zhang, 2001). CSAB cement can be produced either from mixtures of natural materials, including limestone, bauxite, or aluminum clay and gypsum, or from industrial residues such as baghouse dust, low-calcium fly ash, scrubber sludge, lignite fly ash, Al-rich sludge, and red mud (Arjunan et al., 1999; Glasser and Zhang, 2001; Julphunthong, 2018; Luz et al., 2006; Rungchet et al., 2016, 2017). CSAB production has lower CO2 emissions and requires less energy consumption than OPC production. The final properties of CSAB cement include high...
early strength, quick setting time, excellent chemical resistance properties, good dimensional stability, low alkalinity, low permeability, and strength properties comparable to OPC (Chen et al., 2012; Glasser and Zhang, 2001).

CSAB cement clinker can have variable chemical compositions containing different quantities of ye’elimite (CaA3S), ferrite (CaAF), and belite (C3S) phases along with other elements such as anhydrite (CS) or mayenite (C2A2F) (Pinao, 2015). The typical amount of the major component, ye’elimite, is 30–70 w% (Martin et al., 2017). Ye’elimite phase reacts with sources of sulfate (gypsum, anhydrite, basanite), forming ettringite (C₃A·3CS·32H) and aluminum hydroxide (AH₃) phases (Equation (1)). If gypsum is running out, the monosulfate (C₃A·CS·12H) phase starts to form (Equation (2)). These phases are responsible for the strength of the material at early stages (Chen et al., 2012; Winnefeld and Lothenbach, 2010). The other phases of CSAB cement, such as belite (C3S), can form amorphous C–S–H or AFm (strätlingite) phases during hydration, and the ferrite phase can form C-(A,F)–H hydrates as well as an amorphous FH3 gel (Ectors et al., 2013; M Andac and Glasser, 1999).

\[
\begin{align*}
C₃A + 2CSH₂ + 34H & → C₃A·3CS·32H + 2AH₃ \\
C₃A₃S₂ + 18H & → C₃A·CS·12H + 2AH₃
\end{align*}
\]

The amount of sulfate present is an important parameter in the CSAB hydration process. If there is too much sulfate presence, expansion can occur. In addition, the properties of the sulfate source can affect the properties of the final material. Sulfates can be added with pure gypsum or by using the residues from industry, such as phosphogypsum (Chen et al., 2012; Luz et al., 2006; Winnefeld and Lothenbach, 2010).

In addition to the good technical properties and more efficient production process, another advantage of CSAB cement is its capacity for immobilizing harmful species within the hardened structure (Peysson et al., 2005). This immobilization is based on the ability to substitute Ca²⁺, Al³⁺, and SO₄²⁻ ions in the crystal structure of ettringite with other elements such as Fe³⁺, Cr³⁺, Sr²⁺ (replacing Al³⁺), Mg²⁺, Zn²⁺, Co²⁺ (replacing Ca²⁺) and oxyanions (such as As and Cr, replacing SO₄²⁻) (Albino et al., 1996; Arjunan et al., 1999; Chryssochoou and Dermatas, 2006; Kumarashasan et al., 1989; Myneni et al., 1997; Wang et al., 2017). Different elements can be replaced by the elements having similar radius and oxidation state. Heavy metals can also be adsorbed into the negatively charged ettringite structure or precipitate in alkaline conditions, and simultaneously, the physical encapsulation can immobilize hazardous components with chemical stabilization (Chryssochoou and Dermatas, 2006; Hossein, 2000).

Ettringite stabilization is an interesting option for sulfidic tailings. Sulfide rich tailings have been treated by using lime, fly ash and aluminum salt and good immobilization results were obtained based on the ettringite formation (Hossein, 2000). The high sulfidic gold mine tailings, used in this study, had been previously stabilized by using hydrated lime and blast furnace slag, and good immobilization for heavy metals and sulfates was obtained. Ettringite was found in the resulting matrix (Kiventerä et al., 2018b). In addition, CSAB cement has been studied for S/S of galvanic sludge (Luz et al., 2006) and also for stabilization of demolition waste containing calcium sulfate (CaSO₄) (Ambroise and Péra, 2008), with good immobilization results due to ettringite formation during hydration. Based on these findings, the stabilization of gold mine tailings by using CSAB cement was tested in this research. The target was to replace the additional gypsum with sulfates from tailings in the ettringite formation to stabilize the high sulfide content and immobilize heavy metals in the structure. The immobilization of different elements by using different proportions of CSAB cement was investigated, and the mechanical properties of the resulted material were studied. The samples were evaluated by analyzing the compressive strength and heavy metal leachability after 7 d, 28 d, and 90 d of curing. The leaching tests were done according to European leaching standard EN 12457, “Characterization of waste – Leaching - Compliance test for leaching of granular waste materials and sludges”. The phase identification was completed with XRD analysis in order to analyze the ettringite formation in different samples, and the thermogravimetric (TGA) analyses was also made after 7 d and 28 d of curing. The structure of the final materials was studied using FESEM analysis.

2. Materials and methods

2.1. CSAB cement preparation

The CSAB cement used in the present study was synthesized from pure reagent grade chemicals (RGC): CaSO₄, calcium oxide (CaO), aluminum oxide (Al₂O₃), silicon dioxide (SiO₂), and iron (III) oxide (Fe₂O₃). The chemical composition of the RGC used for CSAB clinker preparation is presented in Table 1. A high iron content was chosen because of further interest in using metallurgical slags with high iron content. To remove possible moisture CaO was calcined at 800 °C and anhydrite dried at 500 °C for 12 h.

RGCs were weighed and a tumbling ball mill (Germantec TPR-D; Germantec, Ransbach-Baumbach, Germany) was used to mix the raw materials to achieve a homogenous mixture; a stainless steel jar (10 L) with grinding media of 80 stainless steel balls (d = 30 mm) were used. The RGC mixture was first ground for 15 min and then mixed and again ground for 10 min. After grinding/mixing, the mixture was compressed by hand to three cylinder-shaped corundum crucibles (d = 100 mm and h = 100 mm), and all three crucibles were fired simultaneously in a nabertherm chamber furnace. The crucibles were placed in the furnace at 800 °C and heated at a rate of 10 °C/min to 1300 °C and held for 4 h. After heating, the crucibles were taken out of the furnace and placed on a water-cooled copper table to provide fast cooling.

After firing, each clinker was crushed by using a jaw crusher and then ground into a fine powder by a stainless steel jar with a volume of 10 L and d = 250 mm (Germantec TPR-D; Germantec, Ransbach-Baumbach, Germany). The grinding media of 180 stainless steel balls (d = 30 mm) was utilized. The clinker was first ground for 90 min and then tested with a Beckman Coulter LS 13320 particle size analyzer (Beckman Coulter, Brea, CA, USA). The particle size distribution was found to be too coarse. To achieve a finer particle size, the ground clinker was sieved 63 μm under with an air jet sieve (Alpine e200LS; Hosokawa Micron Corp., Osaka, Japan). The grinding was repeated in small batches until the rest of the clinker passed the 63 μm sieve.

Table 1

<table>
<thead>
<tr>
<th>Chemical composition of RGC used for CSAB cement clinker production.</th>
<th>Mass (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaSO₄</td>
<td>15.3</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>10.0</td>
</tr>
<tr>
<td>SiO₂</td>
<td>12.2</td>
</tr>
<tr>
<td>CaO</td>
<td>44.6</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>24.3</td>
</tr>
<tr>
<td>Total</td>
<td>100.0</td>
</tr>
</tbody>
</table>

* Reagent grade chemicals used in CSAB cement clinker production.
2.2. Mine tailing

The slurry of the studied gold mine tailing slurry was dried at 105 °C to be used as a powder form in this research. The Omnia Pananalytical AXIOS X-ray fluorescence (XRF) spectrometer (Malvern Pananalytical, Malvern, UK) was used to analyze the chemical composition of the mine tailing powder. The microwave-assisted wet digestion (3:1 mixture of HNO₃ and HCl for mine tailing) was used to study the content of trace elements and the inductively coupled plasma-optical emission spectrometer (ICP-OES) (Thermo Electron IRIS Intrepid II XDL Duo; Thermo Scientific, Waltham, MA, USA) was used for determination. A Beckman Coulter LS 13320 (Beckman Coulter, Brea, CA, USA) was used to analyze the mean particle size of the mine tailing powder and the thermogravimetry was used to analyze the Loss on ignition (LOI) at 950 °C of the material. The LOI analysis was made by using a Preparash Precisa Gravimetrics AG prepASH automatic drying and ashing system; Precisa Gravimetrics AG, Dietikon, Switzerland). The chemical composition, pH, LOI and mean particle size of the mine tailing are shown in Table 2.

2.3. S/S sample preparation

The recipes of the S/S specimens produced are presented in Table 3. The amount of additional gypsum is usually between 15 and 25 w-%, but in this study, the CSAB/gypsum ratio of 90/10 was chosen because the tailings included an additional sulfate source, decreasing the required level of additional gypsum. The CSAB/gypsum ratio was kept constant in all formulations. Different proportions of mine tailings were used to replace the CSAB/gypsum content. The CEN standard sand was used as an aggregate, in order to obtain the mechanical strength of the mortar. The water/content. The CEN standard sand was used as an aggregate, in order to vary the microstructure of the mortar. The water/binder (0.5) and binder/aggregate (1/3) ratios were kept constant in all formulations. Different proportions of mine tailings were used to replace the CSAB/gypsum content. The CEN standard sand was used as an aggregate, in order to improve the mechanical strength of the mortar. The water/binder (0.5) and binder/aggregate (1/3) ratios were kept constant in all samples. The S/S samples were prepared by the following steps:

- CSAB cement and gypsum were fully mixed together, and the powdered gold mine tailings were added to the mixture.
- After a homogeneous powder mixture was achieved, it was fully mixed with water and sand. The standard sand was added to the mixture after 0.5 min of mixing.
- The homogeneous paste was molded into cylindrical molds with a diameter of 25 mm. The samples were cured in plastic bags at room temperature for 7 d, 28 d, and 90 d before being further characterized.

2.4. Characterization of S/S samples

Zwick 100 (Zwick GmbH, Ulm, Germany) with a loading rate of 1.2 kN/s was used for compressive strength analysis of the samples and the strength was analyzed after 7d, 28d and 90 d of curing. Five samples of each recipe were analyzed, and the average of the samples was calculated.

The environmental analysis was made by a leaching test according to European standard EN 12457. The sample was crushed and then sieved under the particle size of 4 mm. The crushed and sieved sample was mixed with deionized water for 24 h with liquid/solid weight ratio of 10. ICP-OES was used to determine the concentration of the leachates.

The crystal phases of the specimens produced were analyzed using a 9 kW Rigaku SmartLab (XR D; Rigaku Corporation, Tokyo, Japan) with 45 kV and 200 mA (Cu Kα radiation) for CSAB clinker analysis and for hydrated samples with 40 kV and 150 mA (Co Kα radiation). A step interval of 0.02°/step and scan rate of 4°/min for a scan range of 5°–120° (2θ) were used. The crystalline structures were identified from the data by comparing the diffraction patterns on the International Center for Diffraction Data (ICDD) database using Rigaku PDXL2 software and WPPF (Whole Powder Pattern Fit) analysis. An internal standard method was applied, and XRD analysis by co-grinding the sample with 20% rutile (TiO₂), and the analysis results were calculated based on the internal standard method. The TGA analyses were made using a Preparash Precisa Gravimetrics AG prepASH automatic drying and ashing system (Precisa Gravimetrics AG, Dietikon, Switzerland). Crushed samples were heated from 23 °C to 1000 °C at 10 °C/min in a nitrogen atmosphere, and the mass change was detected.

The microstructure of the samples produced were studied by using the Field Emission Scanning Electron Microscope (FESEM) Ultra Plus. The reaction of the crushed samples was stopped by acetone, and then the samples were impregnated in an epoxy resin under vacuum. The hardened samples in epoxy resin were polished and coated with carbon before FESEM analysis. AZtec software (Oxford Instruments) was used to analyze the BSE pictures and the elemental chemical composition of the selected energy dispersive spectroscopy (EDS) points. Backscattered electrons (BSE) were used for scanning electron microscope (SEM) imaging of the sample, and EDS analysis was used for chemical analysis. Scanning electron images were taken under an acceleration voltage of 15 kV and a working distance of around 8.5 mm.

The main chemical components of LOI (loss on ignition) treated clinker (950 °C, LOI 0.15 w%) was determined using an Omnia Pananalytics Axiosmax 4 kV X-ray fluorescence (XRF) from a melt fused tablet. The melt fused tablet was produced from 1.5 g of clinker melted with 7.5 g of X-ray Flux Type 66:34 (66% LiB₄O₇ and 34% LiBO₂) in a platinum crucible using a Pananalytics Eagoon 2 fluxer operated in 1200 °C.

3. Results

3.1. CSAB cement

The chemical composition of the clinker produced as a normalized XRF results, the calculated/estimated amount of phases based on clinker XRF (normalized) and the results obtained by XRD (results of Rietveld analysis) are shown in Table 4. Through XRD-analysis it was identified that, ye’elimite (C₄A₃S) and belite/larnite (C₃S) are the main phases in this particular cement clinker and they are known to be responsible for early age strength and setting (Luz et al., 2006). Usually the ye’elimite content in the CSAB cement varies between 30 and 70 w% (Martin et al., 2017) being 50 w% of this particular clinker. The belite content in the clinker used in this
study was approximately 30 w%. The belite phase is responsible for the final strength while the hydration reaction of belite is relatively slow (Luz et al., 2006). The other phases formed were andradite, ferrite, anhydrite and mayenite.

### 3.2. Mechanical properties

The strength of the samples was at a good level when the addition of mine tailings was increased up to 50 w% of the total binder amount (Fig. 1). The mechanical properties were improved during longer curing time, meaning the slow hydration of the CSAB cement and the interaction between mine tailings and the cement. A significant decrease in the mechanical strength could be seen with mine tailing content of 75 w% and 90 w% of the binder materials. Similar observations were made by Martin et al. (2017), who used fly ash to partially replace the CSAB cement, obtaining lower mechanical strength of hydration when the amount of fly ash in the matrix was too high. The source of sulfate (gypsum, anhydrite, basanite) and the water to cement ratio are important parameters for the final mechanical properties of CSAB cement based concretes (Chen et al., 2012). In this particular mine tailing, sulfate was previously studied to be as a basanite phase (Kiventerä et al., 2018b).

According to García-Maté et al. (2015), basanite has shown the fastest initial setting time and highest viscosity, with a lower mechanical strength in CSAB cement hydration as compared to anhydrite and gypsum. In this study, the workability of the paste decreased substantially with higher amount of mine tailings, decreasing the consolidation of the matrix (Fig. 2).

#### Table 3

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>MT/CSAB_0/100</th>
<th>MT/CSAB_25/75</th>
<th>MT/CSAB_50/50</th>
<th>MT/CSAB_75/25</th>
<th>MT/CSAB_90/10</th>
</tr>
</thead>
<tbody>
<tr>
<td>CSAB cement (w-%)</td>
<td>22.5</td>
<td>16.9</td>
<td>11.25</td>
<td>5.6</td>
<td>2.25</td>
</tr>
<tr>
<td>Gypsum (VWR) (w-%)</td>
<td>2.5</td>
<td>1.8</td>
<td>1.25</td>
<td>0.65</td>
<td>0.25</td>
</tr>
<tr>
<td>Mine tailing (MT) (w-%)</td>
<td>0</td>
<td>6.3</td>
<td>12.5</td>
<td>18.75</td>
<td>22.5</td>
</tr>
<tr>
<td>CENa sand (w-%)</td>
<td>75</td>
<td>75</td>
<td>75</td>
<td>75</td>
<td>75</td>
</tr>
<tr>
<td>w/b(^{a}) ratio</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
</tr>
</tbody>
</table>

\(^a\) Standard sand.
\(^b\) binder including CSAB + gypsum + mine tailing.

#### Table 4

<table>
<thead>
<tr>
<th>Oxides</th>
<th>Al(_2)O(_3)</th>
<th>CaO</th>
<th>Fe(_2)O(_3)</th>
<th>SiO(_2)</th>
<th>SO(_3)</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>w%</td>
<td>24.3</td>
<td>44.6</td>
<td>10.0</td>
<td>12.2</td>
<td>9.0</td>
<td>100.0</td>
</tr>
</tbody>
</table>

**Normalized XRF result from fired clinker**

<table>
<thead>
<tr>
<th>Oxides</th>
<th>Al(_2)O(_3)</th>
<th>CaO</th>
<th>Fe(_2)O(_3)</th>
<th>SiO(_2)</th>
<th>SO(_3)</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>w%</td>
<td>24.2</td>
<td>45.5</td>
<td>10.3</td>
<td>12.5</td>
<td>7.6</td>
<td>100.0</td>
</tr>
</tbody>
</table>

**Calculated/estimated amount of phases based on clinker XRF (normalized)**

<table>
<thead>
<tr>
<th>Phases</th>
<th>Ye’elimite</th>
<th>Larnite</th>
<th>Andradite</th>
<th>Ferrite</th>
<th>Anhydrite</th>
<th>Mayenite</th>
</tr>
</thead>
<tbody>
<tr>
<td>w%</td>
<td>48.3</td>
<td>29.0</td>
<td>6.8</td>
<td>13.9</td>
<td>2.1</td>
<td>0.0</td>
</tr>
</tbody>
</table>

**Result of Rietveld analysis (WPPF)**

<table>
<thead>
<tr>
<th>Phases</th>
<th>Ye’elimite</th>
<th>Larnite</th>
<th>Andradite</th>
<th>Ferrite</th>
<th>Anhydrite</th>
<th>Mayenite</th>
</tr>
</thead>
<tbody>
<tr>
<td>w%</td>
<td>50.9 ± 0.1</td>
<td>29.7 ± 0.8</td>
<td>4.0 ± 0.3</td>
<td>11.1 ± 0.5</td>
<td>1.78 ± 0.14</td>
<td>2.3 ± 0.2</td>
</tr>
</tbody>
</table>

Fig. 1. The UCS of samples after 7, 28 and 90 days of curing.
3.3. Leaching test

The gold mine tailings used in this study contained As, Cr, Cu, Ni, Mn, Zn, Sb, Pb, Ba, and sulfate (Table 2). According to previous tests, the most challenging elements to immobilize from these mine tailings are oxycations of As and V and sulfates (Kiventerä et al., 2018a). A small amount of sulfate was leached out from the reference sample after 7 d of curing, but the amount decreased substantially after longer curing times (Table 5). These results are in line with the mechanical strength results. The hydration rate of this particular CSAB clinker seems to be slow, and the higher mechanical and chemical properties can be reached with longer curing times. When CSAB cement was replaced with 25 w% of mine tailings, the immobilization of sulfate was still at a good level. With 50 w% of mine tailing content, the leachability of sulfate increased slightly. Overall, more than 60% of sulfates were immobilized, when comparing the calculated theoretical total amount of sulfates in the starting material and the leachable amount from the stabilized material. When the amount of mine tailings increased, the leachability of sulfates increased remarkably. With 75 w% of mine tailings, almost all of the sulfates were leached out.

In addition, cationic species were effectively immobilized. The stabilization mechanism of cationic species is usually adsorption, inclusion, or precipitation, and according to Van der Sloot (2002), the cement stabilized material can immobilize cationic species more easily than it can immobilize oxycations. The immobilization of oxycations such as As, Cr, Se, and V is complicated because of the mobility of oxycations in high alkaline and neutral conditions (Chrysouchou and Dermatas, 2006). As, for example, can have different oxidation states (+5, +3, 0, –3) depending on the environment. The most usual forms are +5 and +3 in groundwater and surface water while the –3 does not occur in natural environment (Kim et al., 2003). Instead under alkaline conditions As occurs usual as –3 making the immobilization challenging. In this study, the most challenging elements (As and V) were immobilized effectively in all sample during 7 d of curing and remained constant or improved after longer curing times. The leachable amount of As was higher when the amount of mine tailings were 90 w% of the total binder content. Cr was leached out from the reference sample indicating that some contamination from crushing and milling equipment occurred during CSAB clinker production. The leaching of Cr decreased when the amount of mine tailings increased, even though the total amount of Cr increases with higher mine tailing content. Cr immobilization is mainly due to the reduction of its toxic Cr(VI) form into the more stable Cr(III) form (Kumpiene et al., 2008). According to Zhang et al. (2008), higher sulfide content could enhance the transformation of Cr(III) to Cr (III), decreasing the leachable amount of Cr.

3.4. Phase structure

The hydration of the CSAB clinker produces ettringite, which is responsible for the early stage strength. If the late ettringite formations occur, it can cause expansion and cracking of the material (Chen et al., 2012). According to XRD analysis (Table 6), the CSAB clinker used in this study was not hydrated completely during the first days of curing. After 7 days and 28 days of curing, 5 w% of ye’elimite (C₃A₅S), 16 w% of larnite (C₂S), and 3 w% of gypsum were unreacted, but the amount of all unreacted phases decreased after 90 d of curing. The unreacted ye’elimite and gypsum could be the reason for the leaching of sulfate from the reference sample. The amount of ettringite phase was decreased after longer curing times, and the total amount of unidentified/amorphous phases increased. Ettringite can form amorphic Al(OH)₃ which is a possible phase forming in this study because of the relatively high amounts of Al (Chen et al., 2012). In addition, the high ferric iron content can lead the brownmillerite (CaAF) transformation into the amorphous FH₃ phase (Meller et al., 2004). Larnite phase was decreased remarkably within 90 d of curing, which may be the reason for the improved mechanical strength after longer curing times (Molén, 2014). Larnite reacts to the amorphous phase, into the so-called C₅S·4H₂O gel. These findings support the mechanical properties and leaching test results in this study.
The main peaks of mine tailings (quartz, dolomite, albite) were found from stabilized mine tailings samples (Fig. 3). Ettringite was found from all samples, and it remained constant after longer curing. The ettringite formation was at a high level (30 w%) in samples containing 25 w% and 50 w% of mine tailings. With a higher amount of mine tailings, the ettringite amount decreased, and the main phases of initial mine tailing powder still occurred. With higher amounts of mine tailings, there was no changes in the phase composition of the samples, which supports the observations of a poor consolidation of the matrix with too high content of mine tailings.

3.5. Thermogravimetric analysis

Ettringite can be characterized by thermogravimetric TGA analysis as an endothermic peak between 165°C and 180°C (Ramachandran, 2003). The clearly endothermic ettringite peak from a CSAB hydrated sample (MT/CSAB_0/100) can be found at around 160°C (Fig. 4a and b). With 25 w% of mine tailings (MT/CSAB_25/75), the ettringite peak still occurred, but with the higher amounts of mine tailings, the ettringite peak decreased substantially. After longer curing times, the ettringite peak remained constant. The endothermic peak around 100°C represents the water loss of the samples. With higher amounts of mine tailings, the sample seems to be relatively wet after 7 d of curing, but after longer curing times, the water loss decreased significantly. The peaks at 97 ± 11°C, 146 ± 18°C, and 156 ± 16°C were observed for calcium silicate hydrate, ettringite, and the first gypsum calcination step, respectively and the peaks at 163 ± 17°C, 201 ± 3°C, 275 ± 7°C, and 496 ± 26°C are reported to represent the second gypsum calcination, monosulfate, aluminum hydroxide, and calcium hydroxide, respectively (Telesca et al., 2014). In this study, the small endothermic peak can be seen between 250°C and 300°C. This peak can illustrate the AH₃ phase according to the previous list or it can be the AFm phases which both can have endothermic peak between 250°C and 300°C (Collier, 2016; De Weerdt et al., 2011; Telesca et al., 2014). These findings are in line with the XRD analysis. The ettringite is the main phase in the CSAB hydrated sample, and it is produced during the early stage of curing. With higher amounts of mine tailings, the ettringite and other hydrated phase formations decreased, resulting the poor strength and immobilization of the material.

3.6. Microstructural analysis

Using FESEM analysis, arsenic was found, together with sulfur and iron, as arsenopyrite particles (Fig. 5). Arsenopyrite was surrounded by ettringite and by other hydration phases, which means that arsenopyrite particles were physically encapsulated in the matrix. The clear observation of the reaction between arsenopyrite and ettringite/C–S–H gel or chemical stabilization cannot be seen at the resolution of FESEM analysis. Zhang et al. (2019) investigated the immobilization of arsenic-rich mine tailings using metallurgical slag cement materials. They obtained good immobilization results of arsenic, and the stabilization was found to be mainly solidification as alkaline arsenate. Arsenic can also partly enter the ettringite crystal, via ion exchange, or become encapsulated by C–S–H gel. Similar observations were made by Phenrat et al. (2005), who studied S/S of arsenic–iron hydroxide sludge. According to their research, the stabilization of arsenic could be from either sorption onto the C–S–H surface, replacing SO₄ in the ettringite structure, or solidifying as a calcium–arsenic compound having low solubility properties.

Even though the immobilization of heavy metals was at good levels and had good mechanical properties, the stabilization mechanism is still unclear. When the waste material contains several different elements, the stabilization mechanism is more complex. It should also be kept in mind that this was the situation before the crushing and environmental leaching analysis: some hazardous elements may have reacted with ettringite and other phases during water leaching. Sulfate, if present in solution after substituted ettringite has already formed, can still displace the oxyanions, being the most stable component in the ettringite stabilization system (Chrysochoou and Dermatas, 2006). A more detailed analysis should be made in order to better understand the stabilization mechanism. In addition, the sludge after a leaching test should be analyzed in order to see the possible reactions during immersion in water. The long-term stability and durability of the matrix produced needs further investigation, while the ettringite can be unstable in different environmental conditions, leading to reduction of stabilization and mechanical structure (Baur and Johnson, 2003; Damidot and Glasser, 1992; Perkins and Palmer, 2000).

4. Conclusion

The aim of this study was to stabilize sulfidic gold mine tailings by using CSAB cement as a co-binder. The mechanical strength and
the leaching rates of heavy metals and sulfates were analyzed after 7 days, 28 days and 90 days of curing. High mechanical strength of the stabilized samples is able to obtain with 25 w% and 50 w% of mine tailing content. The mechanical strength was 70% when compared with CSAB hydrated reference sample. The strength was increasing during longer curing time indicating slow hydration of CSAB cement and interactions between the mine tailings and cement. High immobilization efficiency of many harmful substances, including arsenic and vanadium, is able to achieve with gold mine tailing content 25 w% and 50 w%. Small amount of sulfates was leached out from the reference sample after 7 days of curing but was highly decreased after longer curing time. However, over 60% of the sulfates were immobilized with 25 w% and 50 w% of mine tailing content when comparing the leachable amount and calculated theoretical amount of sulfates in the structure. The hydration of CSAB cement achieved relatively high ettringite content during the early stages of curing, and the ettringite remained constant during longer curing times. Ettringite substitution can be one reason for good stabilization results. It was also observed that the main stabilization mechanism for arsenic seems to be physical encapsulation, while some arsenopyrite particles surrounded by the ettringite structure were found from the sample containing 50 w% of mine tailings.

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