

# **Immobilization of sulfates and heavy metals in gold mine tailings by sodium silicate and hydrated lime**

Jenni Kiventerä<sup>a</sup>, Harisankar Sreenivasan<sup>a</sup>, Christopher Cheeseman<sup>b</sup>, Paivo Kinnunen<sup>a</sup> Mirja Illikainen<sup>a\*</sup>

<sup>a</sup>University of Oulu, Fiber and Particle Engineering, P.O. Box 4300, FIN-90014 University of Oulu, Oulu, Finland

<sup>b</sup>Department of Civil and Environmental Engineering, Imperial College London, London, UK

\*Corresponding author: E-mail: [mirja.illikainen@oulu.fi](mailto:mirja.illikainen@oulu.fi) (M.Illikainen). Tel: +358 40 588 5904

## **Abstract**

Gold mining produces hazardous tailings wastes with elevated sulfur content and high levels of heavy metals including oxyanion elements such as V and As. This research investigated activation of these tailings with calcium hydroxide and sodium hydroxide/sodium silicate as a way to stabilize the material and limit leaching of harmful components. The effects of thermal treatment on the reactivity of the tailings and the use of different activating solutions on the physical properties, microstructure and leaching of harmful components are reported. The effect of adding ground granulated blast furnace slag to the tailings is also assessed. The use of 5 wt % Ca(OH)<sub>2</sub> activating solution produces optimum performance increasing the immobilization efficiency of sulfates, arsenic and the other harmful elements. Heat-treating mine tailings at 900°C slightly improves the reactivity but did not improved the immobilization efficiency. Microstructural analysis by TEM and XRD confirmed that stabilization is based on calcium sulfate and/or ettringite formation during alkali-activation. All materials achieved reasonable compressive strength after 28 days of curing and the potential for using alkali activation as a method to treat tailings from mining is discussed.

**Keywords:** geopolymer; alkali activated material; immobilization of heavy metals; thermal treatment; STEM, In situ XRD

## **1. Introduction**

Gold mine tailings are produced after extraction and subsequent mineral processing and are a hazardous waste that is normally landfilled close to the mining site. They typically contain high levels of sulfides that are oxidized in the presence of air and moisture to produce sulfuric acid and as a result low pH in surrounding waters. Gold mine tailings also contain Cu, Cr, Cd, Pb, Sb, Ni, Zn, V and As and these leach under the acidic conditions causing additional environmental degradation and risks to human health [1].

Hazardous heavy metal elements, such as Cd, Ni, Cu, Pb and Zn, can be encapsulated and immobilized in alumino-silicate based wastes by using alkali-activation to form monolithic treated waste products [2–11]. Alkali activation of alumino-silicates hydrolyses aluminum and silicon species into solution. The dissolved species then undergo speciation equilibrium, gelation, reorganization, polymerization and hardening reactions to form a solid alkali-activated monolithic

material [12]. The alkali-activated material formed has a 3-dimensional network structure consisting of aluminum and silica tetrahedra. The presence of  $\text{Al}^{3+}$  ions in the network requires a charge balancing cation from the alkaline solution or the waste material [13]. Heavy metals are immobilized by forming hydroxides in highly alkaline conditions [9] or they can be encapsulated within the network structure [14]. All these methods can occur simultaneously. However high leaching of elements such as As and Cr after alkali activation has also been reported [1,15,16].

Gold mine tailings are reported to have low reactivity and need the addition of co-binder to achieve a strong matrix [17]. Large amount of different cationic elements from gold mine tailings can be immobilized by alkali activation of optimized system [11,18]. High levels of As and V were leached out from the alkali-activated mine tailing materials at the early stage of curing. Longer curing periods improved the immobilization effectively. Poor immobilization of As and V results because of the oxyanionic nature of these elements. For example, As can have oxidation states of +5, +3, 0 and 3- which depends on the environment. The most common states are As (III) and As (V) in groundwater and surface water system [19] when the valence stages 0 and -3 cannot usually be find in natural environment [20]. Oxyanions have high solubility in highly alkaline conditions and are not chemically bound into the alkali-activated alumino-silicate structure. They also cannot precipitate as a hydroxides under highly alkaline conditions [21].

Since alkali activation is not an effective method to stabilize poorly reactive gold mine tailings, other approaches are needed. The present study is divided in two different parts. The first part investigates thermal treatment of mine tailings as a method to increase the reactivity of the material, as shown previously with other materials like clay minerals, and mine tailings [22–24]. The aim is to study if the increased reactivity of the material can enhance the stabilization of mine tailings in alkali activation. The second part investigates the use of  $\text{Ca}(\text{OH})_2$  as an activator instead of  $\text{NaOH}/\text{Na}_2\text{SiO}_3$  in heavy metal and sulfate stabilization.  $\text{Ca}(\text{OH})_2$  solution has been used to stabilize expansive clays

with good results; the reaction products formed, such as ettringite, have the ability to immobilize sulfates, heavy metals and oxyanions effectively [21].

The mine tailings were treated thermally, and the phase changes during thermal treatment were studied by in situ X-ray diffraction (XRD). The solubility of Si and Al in alkaline conditions was analyzed to show the increase in the reactivity of the materials during thermal treatment. Both untreated and thermally treated mine tailings were activated using sodium hydroxide/sodium silicate solutions and  $\text{Ca(OH)}_2$  solution and the mechanical properties were measured. Ground granulated blast furnace slag (GBFS) was used as an additional pozzolanic additive to increase the levels of Al, Si and Ca ions. Leaching of sulfates and heavy metals was analyzed and the microstructure of the specimens produced were characterized by scanning transmission electron microscopy (STEM) and by XRD.

## **2. Materials and Methods**

### **2.1 Materials**

Sulfidic mine tailings (MT) were received as a slurry from a gold mining site in North of Finland. The slurry was dried in oven at  $105^\circ\text{C}$  and milled with a vibratory disc mill (Retsch RS 200) for 2 minutes with 1000 rpm to form a fine powder. Part of the powder was heated to  $900^\circ\text{C}$  for 6 hours in order to study the effect of calcination on reactivity of tailings and on the efficiency of stabilization. The heat-treated mine tailings were cooled and then reground in the disc mill for 3 minutes at 1000 rpm. A commercial ground granulated blast furnace slag (KJ 400 from Finnsementti) containing a high glassy fraction was used in selected mixes.

The alkali activation has used two different solutions. First solution was formed by mixing solid NaOH pellets (>99%, Merck, Germany) with commercial sodiumsilicate solution (with  $\text{Na}_2\text{O}/\text{SiO}_2$

ratio of 3.3) and water. The second activating solution was formed by mixing  $\text{Ca(OH)}_2$  pellets (>99%, Merck, Germany) with distilled water to form a 5 wt %  $\text{Ca(OH)}_2$  solution.

## 2.2 Sample preparation

The alkali-activated samples prepared are presented in Table 1. Alkali-activated samples were formed by mixing the mine tailings powder with 0, 10 or 25 wt % of GBFS. The powder mixture were intensively mixing with the alkali-activating solution for 5 minutes. Additional water was added to produce a paste with appropriate workability. The homogeneous pastes were then casted into 25 mm diameter cylindrical molds and cured in 90% relative humidity at room temperature for 7 and 28 days.

**Table 1.** Geopolymer formulations from a mixture of mine tailings (MT) and blast furnace slag (GBFS). All the samples were made from Original and heat treated mine tailing powder.

		MT/GGBFS_75/25	MT/GGBFS_75/25	MT/GGBFS_90/10
		NaOH/NaSil	CaOH2	CaOH2
MT	(g)	75	75	90
GBFS	(g)	25	25	10
NaOH	(ml)	30	0	0
NaSil	(ml)	50	0	0
$\text{Ca(OH)}_2$	(ml)	0	30	30

## 2.3 Characterization of the raw materials and specimens produced

The chemical composition of the mine tailings before and after heating were analyzed by Omnia Panalytix Axios X-ray fluorescence (XRF) spectrometer. The content of trace elements was analyzed by microwave-assisted wet digestion using a 3:1 mixture of  $\text{HNO}_3$  and  $\text{HCl}$  for mine tailing and determination was made using a inductively coupled plasma-optical emission spectrometer (ICP-OES) (Thermo Electron IRIS Intrepid II XDL Duo, Thermo Scientific). The particle size distribution was measured using a Beckman Coulter LS 13320. Specific surface area measurement was based on

the physical adsorption of gas molecules on a solid surface using a physisorption analyzer (ASAP 2020, Micrometrics) and the results were reported in a form of a BET isotherm.

The phase changes occurring during the thermal treatment of mine tailing were analysed using in-situ x-ray diffraction. An Anton Paar DHS1100 furnace containing the sample was placed inside a Rigaku SmartLab 9 kW XRD equipment. The sample was heated at 20°C/min to 900°C and the XRD pattern was recorded at 20°C temperature intervals. XRD analysis used Co K $\alpha$  radiation (K $\alpha$ 1=1.78892 Å; K $\alpha$ 2=1.79278 Å; K $\alpha$ 1/K $\alpha$ 2=0.5) with a scan rate of 3°/min between 5° and 90° (2 $\theta$ ) with a 0.02°/step. For phase identification “X'pert HighScore Plus” (PANalytical software) was used.

Reactivity of the samples were assessed using alkaline solubility tests. All the samples were milled to have an average particle size of between 1  $\mu$ m and 10  $\mu$ m. During the solubility test, the sample was mixed with 6M NaOH solution in polypropylene container with a liquid to solid ratio of 40 w/w. The polypropylene container was placed in a horizontal shaking table (IKA KS 260 orbital shaker) under shaking motion (Mot = 150/min) at 23  $\pm$  0.5°C for 24 h. At the end of the test, sample was filtered using a 0.45  $\mu$ m filter paper. Filtrate was then acidified with 6M HNO<sub>3</sub> to pH around 2 and was later analyzed by AAS (AAS Perkin Elmer 600) to determine elemental concentrations. For the determination of Si, a wavelength of 251.6 nm with atomization temperature of 2350°C was used. Similar parameters used in case of Al were 309.3 nm and 2300°C respectively.

The compressive strength of the samples produced was determined with Zwick 100 using loading rate of 1.2 kN/s. Three samples of each composition were analyzed and the average of the results calculated. The samples were tested after 7 or 28 days of curing.

The leachability analysis were carried out according to the European standard EN 12457 “Characterization of waste-Leaching-Compliance test for leaching of granular waste materials and

sludge.” After being crushed and sieved to a particle size  $<4$  mm, the samples were placed in bidistilled water with a liquid/solid weight ratio of 10 l/kg and rotated for 24 h. After the extraction and filtration of the leachates, the concentrations of heavy metal ions were determined with ICP-OES. Before ICP-OES analysis, the samples were acidified with  $\text{HNO}_3$  to  $\text{pH}=2$ . The analysis were made after 7 and 28 days of curing. This way it can be analyzed how the samples are strengthening by time and how does it influence to the immobilization of the different components.

The crystalline phases present in samples were identified using a Siemens 5000 X-ray diffractometer. The step interval, integration time, and angle interval used were  $0.04^\circ/\text{step}$ , 4 s/step, and  $10\text{-}50^\circ 2\Theta$ , respectively. The ICDD-database (PDF-2, 2006) was used to identify the crystal phases of the material. Microstructural analysis of the samples produced were analyzed by scanning transmission electron microscope (STEM) with a LEO 912 OMEGA EFTEM, with an energy-dispersive X-ray spectroscopy (EDS) detector (Oxford Instruments, X-Max 80).

### **3. Results**

#### **3.1. Properties of mine tailings**

The mine tailings are rich in silicate, aluminum, calcium and iron (Table 2). They also have fine particle size ( $d_{50}$  45  $\mu\text{m}$ ). The minor elements present in mine tailings are shown in Table 3. The main problematic elements are sulfur and arsenic, especially sulphur is in leachable form.

**Table 2.** The chemical composition of the original mine tailing (MT) and GBFS powder.

Component	MT (original)	GBFS
SiO <sub>2</sub> (%)	49.9	32.3
Al <sub>2</sub> O <sub>3</sub> (%)	10.4	9.6
Fe <sub>2</sub> O <sub>3</sub> (%)	9.1	1.2
CaO (%)	11.7	38.5
SO <sub>3</sub> (%)	3.9	3.9
MgO (%)	6.8	10.2
K <sub>2</sub> O (%)	1.3	0.5
TiO <sub>2</sub> (%)	1.2	2.2
BET surface area (m <sup>2</sup> /g)	7.2	
pH	9.6	
LOI 525°C	0.7	
LOI 950°C	12.9	
Particle size d <sub>50</sub> (μm)	45	10.8



**Table 3.** The total amount in MT powder, leaching amount from MT powder and waste law limits of minor elements.

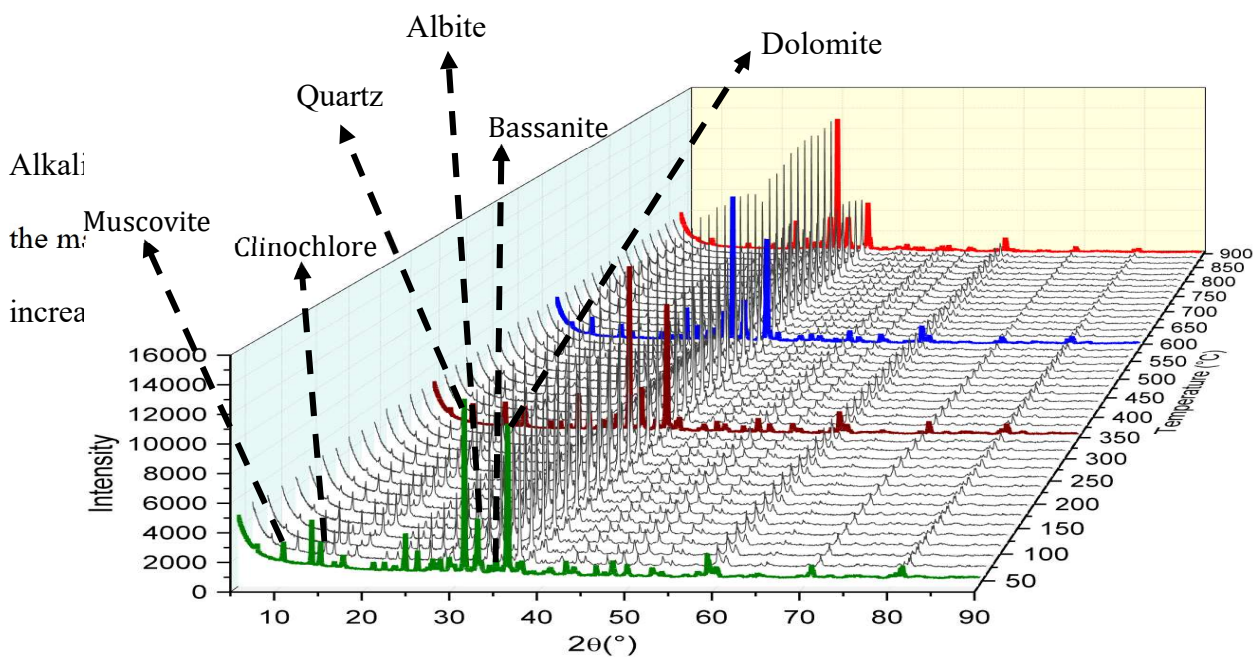
Component	Total amount in MT (mg/kg)	Leaching from MT (mg/kg)	Inert waste limit (mg/kg)	Regular waste limit (mg/kg)
S	18900	> 20 000	1000	20 000
As	1520.0	1.5	0.5	2
Cd	<0.3	0.05	0.04	1
Cr	74.0	0.5	0.5	10
Cu	120.0	0.05	2	50
Ni	100.0	0.5	0.4	10
Mn	1500	< 0.3		
Pb	4.3	0.1	0.5	10
Zn	71.0	0.1	4	50
B	9.6			
Be	<1	< 0.02		
Co	22.0	0.03		
Mo	1.5	0.1	0.5	10
Sb	32.0	0.2	0.06	0.7
Se	<3	0.06	0.1	0.5
Sn	<3	< 0.1		
V	59.0	0.05		
Ba	29	0.09	20	100

### 3.2 The effect of calcination on tailings' reactivity

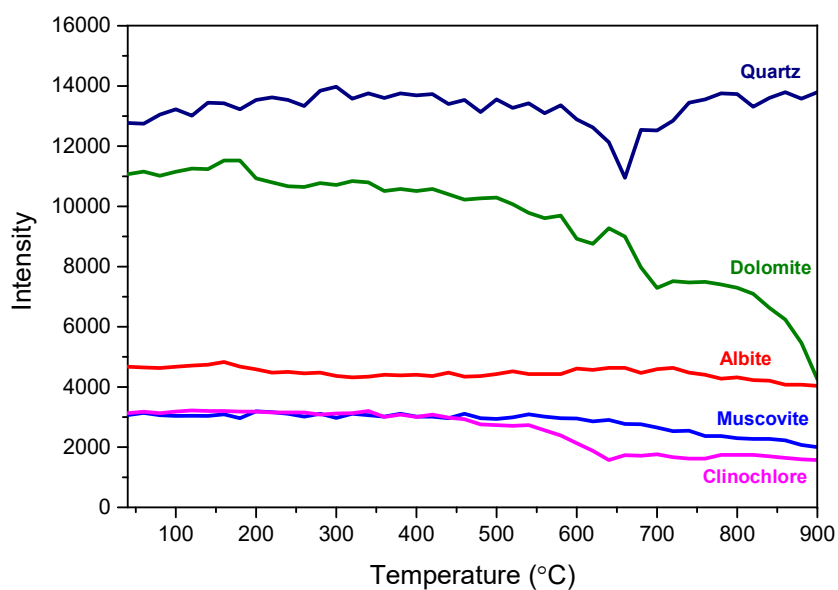
Even if the chemical composition of tailings is suitable for alkali activation (Table 2), the mine tailings are naturally-forming minerals and have shown poor reactivity [25]. In order to increase the reactivity of tailings, they were treated thermally.

The chemical composition of mine tailings did not change during the thermal treatment (results not shown). However, there were some mineralogical changes (Fig 1a and 1b). A reduction of the dolomite ( $(\text{CaMg}(\text{CO}_3)_2)$ ) peak can be seen after heat treatment at  $\sim 600^\circ\text{C}$  (Fig 1b). Decomposition of dolomite can produce reactive CaO and MgO which can improve the strength of the final material.

Sulfur in the untreated mine tailings is reported to be present in basanite (Fig. 1(a)). Basanite transforms into anhydrite when heated above 400°C [26] and decomposition of anhydrite occurs at temperature between 1050 °C and 1150 °C [24]. Hence, sulfur is not removed during thermal treatment to 900 °C. The quartz content remained constant apart from a small reduction at ~650 °C ((Fig. 1(b)). Other crystalline phases such as albite, muscovite, and clinochlore have high temperature stability (Fig 1a and 1b).



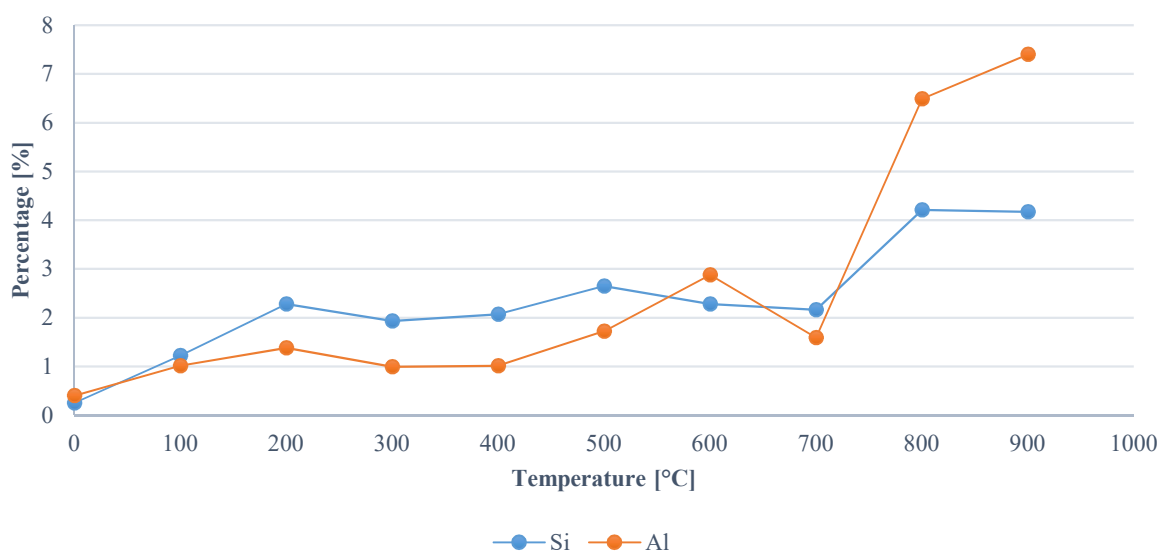
(a)



(b)

**Fig. 1.** (a) In-situ XRD analysis of mine tailings during heat treatment. (b) Intensity variation (based on the highest intensity) for some major components.

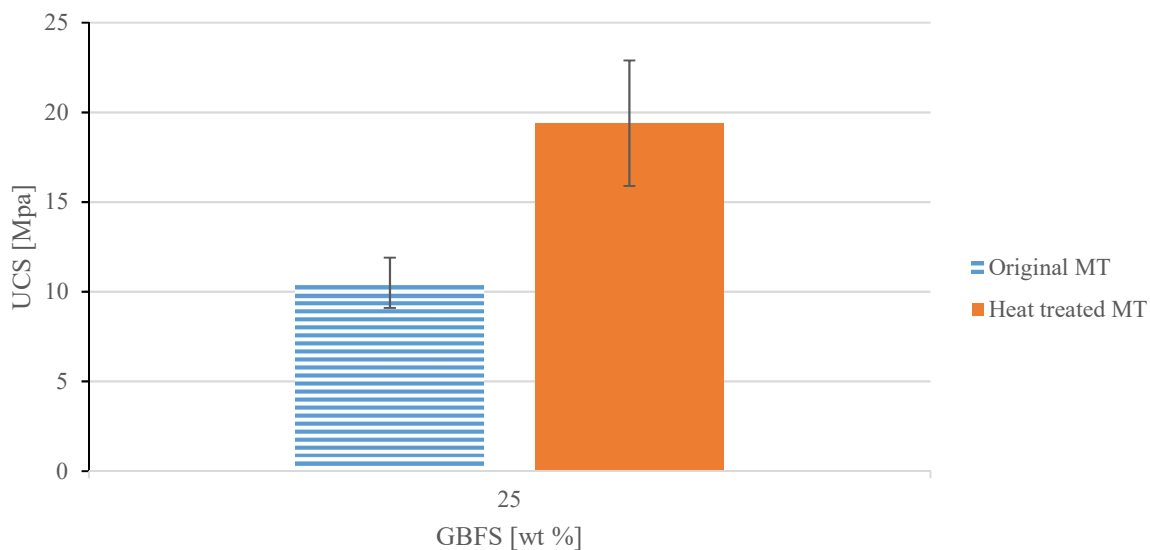
Alkali-reactivity of the material was found to increase during the heat treatment (Fig. 2). Initially, the material can be considered inert ( $< 0.5\%$  Al dissolution), and the amount of reactive Si gradually increased to  $4\%$  while that of Al  $6.8\%$ .



**Fig. 2.** The amount of reactive Si and Al in mine tailings during the heat treatment.

### 3.3. Stabilization of tailings by sodium hydroxide/sodium silicate solution

Thermal treatment had clear effect on strength of sodium hydroxide/sodium silicate ( $\text{NaOH}/\text{Na}_2\text{SiO}_3$ ) activated mine tailing samples (Fig. 3). The sample containing 25 % of GBFS had strength of approximately 10 MPa and when treated mine tailings were used; the compressive strength achieved almost 20 MPa. However, the leaching of sulfur, arsenic and vanadium remained at high level before and after the thermal treatment (Table 4). Samples activated by sodium hydroxide / sodium silicate activator increased also the leaching of Zn, Sb and Pb. Ba was stabilized most effectively by sodium hydroxide / sodium silicate solution. Since alkali-activation with sodium hydroxide / sodium silicate solution was not promising alternative for the stabilization, this work focused more on stabilization by hydrated lime.



**Fig. 3.** UCS of the sodium hydroxide / sodium silicate activated samples after 28 days of curing.

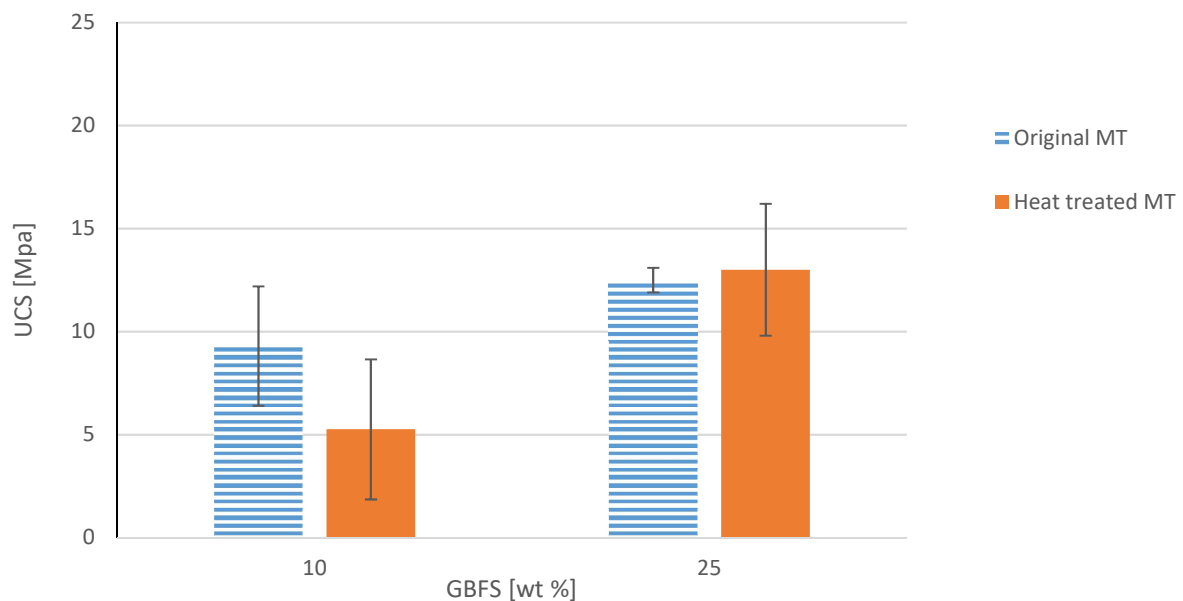
**Table 4.** The total concentration, leachable amount from MT powder, and leachable amount from sodium silicate/sodium hydroxide activated samples after 28d of curing.

	S ppm	As ppm	V ppm	Cr ppm	Cu ppm	Ni ppm	Zn ppm	Sb ppm	Pb ppm	Ba ppm
Total concentration in MT powder	> 20 000	1520	59	74	120	100	71	32	4,3	29

Leaching from MT powder	> 20 000	1,5	0,05	0,1	0,05	0,5	0,1	0,3	0,1	0,09
Original MT MT/GGBFS_75/25	20 000	70,7	16,7	0,5	0,25	0,25	0,5	0,75	0,75	0,25
Heat treated MT MT/GGBFS_75/25	19 000	28	29	1	0,5	0,5	1	1,5	1,5	0,5

### 3.4. Stabilization of tailings by hydrated lime

The tailings stabilized by hydrated lime ( $\text{Ca}(\text{OH})_2$ ) with GBFS content of 10 and 20 % achieved the strength of approximately 10 MPa during 28 days of curing (Fig. 4.) which is good level when considering for example mine backfilling, which requires strength of below 5 MPa. Higher slag content increased the strength of all samples which was noticed also in the previous work [17]. The heat treatment did not significantly affect the strength of the lime activated materials.



**Fig. 4.** UCS of the  $\text{Ca}(\text{OH})_2$  activated samples after 28 days of curing.

As it was previous mentioned, mine tailing powder was found to have high levels of S, As, V, Cr, Cu, Ni, Zn, Sb, Pb and Ba content (Table 3). Using  $\text{Ca}(\text{OH})_2$  solution as an activator the

immobilization of these elements were achieved (Table 5). The leaching was constant after longer curing period. When comparing the theoretical total amount in the geopolymer based on the value of the starting material (MT) and the leachable amount of the element from the geopolymer structure the immobilization efficiency were almost 100 % by  $\text{Ca}(\text{OH})_2$  activation after 28 days of curing (Fig. 5). Heat treatment did not improve the stabilization of any elements (Table 4).

Sulfates were stabilized more effectively with higher slag content in the matrix (Table 5). Higher slag content increases the reactive amount of Si and Al and provides more available Ca ions into the reaction. When sulfates react with calcium coming from slag or lime, it can form calcium sulfates. Calcium sulfates have much lower water solubility than sodium sulfates which can be the reason for the lower leachability of the sulfates. On the other hand calcium can react with aluminum and sulfates producing pozzolanic products such as ettringite which have an ability to immobilize sulfates effectively [21]. Arsenic stabilization is possible when precipitated as  $\text{Ca}_3(\text{AsO})_2$  [28]. On the other hand ettringite formation is known to be able to stabilize also oxyanions such as As, B, Se and V [29].

**Table 5.** The total concentration, leachable amount from MT powder, and leachable amount from Ca(OH)<sub>2</sub> activated samples.

	S ppm	As ppm	V ppm	Cr ppm	Cu ppm	Ni ppm	Zn ppm	Sb ppm	Pb ppm	Ba ppm
Total concentration in MT powder	> 20 000	1520	59	74	120	100	71	32	4,3	29
Leaching from MT powder	> 20 000	1,5	0,05	0,1	0,05	0,5	0,1	0,3	0,1	0,09
Original MT										
MT/GGBFS_90/10 (7d)	8 700	0,37 (±2%)	0,47 (±3%)	0,19 (±0,12%)	0,19	0,2 (±0,4%)	0,19 (±0,3%)	0,18 (±0,1%)	0,19 (±0,2%)	1 (±9%)
MT/GGBFS_90/10 (28d)	5 500	0,3 (±10%)	0,33 (±10%)	0,19 (±0,12)	0,2 (±10%)	0,2 (±0,12%)	0,23 (±10%)	0,2 (±10%)	0,2 (±10%)	0,7 (±10%)
MT/GGBFS_75/25 (7d)	2 800	0,6 (±4%)	0,52 (±3%)	0,2 (±0,12%)	0,2 (±0,08%)	0,22 (±0,3%)	0,21 (±0,3%)	0,2 (±0,04%)	0,2 (±0,1%)	1,5 (±13%)
MT/GGBFS_75/25 (28d)	1500	1 (±10%)	0,44 (±10%)	0,2 (±0,12%)	0,2 (±10%)	0,2 (±10%)	0,23 (±10%)	0,19 (±10%)	0,19 (±10%)	0,68 (±10%)
Heat treated MT										
MT/GGBFS_90/10 (7d)	13 000	0,3 (±1%)	0,49 (±3%)	0,2 (±1%)	0,2 (±0,1%)	0,2 (±0,1%)	0,2 (±0,3%)	0,19	0,19 (±0,1%)	1,6 (±14%)
MT/GGBFS_90/10 (28d)	7600 (±8%)	0,44 (±10%)	0,26 (±10%)	0,49 (±10%)	0,25 (±10%)	0,23 (±10%)	0,25 (±10%)	0,23 (±10%)	0,23 (±0,3%)	0,94 (±10%)
MT/GGBFS_75/25 (7d)	9300	0,19 (±0,2%)	0,17 (±3%)	0,19 (±0,3%)	0,18 (±0,1%)	0,19 (±0,1%)	0,19 (±0,3%)	0,2	0,17 (±0,2%)	1,7 (±15%)
MT/GGBFS_75/25 (28d)	3400 (±8%)	0,19 (±10%)	0,46 (±10%)	0,18 (±10%)	0,19 (±10%)	0,18 (±10%)	0,2 (±10%)	0,17 (±10%)	0,18 (±0,3%)	0,94 (±10%)

Lime acts as a cementitious agent yielding alkaline conditions to the reaction. Available alumina, coming from blast furnace slag or partly from mine tailings, reacts with Ca ions and sulfates producing ettringite ( $3\text{CaO} - \text{Al}_2\text{O}_3 - 3\text{CaSO}_4 - 32\text{H}_2\text{O}$ ) structure [21]. Ettringite consist of columns  $\{\text{Ca}_6[\text{Al}(\text{OH})_6]_2 \cdot 24\text{H}_2\text{O}\}$  and channels  $\{(\text{SO}_4)_3 \cdot 2\text{H}_2\text{O}\}^{6-}$  [30]. In the structure  $\text{Ca}^{2+}$ ,  $\text{Al}^{3+}$  or  $\text{SO}_4^{2-}$  can

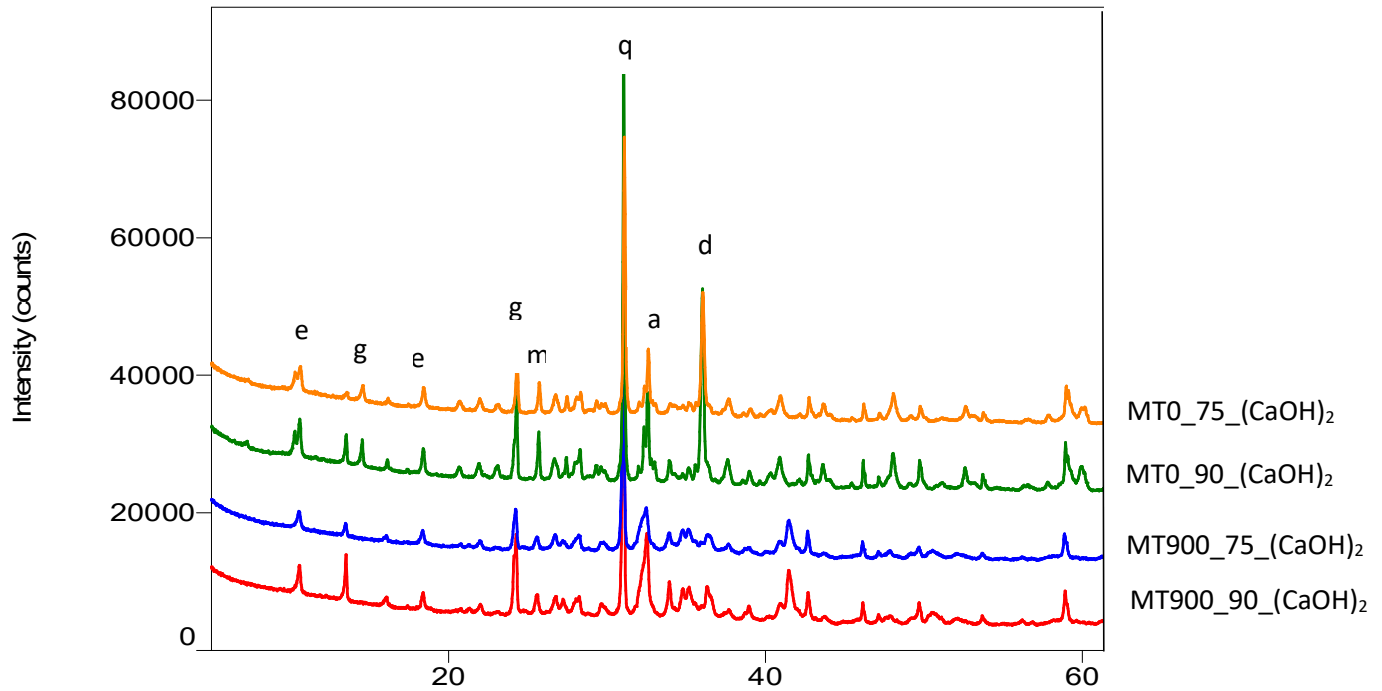
be replaced by other metal ions such as  $\text{Fe}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Sr}^{3+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Co}^{2+}$ , or by some ion group being suitable to stabilize heavy metals effectively in the matrix. Oxyanions such as As can also be substituted either by reacting with surface sites of the ettringite matrix or by substituting into the ettringite channels replacing sulfate. The substitution of the different elements is based on the ion charge and ion size [31]. When multiple anions are present the dominant anion will form ettringite more likely than the others [21].

All harmful components stabilized more efficiently by  $\text{Ca}(\text{OH})_2$  activation compared to  $\text{NaOH}/\text{Na}_2\text{SiO}_3$  activation, with the exception of barium. Stabilization results were improved across the board with longer curing period and the immobilization can be expected to increase further more by longer curing time [11]. Leaching of harmful components were all below the Finnish regular waste law limits and most of them under inert waste law limits after only seven days of curing when activated by  $\text{Ca}(\text{OH})_2$  (Table 4).

### **3.5 Microstructure analysis of the samples**

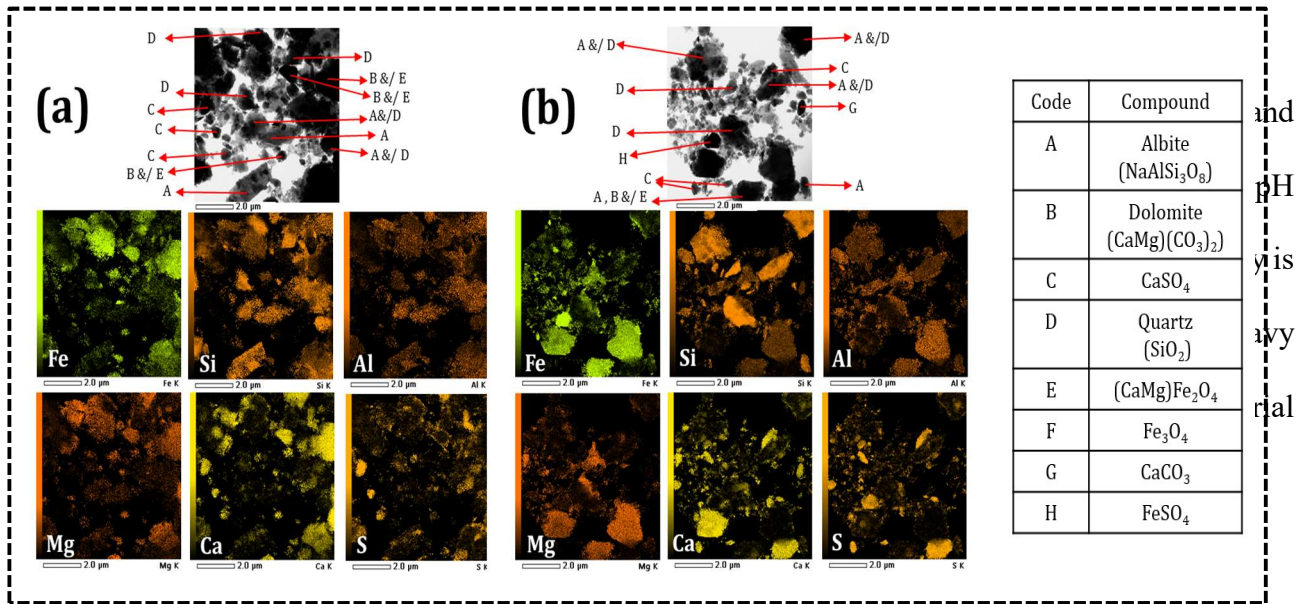
The main peaks quartz, albite and muscovite were found by XRD in all samples after 7d and 28d of curing indicating that they are inert in alkali activation (Fig. 5). Ettringite were found in all samples which can be the one reason for higher immobilization of hazardous element. Dolomite were not found from untreated mine tailings based samples, which is in line with the in situ XRD-analysis results.





**Fig. 5.** XRD analysis of the samples after 7d of curing. (q = quartz, e=ettringite, a=albite, d=dolomite, g=gypsum, m=muscovite.)

Almost all phases that were identified by XRD were also confirmed by TEM analysis (Fig. 6). TEM analysis show that calcium and sulphur form together calcium sulfates. As stated earlier, sulfate preferably form sodium sulfates during alkali activation with NaOH/Na<sub>2</sub>SiO<sub>3</sub> solution. Whereas activation by Ca(OH)<sub>2</sub> promotes the existence of calcium sulfate with lower solubility than sodium sulfate [32,33]. Other phases found from TEM observation includes Fe<sub>3</sub>O<sub>4</sub>, FeSO<sub>4</sub>, (CaMg)Fe<sub>2</sub>O<sub>4</sub>, and CaCO<sub>3</sub>.



**Fig. 6.** STEM Dark-Field Images of two different regions (a and b) after 28d of curing.

#### 4. Conclusion

Activation of sulfidic gold mine tailings with Ca(OH)<sub>2</sub> and 10-25% of GGBFS can effectively stabilize sulfates and arsenic that are the most problematic elements in these mining residues. Over 90 % of sulfates and more than 99 % of arsenic can be stabilized only after a week of curing. The high immobilization of other harmful substances can be also achieved. On the other hand, alkali activation with NaOH/Na<sub>2</sub>SiO<sub>3</sub> does not produce stabilized products. Thermal treatment of the tailings increases the reactivity, but does not significantly improve stabilization of harmful components.

The most probable mechanisms for the effective immobilization by Ca(OH)<sub>2</sub> is formation of calcium sulfate and As precipitation as Ca<sub>3</sub>(AsO)<sub>2</sub>. In this study, calcium sulfate was found by microstructural analysis (TEM) and it is known to have low solubility in comparison to sodium sulfates. Other form of potential immobilization is ettringite formation, and the presence of ettringite was confirmed by XRD in all Ca(OH)<sub>2</sub> activated samples. All final materials had reasonable compressive strength and

could be used for example as mine backfilling materials. The results are encouraging for the utilization capability of sulfidic mine tailings but long-term durability and the immobilization mechanism warrants further research.

## **Acknowledgements**

This work was conducted as part of the ERA-MIN project entitled 'GEOSULF,' which is supported by the Finnish Agency for Technology and Innovation (TEKES); the Portuguese National Funding Agency for Science, Research and Technology (FCT); The National Centre for Research and Development (BR); and various companies (Outotec, Agnico Eagle, and First Quantum Minerals). The authors would like to thank the Renlund Foundation for its financial support. The support of Jenny ja Antti Wihuri Foundation is also appreciated. Ms Katri Piekkari is acknowledged for her contributions to laboratory analyses.

- [1] S. Ahmari, L. Zhang, Durability and leaching behavior of mine tailings-based geopolymer bricks, *Constr. Build. Mater.* 44 (2013) 743–750. doi:10.1016/j.conbuildmat.2013.03.075.
- [2] P. Bankowski, L. Zou, R. Hodges, Reduction of metal leaching in brown coal fly ash using geopolymers, *J. Hazard. Mater.* 114 (2004) 59–67. doi:10.1016/j.jhazmat.2004.06.034.
- [3] E. Ivan Diaz-Loya, E.N. Allouche, S. Eklund, A.R. Joshi, K. Kupwade-Patil, Toxicity mitigation and solidification of municipal solid waste incinerator fly ash using alkaline activated coal ash, *Waste Manag.* 32 (2012) 1521–1527. doi:10.1016/j.wasman.2012.03.030.
- [4] M. Izquierdo, X. Querol, Leaching behaviour of elements from coal combustion fly ash: An overview, *Int. J. Coal Geol.* 94 (2012) 54–66. doi:10.1016/j.coal.2011.10.006.
- [5] I. Lancellotti, E. Kamseu, M. Michelazzi, L. Barbieri, A. Corradi, C. Leonelli, Chemical stability of geopolymers containing municipal solid waste incinerator fly ash, *Waste Manag.* 30 (2010) 673–679. doi:10.1016/j.wasman.2009.09.032.
- [6] V. Nikolić, M. Komljenović, N. Marjanović, Z. Baščarević, R. Petrović, Lead immobilization by geopolymers based on mechanically activated fly ash, *Ceram. Int.* 40 (2014) 8479–8488. doi:10.1016/j.ceramint.2014.01.059.
- [7] J.G.S. Van Jaarsveld, J.S.J. Van Deventer, L. Lorenzen, Factors affecting the immobilization of metals in geopolymerized flyash, *Metall. Mater. Trans. B.* 29 (1998) 283–291. <http://link.springer.com/article/10.1007/s11663-998-0032-z> (accessed August 24, 2016).
- [8] J. Yliniemi, J. Pesonen, M. Tiainen, M. Illikainen, Alkali activation of recovered fuel–biofuel fly ash from fluidised-bed combustion: Stabilisation/solidification of heavy metals, *Waste Manag.* 43 (2015) 273–282. doi:10.1016/j.wasman.2015.05.019.
- [9] J. Zhang, J.L. Provis, D. Feng, J.S.J. van Deventer, Geopolymers for immobilization of Cr<sup>6+</sup>, Cd<sup>2+</sup>, and Pb<sup>2+</sup>, *J. Hazard. Mater.* 157 (2008) 587–598. doi:10.1016/j.jhazmat.2008.01.053.
- [10] L. Zheng, W. Wang, X. Gao, Solidification and immobilization of MSWI fly ash through aluminate geopolymerization: Based on partial charge model analysis, *Waste Manag.* 58 (2016) 270–279. doi:10.1016/j.wasman.2016.08.019.
- [11] J. Kiventerä, I. Lancellotti, M. Catauro, F.D. Poggetto, C. Leonelli, M. Illikainen, Alkali activation as new option for gold mine tailings inertization, *J. Clean. Prod.* 187 (2018) 76–84. doi:10.1016/j.jclepro.2018.03.182.
- [12] P. Duxson, A. Fernández-Jiménez, J.L. Provis, G.C. Lukey, A. Palomo, J.S.J. van Deventer, Geopolymer technology: the current state of the art, *J. Mater. Sci.* 42 (2007) 2917–2933. doi:10.1007/s10853-006-0637-z.
- [13] J.G.S. Van Jaarsveld, J.S.J. Van Deventer, L. Lorenzen, The potential use of geopolymeric materials to immobilise toxic metals: Part I. Theory and applications, *Miner. Eng.* 10 (1997) 659–669. doi:10.1016/S0892-6875(97)00046-0.
- [14] L. Zheng, W. Wang, Y. Shi, The effects of alkaline dosage and Si/Al ratio on the immobilization of heavy metals in municipal solid waste incineration fly ash-based geopolymer, *Chemosphere.* 79 (2010) 665–671. doi:10.1016/j.chemosphere.2010.02.018.
- [15] E. Alvarez-Ayuso, X. Querol, F. Plana, A. Alastuey, N. Moreno, M. Izquierdo, O. Font, T. Moreno, S. Diez, E. Vázquez, M. Barra, Environmental, physical and structural characterisation of geopolymer matrixes synthesised from coal (co-)combustion fly ashes, *J. Hazard. Mater.* 154 (2008) 175–183. doi:10.1016/j.jhazmat.2007.10.008.
- [16] M. Izquierdo, X. Querol, J. Davidovits, D. Antenucci, H. Nugteren, C. Fernández-Pereira, Coal fly ash-slag-based geopolymers: Microstructure and metal leaching, *J. Hazard. Mater.* 166 (2009) 561–566. doi:10.1016/j.jhazmat.2008.11.063.

- [17] J. Kiventerä, L. Golek, J. Yliniemi, V. Ferreira, J. Deja, M. Illikainen, Utilization of sulphidic tailings from gold mine as a raw material in geopolymerization, *Int. J. Miner. Process.* 149 (2016) 104–110. doi:10.1016/j.minpro.2016.02.012.
- [18] I. Lancellotti, J. Kiventerä, M. Catauro, Dal Poggetto, Francesco, Illikainen, Mirja, Inertization of mine tailing via cold consolidation in geopolymer matrix, *Non-Tradit. Cem. Concr.* (n.d.) 120–121.
- [19] J.-Y. Kim, A.P. Davis, K.-W. Kim, Stabilization of available arsenic in highly contaminated mine tailings using iron, *Environ. Sci. Technol.* 37 (2003) 189–195. <http://pubs.acs.org/doi/full/10.1021/es020799+> (accessed August 24, 2016).
- [20] W.-H. Choi, S.-R. Lee, J.-Y. Park, Cement based solidification/stabilization of arsenic-contaminated mine tailings, *Waste Manag.* 29 (2009) 1766–1771. doi:10.1016/j.wasman.2008.11.008.
- [21] M. Chrysochoou, D. Dermatas, Evaluation of ettringite and hydrocalumite formation for heavy metal immobilization: Literature review and experimental study, *J. Hazard. Mater.* 136 (2006) 20–33. doi:10.1016/j.jhazmat.2005.11.008.
- [22] G. Habert, N. Choupay, G. Escadeillas, D. Guillaume, J.M. Montel, Clay content of argillites: Influence on cement based mortars, *Appl. Clay Sci.* 43 (2009) 322–330. doi:10.1016/j.clay.2008.09.009.
- [23] H. Sreenivasan, P. Kinnunen, E.-P. Heikkinen, M. Illikainen, Thermally treated phlogopite as magnesium-rich precursor for alkali activation purpose, *Miner. Eng.* 113 (2017) 47–54. doi:10.1016/j.mineng.2017.08.003.
- [24] H. Xu, J.S. Van Deventer, Geopolymerisation of multiple minerals, *Miner. Eng.* 15 (2002) 1131–1139. <http://www.sciencedirect.com/science/article/pii/S0892687502002558> (accessed September 29, 2017).
- [25] F. Yang, Geopolymerization of copper mine tailings, The University of Arizona. (2014).
- [26] T. Sida, Z. Yuqun, S. Xinqian, C. Changhe, The Chemical Transformation of Calcium in Shenhua Coal During Combustion in a Muffle Furnace, in: H. Qi, B. Zhao (Eds.), *Clean. Combust. Sustain. World*, Springer Berlin Heidelberg, Berlin, Heidelberg, 2013: pp. 143–147. doi:10.1007/978-3-642-30445-3\_22.
- [27] W.M. Swift, A. Panek, G. Smith, G.J. Vogel, A.A. Jonke, Decomposition of calcium sulfate : a review of literature., *Argonne Natl. Lab. Rep. ANL.* (1976 ) 76–122.
- [28] S. Coussy, M. Benzaazoua, D. Blanc, P. Moszkowicz, B. Bussière, Assessment of arsenic immobilization in synthetically prepared cemented paste backfill specimens, *J. Environ. Manage.* 93 (2012) 10–21. doi:10.1016/j.jenvman.2011.08.015.
- [29] P. Kumarathan, G.J. McCarthy, D.J. Hassett, D.F. Pflughoeft-Hassett, Oxyanion Substituted Ettringites: Synthesis and Characterization; and their Potential Role In Immobilization of As, B, Cr, Se and V, *MRS Proc.* 178 (1989). doi:10.1557/PROC-178-83.
- [30] H.F.W. Taylor, Crystal Structures of Some Double Hydroxide Minerals, *Mineral. Mag.* 39 (1973) 377–389. doi:10.1180/minmag.1973.039.304.01.
- [31] S.C. Myneni, S.J. Traina, T.J. Logan, G.A. Waychunas, Oxyanion behavior in alkaline environments: sorption and desorption of arsenate in ettringite, *Environ. Sci. Technol.* 31 (1997) 1761–1768. <http://pubs.acs.org/doi/abs/10.1021/es9607594> (accessed September 14, 2017).
- [32] R. Wells, Sodium sulphate: Its sources and uses, Wash. Gov. Print. Off. (1923).
- [33] E.P. Partridge, A.H. White, The solubility of calcium sulfate from 0 to 200°, *J. Am. Chem. Soc.* 51 (1929) 360–370. doi:10.1021/ja01377a003.