

HOSTED BY



ELSEVIER

Contents lists available at ScienceDirect

Journal of Sustainable Mining

journal homepage: [www.elsevier.com/locate/jsm](http://www.elsevier.com/locate/jsm)

Research paper

# Efficiency of MgO activated GGBFS and OPC in the stabilization of highly sulfidic mine tailings

Minna Sarkkinen<sup>a,\*</sup>, Kauko Kujala<sup>b</sup>, Seppo Gehör<sup>c</sup><sup>a</sup> Kajaani University of Applied Sciences, P.O.Box 52, FI-87101, Kajaani, Finland<sup>b</sup> Kajaani University of Applied Sciences/Solid Liner Ltd, P.O.Box 52, FI-87101, Kajaani, Finland<sup>c</sup> University of Oulu, P.O. BOX 8000, FI-90014, University of Oulu, Finland

## ARTICLE INFO

## Keywords:

AMD  
Stabilization  
Tailings  
Diffusion  
Alkali-activation

## ABSTRACT

MgO activated ground granulated blast furnace slag (GGBFS) is a form of alkali-activated composite, which is successfully used as a binder in the stabilization of highly sulfidic mine tailings. The aim of this study was to compare alkali activated composite (AAC) and ordinary Portland cement (PC) as stabilization agents, as well as their efficiency to stabilize sulfidic tailings and the results of three different diffusion and leaching methods. The Life Cycle Assessment (LCA) method was used to compare the environmental impacts of the binders. The lab-scale program covered hydraulic conductivity, compression strength, and freeze-thaw resistance tests of the stabilized tailings. The results indicate that the hydraulic conductivity ( $6.08 \cdot 10^{-9}$  m/s) and compressive strength (11.5 MPa at 28 days) of AAC were better in comparison, if the corresponding amount of PC ( $2.04 \cdot 10^{-8}$  m/s and 10.3 MPa at 28 days) was used. LCA shows clear ecological benefits when using AAC instead of PC in terms of lower global warming potential. Diffusion and leaching tests indicated better immobilization efficiency of AAC than PC concerning As, Cr, Cu, Ni, Se, Zn, and especially Mo. In comparison with plain tailings, AAC stabilization reduced leaching of As, Cr, Cu, Mo, Ni, Pb, Se, Zn, Cl, and  $\text{SO}_4$  better than PC.

## 1. Introduction

The various branches of the mining industry are the biggest producers of waste materials in the form of waste rock and tailings. About 7 gigatons of tailings are produced by the mining industry annually, in addition to the billions of tons that already exist, and production is increasing (Mudd & Boger, 2013; Wang, Harbottle, Liu, & Xu, 2014).

Hazardous substances in the tailings and the toxic additives used in the metal processing phase create potential ecological risks (Manjunatha & Sunil, 2013). Sulfides in the tailings can oxidize when exposed to oxygen and water, generating harmful acid mine drainage (AMD) as well as other harmful substances, which is an important ecological challenge for the mining industry. Serious environmental accidents worldwide have increased public awareness, and increasingly stringent environmental regulations have promoted research which aims to develop new innovative approaches of mitigating the risks caused by tailings. More common extreme weather phenomena due to climate change are also likely to increase safety risks created by tailings (Edraki et al., 2014). In addition, more than 18 400 tailing dams worldwide have potential failure risks (Azam & Li, 2010). For example, in China tailing storage is defined as one the most dangerous

environmental risk sources (Xie, Tian, Wang, and Zhan., 2009).

The chemical stabilization of tailings is a commonly used technology to prevent the leaching of hazardous substances into the natural environment. Stabilization captures the harmful substances in an immobile form in a binder matrix (Lange, Hills, & Poole, 1995). According to the literature, the MgO activated ground granulated blast furnace slag (GGBFS) binder has not yet been studied or used in the stabilization of highly sulfidic tailings, whereas PC is a commonly used stabilization binder (e.g. Desogus, Manca, Orru, & Zucca, 2013; Jin & Al-Tabbaa, 2014; Yi, Liska, & Al-Tabbaa, 2014). However, the long-term durability of PC, especially in highly sulfidic environments, is questionable due to its vulnerability to sulfate attacks and ecological impacts (e.g. Cihangir, Ercikdi, Kesimal, Turan, & Deveci, 2012; Tariq & Yanful, 2013). It is also known that several metals have negative effects on the hydration processes of PC, which needs to be accounted for when using PC as a stabilization agent.

Cement reaction in tailings occurs in two phases (Nehdi & Tariq, 2007). During the first phase tricalcium silicate ( $\text{C}_3\text{S}$ ) or ( $3\text{CaO}\cdot\text{SiO}_2$ ) releases  $\text{Ca}^{2+}$ ,  $\text{H}_2\text{SiO}_4^{2-}$  and  $\text{OH}^-$  ions in the cement dissolving reaction. Calcium ion content increases rapidly in the early phase until the saturation point is achieved. In the second phase, binder hydrate phases

\* Corresponding author.

E-mail addresses: [minna.sarkkinen@kamk.fi](mailto:minna.sarkkinen@kamk.fi) (M. Sarkkinen), [kauko.kujala@oulu.fi](mailto:kauko.kujala@oulu.fi) (K. Kujala), [seppo.gehor@oulu.fi](mailto:seppo.gehor@oulu.fi) (S. Gehör).

(e.g. C–S–H) promote the strength development of the tailing-cement paste. However, sulfate can cause a strength decrease in cement. It is also known that the presence of a combination of high pH, soluble Al, Ca, sulfides, and water constitutes a risk to generate expansive ettringite (Seco et al., 2017).

Binder reactions of GGBFS have been activated and modified, for instance with reactive magnesia and different combinations of magnesia, dolomite, calcium hydroxide, and oxide (Gu, Jin, Al-Tabbaa, Shi, & Liu, 2014; Sarkkinen, Tuomikoski, Kujala, Kemppainen, & Gehör, 2017). Jin, Gu, and Al-Tabbaa (2015) compared hydrated lime and reactive MgO for activating GGBFS and found that MgO was the more efficient activator and was more efficient at immobilizing lead and zinc (Jin & Al-Tabbaa, 2014). Furthermore, Yi, Liska, Jin, and Al-Tabbaa (2016) compared reactive MgO, brucite, and hydrated lime activated GGBFS in soil stabilization and stated that reactive MgO had the highest activating efficacy. Yi, Gu, Liu, and Jin (2016) studied how different reactivity degrees and dosages of MgO influence the activation of GGBFS in soft clay stabilization. According to their results, higher reactivity of MgO was beneficial but excessive MgO content reduced the strength development of stabilized clay. In addition, Jin, Wang, and Al-Tabbaa (2016) compared different MgO-bearing binders in the stabilization of highly contaminated soil and concluded that MgO activated GGBFS had superior performance compared to Portland cement after three years.

The reactivity rate and the generation of hydration products, such as C–S–H and hydrotalcite (Ht), are influenced by activator composition and amount, and thus the binder can be optimized according to the needs of specific applications. There have previously been some results, which are conflict to some extent, on the performance of MgO activated GGBFS in sulfate bearing soils. According to some studies (e.g. Gu et al., 2014), sulfate can form ettringite and expansive reactions in the long term, especially when using reactive magnesia. According to other results, MgO activated GGBFS had better resistance against sulfate and acid, compared to PC as a stabilization agent, and no expansion due to non-controlled ettringite formation was observed (Yi, Li, et al., 2014). In addition, it has been stated that MgO is a better activator of GGBFS than lime in terms of mechanical characteristics and the formation of expansive minerals when used in the stabilization of sulfate-bearing soils (Seco et al., 2017). On the other hand, excessive MgO can generate expansion due to magnesia hydration to brucite and cracking due to excessive Ht formed in the reaction between MgO and GGBFS (Gu et al., 2015).

In addition, commonly used liquid alkali activators, such as sodium and potassium hydroxides and silicates, present safety concerns due to the handling risks of high alkali solutions, relatively high costs, and ecological issues regarding the resources needed in their production. For example, about 20 megatons of magnesia are produced annually, mainly in China, and its price is typically between US\$180–US\$350/t in China. This is less than, for instance, the price of NaOH (ca. US\$500/t in China), the most commonly used alkali-activator of GGBFS. The main goals of this study were: a) to compare the chemical and physical performance of PC and AAC as the stabilization binders of sulfide tailing material, b) to study the efficiency of AAC and PC stabilization to capture hazardous substances in high sulfide tailings, and c) to compare three different diffusion analysis methods to obtain information on the variability of the results in terms of the method. A range of laboratory tests and analyses were conducted in addition to LCA.

## 2. Materials and methods

### 2.1. Materials

The Pyhäsalmi mine in Finland is one of the largest massive sulfidic ore mine in the world. The total area of the tailing ponds is 150 ha, which approximately 50% of this space had been covered using conventional methods (till) by the beginning of the millennium. The

tailings potentially generate acid, mostly due to the oxidation of iron sulfides (58%). The mine will be closed in the near future, and the principal aim of the tailing recovery plan is to decrease environmental risks in the long term by restricting acid generation caused by water and oxygen ingress. Several different cover liner options for tailing ponds have been considered.

Tailings samples were collected from a maximum depth of 500 mm from the tailings pond of the mine, during 2017. The samples were stored in a sealed container before analysis. PC of class CEM II/B-M (3-LL) 42,5 N by Finnsementti Ltd, included GGBFS and limestone as additives, circa 21–35%. GGBFS (KJ100) was delivered by Finnsementti Ltd. The magnesia was of a reactive type, derived from the talc mine byproducts and calcined at 700 °C.

### 2.2. Test methods

The particle size distribution (PSD) of the tailings was determined by an Alpine wind sieve in addition to a normal sieve series. Tailings, GGBFS, and MgO were characterized chemically by an x-ray fluorescence analyzer (XRF).

The binders (10 w%) were mixed with tailing materials in the Hobart mixer. The mixes were consolidated using a vibrating table. The size of the cube specimens was 100 × 100 × 100 mm and the diameter of the cylinder specimens used for the measurement of hydraulic conductivity was 100 mm. The specimens were covered with a plastic sheet and stored in air at the temperature of 18 °C. The compressive strength was measured from separate cubes after 28 days of being cured under normal conditions and after 10 freeze-thaw cycles. Repeating freeze-thaw cycles can lead to physical damage in stabilized matrices in cold regions. The freeze-thaw resistance test was executed by using PC and AAC as stabilization agents. The compressive test was performed using the universal compressive testing machine Matest C089–04 N and Standard SFS-EN 12390–4. The freeze-thaw test was executed by applying the method described in the standard for unbound and hydraulically bound mixtures (CEN/TS 13286–54). The minimum temperature used was –5 °C, because in practice the temperature does not go below –5 °C due to protective till layers.

The greatest value of hydraulic conductivity defines the main criteria for tailing cover of the mine in the environmental permit. The hydraulic conductivity of stabilized test samples was measured after 28 days of being cured in the air, according to the Standard ASTM D 5084 using the flexible cell method.

#### 2.2.1. Diffusion tests

Three diffusion and leaching test procedures (surface leaching from a monolithic sample, leaching from a crushed material, and a column leaching test) were performed to recognize the usability of the test methods and to receive reliable results. The specimens used in the test were 100 × 100 × 100 mm cubes prepared using PC and AAC stabilized tailings. For each test method one AAC and PC cube was prepared. A monolithic sample was employed in the surface leaching test method and crushed samples for the other two methods.

The first diffusion test was performed according to the Standard NEN 7345/7347. The Standard method for the test arrangement was followed. It states that leaching is to be restricted to one surface of the cubic sample. The water used was pH neutral ultra-pure (UP) water (conductivity 0.055 µS/cm). The sample cube was isolated except for on one surface, using paraffin or Teflon tape to prevent diffusion. The fractions used were 0.25; 1; 2.25; 4; 9; 16; 36; 64 days.

Dutch diffusion test NEN 7345 measures the leaching of the materials used, especially in soil construction. The diffusion leaching test presumes that the leaching in the storage location is based on diffusion leaching. This requirement is met when water penetration into the material is restricted by using material with low hydraulic conductivity ( $k < 10^{-8}$  m/s) or when material (e.g. stabilized tailings) has a compressive strength of  $> 1$  MPa and hydraulic conductivity of  $< 10^{-9}$  m/

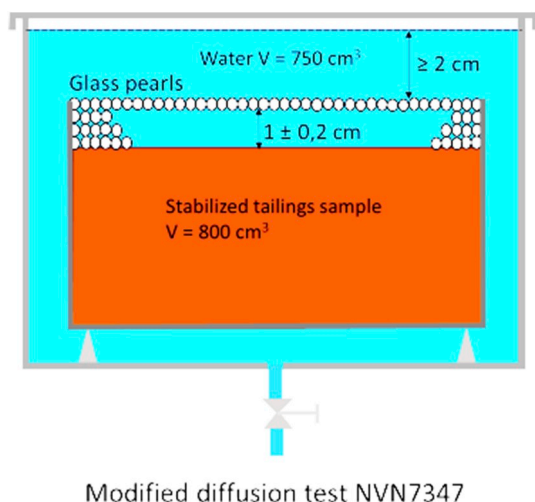


Fig. 1. The arrangement of the test methodology of the modified diffusion test NVN 7347.

s. The stabilized AAC and PC test specimens were stored in water for 64 days. The pH of the water was adjusted to pH 4 and the water volume ratio to specimen volume was 5 (Fig. 1 illustrates the principle of the test arrangement only). The water was changed 8 times during the test after 6 h, 1 day, 2.25 days, 4 days, 9 days, 16 days, 36 days, and 64 days from the beginning of the test to simulate natural conditions and the impact of rainwater (Mäkelä, Wahlström, Pihlajaniemi, & Mroueh, 1998). The test arrangements for the modified diffusion test NEN 7345/7347, based on the Dutch diffusion test for solidified materials, is presented below.

The test material was placed into the test box and the surface of the sample was covered with glass pearls. The test box was placed into the water, which was changed 8 times in 64 days. The mass of the leached material ( $\text{mg}/\text{m}^2$ ) was measured in relation to time.

The second diffusion test was made from a crushed sample. This simulates contaminant migration into the material, in case the stabilized material breaks in extreme conditions. The test was conducted according to the Standard NEN 7347/CEN/TS 16637–2. The sample material was crushed to  $< 4$  mm and the test was conducted at pH 7. The measured fractions were 0.25; 1; 2.25; 4; 9; 16; 36, and 64 days.

The third test was conducted according to the Standard CEN/TS 14405:04 and using crushed sample material of  $< 4$  mm. The test comprised of 7 fractions: (liquid to solid ratio) L/S 0.1; L/S 0.2; L/S 0.5; L/S 1; L/S 2, L/S 5, and L/S 10. All three test methods consisted of elemental analysis for 30 elements determined by ICP-MS/ICP-OES using MS for Al, As, B, Ba, Be, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sb, Se, Sn, Sr, Tl, V, Zn, Hg, and U. An optical emission spectrometer (OES) was used for the determination of Ca, K, Mg, Na, S, P, and Si. In addition, chloride, sulfate, fluoride, pH, and conductivity were also measured.

### 3. Results

#### 3.1. Tailing characteristics

According to the PSD analysis, the tailing material is comprised partly of silt and partly of clay. PSD of the tailings is presented in Table 1.

The PSD of the tailings varied which was related to the sampling point being coarser close to the spigot.

The chemical compositions of the tailings, GGBFS, and MgO based on XRF are presented in Table 2.

According to the analysis, the solid tailings sample contained over 34%  $\text{SO}_3$ , up to 20.8%  $\text{Fe}_2\text{O}_3$  and 17.3%  $\text{SiO}_2$  as major components.

Table 1  
Average particle size distribution of the tailings.

Characteristics	Average
Sand (75 $\mu\text{m}$ – 4,75 mm) %	40
Silt (2–75 $\mu\text{m}$ ) %	46
< 20 $\mu\text{m}$ (%)	18
< 30 $\mu\text{m}$ (%)	45
< 60 $\mu\text{m}$ (%)	100

Table 2  
Chemical composition of the studied material (%) by XRF.

Characteristics	Tailing average	Tailing standard deviation	GGBFS	MgO
$\text{SiO}_2$ (%)	17.292	4.67	26.676	0.816
$\text{Al}_2\text{O}_3$ (%)	4.716	1.14	7.488	0.000
$\text{Fe}_2\text{O}_3$ (%)	20.845	3.84	0.646	7.449
MgO (%)	5.164	0.72	8.712	78.773
CaO (%)	8.274	3.56	39.752	7.466
$\text{SO}_3$ (%)	34.145	8.76	2.420	0.233
$\text{K}_2\text{O}$ (%)	0.626	0.21	0.591	0.000

#### 3.2. Compressive strength and freeze-thaw resistance

Table 3 illustrates the change in compressive strength and density after 10 freeze-thaw cycles.

The compressive strength after 28 days was 8.9 MPa when using PC and 10.2 MPa when using AAC. The strength is sufficient when considering the strength requirement for the general soil mixing applications of 0.1–5.0 MPa (Bruce, 2001) and the 1 MPa threshold criterion for landfill disposal (Environment Agency, 2006). The results indicate that there was no visible cracking or other damage in the specimens due to freeze-thaw cycles because the compressive strength and density increased after 10 cycles, which was likely caused by an increase in the binder products formed due to extra moisture and higher temperatures during the warmer cycle period. The test duration was 10 days which may also positively affect the strength development during the test. However, the strength change was not very significant during the test. In general, the slight increase in strength indicates denser structure which improves stabilization. Higher density indicates lower hydraulic conductivity and lower leaching, which is visible in the diffusion and leaching results of AAC and PC samples. Moreover, the change was a few MPa only, which means that closer leaching testing is not needed.

#### 3.3. Hydraulic conductivity

The hydraulic conductivity indicates the transport of leachate substances through the stabilized tailings into underlying layers and into groundwater. The results show that AAC had slightly lower hydraulic conductivity than PC (Fig. 2).

Hydraulic conductivity is influenced by several factors, including material PSD and packing density, properties of the reactive binder products, and the consolidation of the interfacial transition zone (ITZ) between binder paste and tailing particles (Nehdi & Mindess, 1999). According to the tests, both binder types decreased hydraulic conductivity when using 10 w% dosage. With plain tailing material, the hydraulic conductivity was  $3.7 \times 10^{-7}$  m/s with PC  $2.0 \times 10^{-8}$  m/s and AAC  $6.0 \times 10^{-9}$  m/s. The threshold of  $10^{-9}$  m/s is the most commonly used limit for in-ground treatment (Kogbara, Al-Tabbaa, & Stegemann, 2014). One likely explanation for the lower hydraulic conductivity of AAC stabilized tailings is their higher packing density. The result also supports the presumption that the replacement of PC with GGBFS improves sulfate resistance and forms a denser binder matrix which reduces hydraulic conductivity (Obuzor, Kinuthia, & Robinson, 2012).

**Table 3**  
Change in compressive strength and density after 10 freeze-thaw cycles.

	After 28 days curing at 18 °C Tailings: PC	Tailings: AAC	After 10 freeze-thaw cycles Tailings: PC	Tailings: AAC
Compressive strength (MPa)	8.9	10.2	11.42	13.5
Density (kg/m <sup>3</sup> )	2281	2385	2321	2408

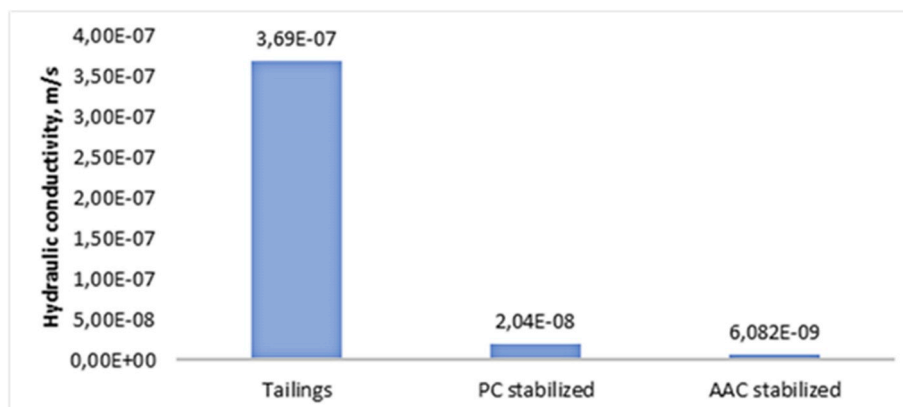


Fig. 2. The hydraulic conductivity of the tailings, tailings stabilized with PC 10 w%, and tailings stabilized with AAC 10 w%.

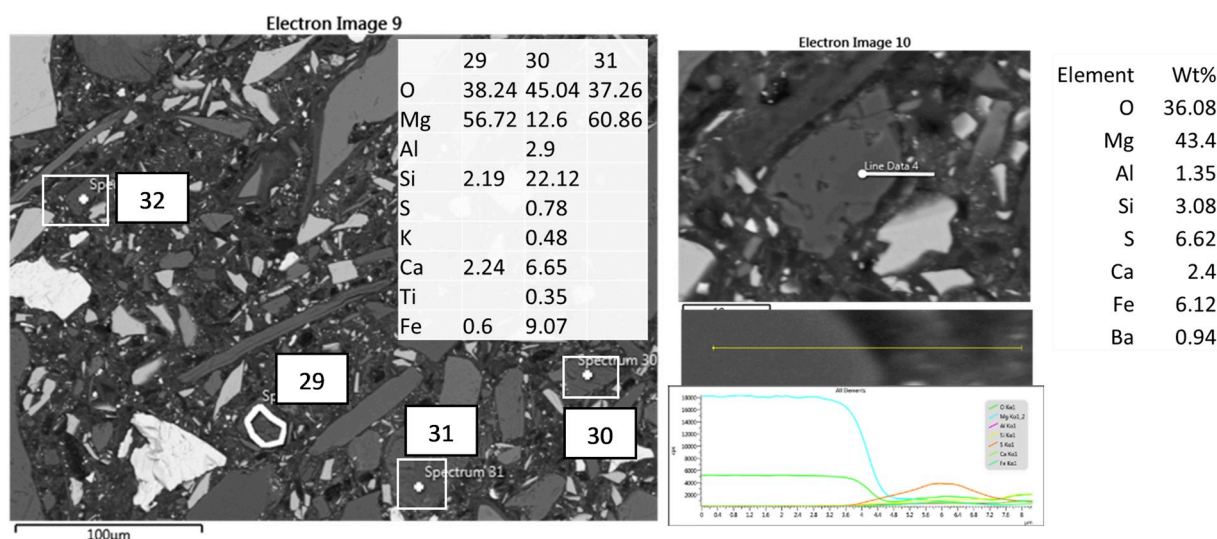


Fig. 3. BEI and EDS analyses on the AAC stabilized tailings on the left. Magnification of MgO grain in spectrum 32 on the right.

3.4. Microscopic analyses

Backscattered electron image (BEI) and energy-dispersive detector (EDS) analyses on the AAC stabilized tailings highlight the better efficiency of the binder in the encapsulation of harmful substances (Fig. 3). It is known that activator quality and processing (e.g. calcination and particle size optimization) influence hydration properties (Jin, Abdollahzadeh, & Al-Tabbaa, 2013). For example, MgO can accelerate the formation of hydrotalcite and develop denser pore structure (Jin, 2014). Magnesia can also encapsulate heavy metals more efficiently than ordinary PC, which has led to an interest in studying the usage of magnesia within the rehabilitation of contaminated soils (Al-Tabbaa, Evans, & Barker, 2011). The reactions of MgO form suitable pH (ca. 10.5) for the encapsulation of heavy metals and this reaction produces brucite (Mg(OH)<sub>2</sub>) which efficiently encapsulates heavy metals and organic compounds through hydrogen bonds or ion exchanges (Tresintsi et al., 2014).

Magnesium oxide (MgO) and BFS are both known to present high adsorption capacity at certain pH, especially for As, F, P, and for

divalent cations like Ni, Cd, and Pb. The BEI images and EDS-analyses of AAC stabilized tailings indicate the presence of slag and MgO particles in the binder, which represent a reaction surface for infiltrating contaminants.

3.5. Diffusion tests

The results of the modified diffusion test NEN 7345/7347 on the monolithic sample (mg/m<sup>2</sup>/64d) of the PC and AAC stabilized tailings were compared to the results of the diffusion test using a crushed sample applying NEN 7347 (mg/m<sup>2</sup>/64d) for solidified soil construction materials. The results presented in Figs. 4–6 were compared to Dutch and Finnish guidelines. Dutch class 1A is for wet placement, Dutch class 1B and Finnish Environmental Institute’s (FEI) values are for occasionally wet placement.

The results indicate that most of the values met Class 1A, except the leaching of Mo and Se. The difference is significant when compared to the maximum values of the presented guidelines’ classification. When using AAC the stabilized tailings could be classified as 1B, but when

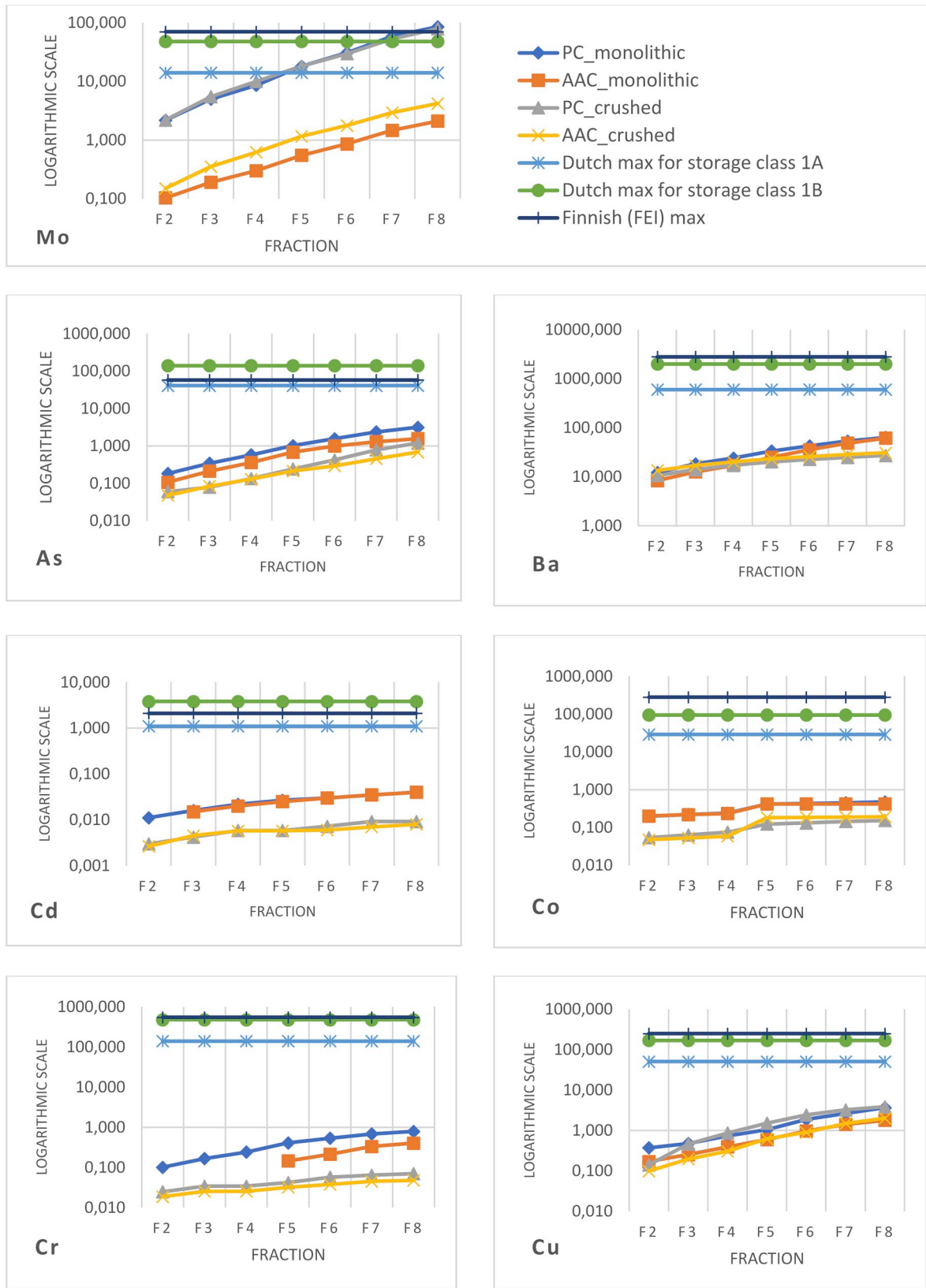


Fig. 4. Diffusion ( $\text{mg}/\text{m}^2/64\text{d}$ ) of Mo, As, Ba, Cd, Co, Cr and Cu from monolithic and crushed samples.

using PC the values did not meet the guidelines.

The results were on the whole similar when comparing the two test methods. The leaching trend clearly rose with Mo, Sb, Se, Cu, As, and V in all the measurements. The leaching of Mo and Se and also of Cu, Ni,

Pb, and Zn from PC stabilized tailings in crushed samples was higher, but slightly lower for Ti and V in comparison with the AAC stabilized tailings. The leaching from monolithic samples was higher from PC stabilized tailings with regard to Cr, Sb and Zn but lower for V. The only

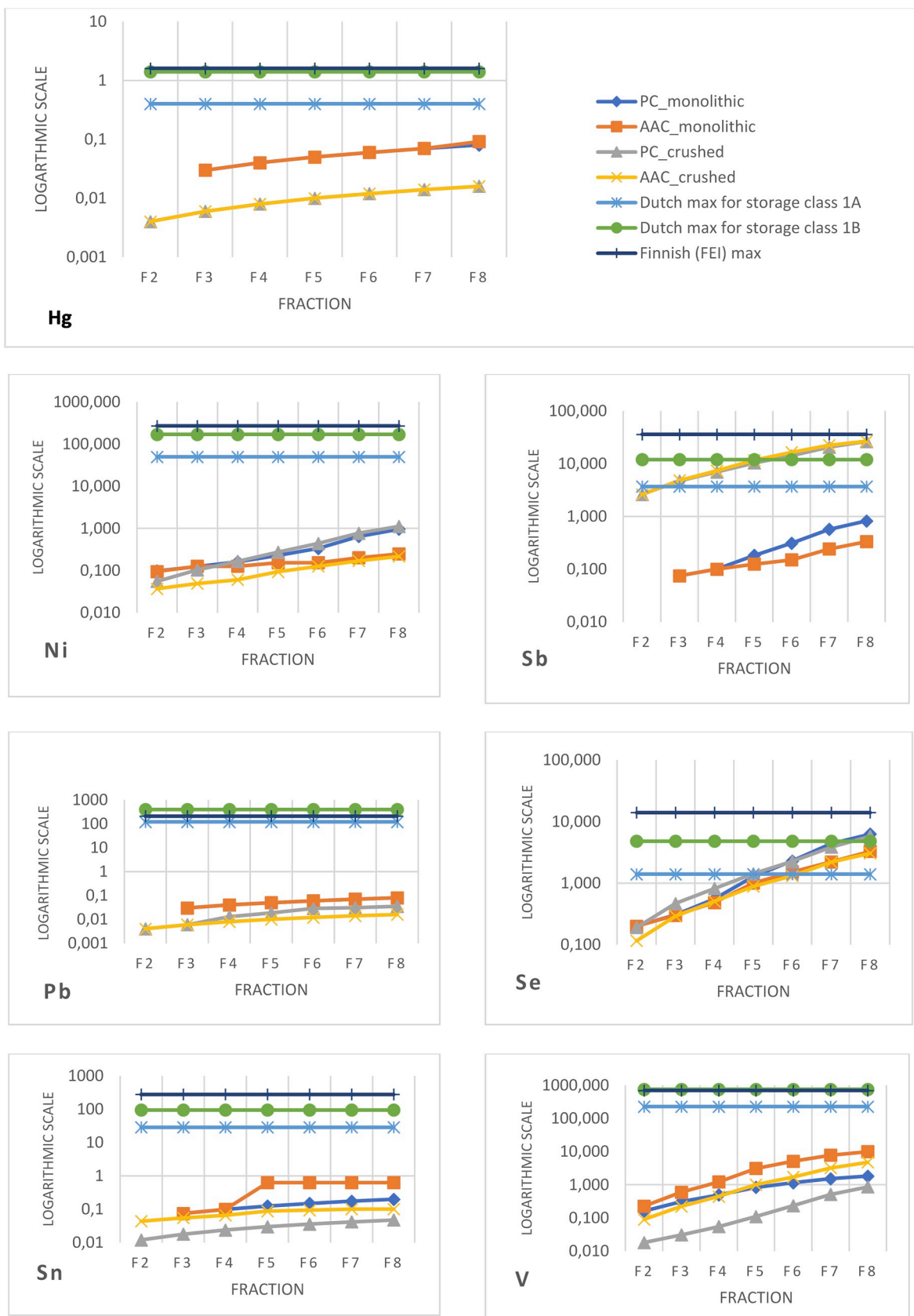


Fig. 5. Diffusion (mg/m<sup>2</sup>/64d) of Hg, Ni, Sb, Pb, Se, Sn and V from monolithic and crushed samples.

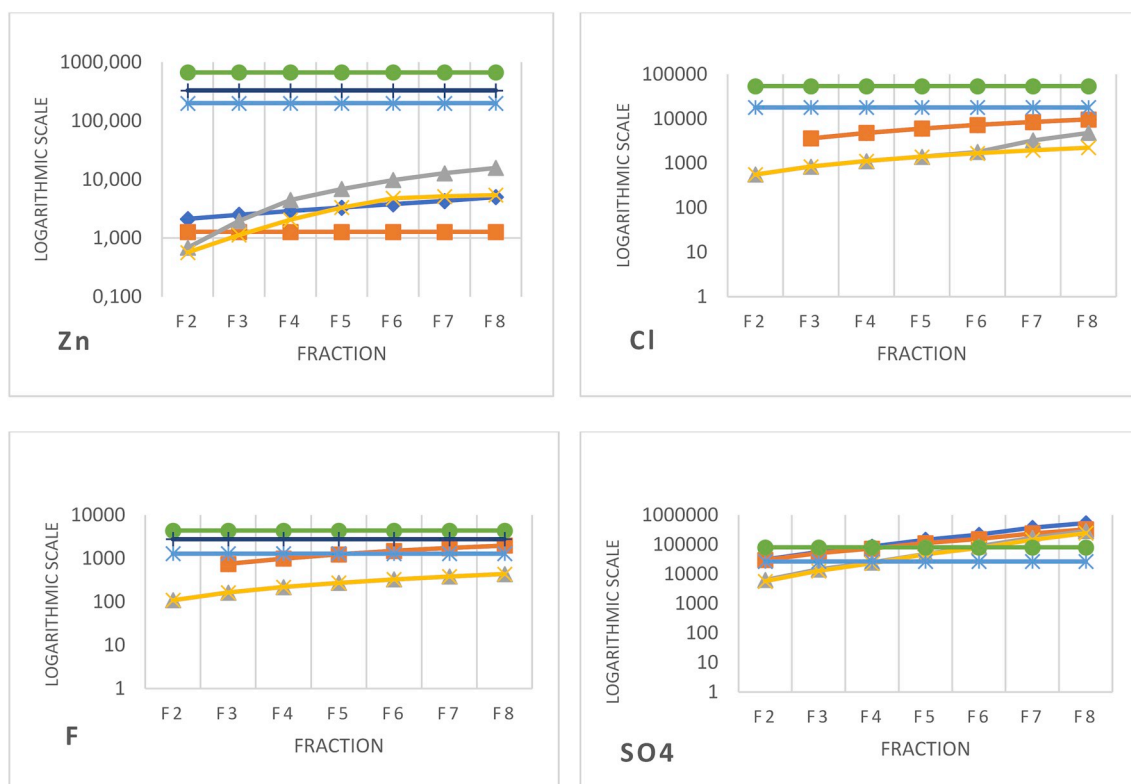


Fig. 6. Diffusion (mg/m<sup>2</sup>/64d) of Zn, Cl, F, and SO<sub>4</sub> from monolithic and crushed samples.

difference between the two results was the values for the leaching of Sb, which were higher when using the crushed sample. However, the difference for the leaching of Sb was minor when compared to the stabilization with AAC and PC.

The results of the two diffusion tests of monolithic and crushed samples were compared with the results of the up-flow percolation leaching test (Fig. 7 and Fig. 8). The results were compared using the Finnish criteria for contaminated soils which identifies three different classes: contaminated soil applicable for inert waste storage (class 1), non-hazardous waste storage (class 2), and hazardous waste (class 3), regarding As, Ba, Cd, Cr, Cu, Sb, Ni, Pb, Mb, Se, Zn, Hg, F, SO<sub>4</sub>, and Cl. In addition, results from the plain tailings sample are presented in the figures below.

In general, the results for the stabilized tailings are in line with the previous two tests. Both stabilization binders reduce the leaching of Cd, Cu, Ni, Pb, Zn, SO<sub>4</sub>, Co, Al, Fe, Mn, U, Mg, S, and Si. When comparing the efficiency of AAC and PC, as stabilization agents, the leaching values of Se and Mo were clearly lower when using AAC compared to PC and this influenced waste classification. With regards to the plain tailings, Zn leaching was above all accepted values, but the stabilization was below Class 1. Cd and SO<sub>4</sub> content were in Class 3, but stabilized tailings could be classified as inert waste when considering Cd and as non-hazardous waste when considering SO<sub>4</sub>. Ni leaching from tailings without stabilization was higher than expected for Class 1, but below the limit from tailings with stabilization. The leaching trend was rising in all cases and this was stronger for SO<sub>4</sub>, F, Hg, Sb, and Se. Generally, leaching was approaching the limit values with higher fractions. The tailings sample was from a different batch than the tailings material used in the studied stabilized samples, thus explaining the lower leaching of Se and Mb in comparison with the stabilized samples.

### 3.6. Life cycle assessment

The aim of the LCA is to compare the ecological impacts of the two stabilization binders. Life cycle assessment (LCA) was conducted using

SimaPro software, which uses the EcoInvent database. The method used was the Greenhouse Gas Protocol V102. The production and transportation distances by trucks to the site were considered to be influencing factors, while the need for equipment and related environmental impacts were the same for the both binders (Fig. 9).

The LCA indicates the negative impact of PC, especially in terms of fossil CO<sub>2</sub> eq. The positive impact of the AAC binder compared to PC is visible in terms of fossil eq, biogenic CO<sub>2</sub> eq, CO<sub>2</sub> eq from the land transformation, and CO<sub>2</sub> uptake. Exploitation of waste-based binders for AAC indicates clear ecological benefits when compared to PC. In this case, the production of materials has a significant impact while transport only has a minor impact. This is typical for stabilization binder materials, as the material demand is much lower compared to the use of tailing cover alternatives, based on, for example, the use of till.

## 4. Discussion

The main goals of this study were: a) to compare the chemical and physical performance of PC and AAC as stabilization binders of sulfide tailings material, b) to study the efficiency of AAC and PC stabilization to encapsulate hazardous substances in sulfide tailings and c) to compare the results of three analysis methods simulating diffusion and leaching under different conditions from monolithic or crushed samples. Table 4 and Table 5 summarize the relative differences between the diffusion test results.

Considering the first goal, a) on differences between the performance of AAC and PC as stabilization agents, the compressive strength development and durability test results showed the better performance of MgO activated GGBFS than PC in the sulfidic environment. Furthermore, hydraulic conductivity was lower with AAC than with PC stabilization. According to earlier studies, MgO activated GGBFS forms hydrotalcite, which fills the pores which in turn compacts and strengthens the soil structure (Yi, Liska, Jin, & Al-Tabbaa, 2016). Expansion or cracking was not observed in this research. According to the diffusion tests, AAC stabilization could clearly reduce the leaching of

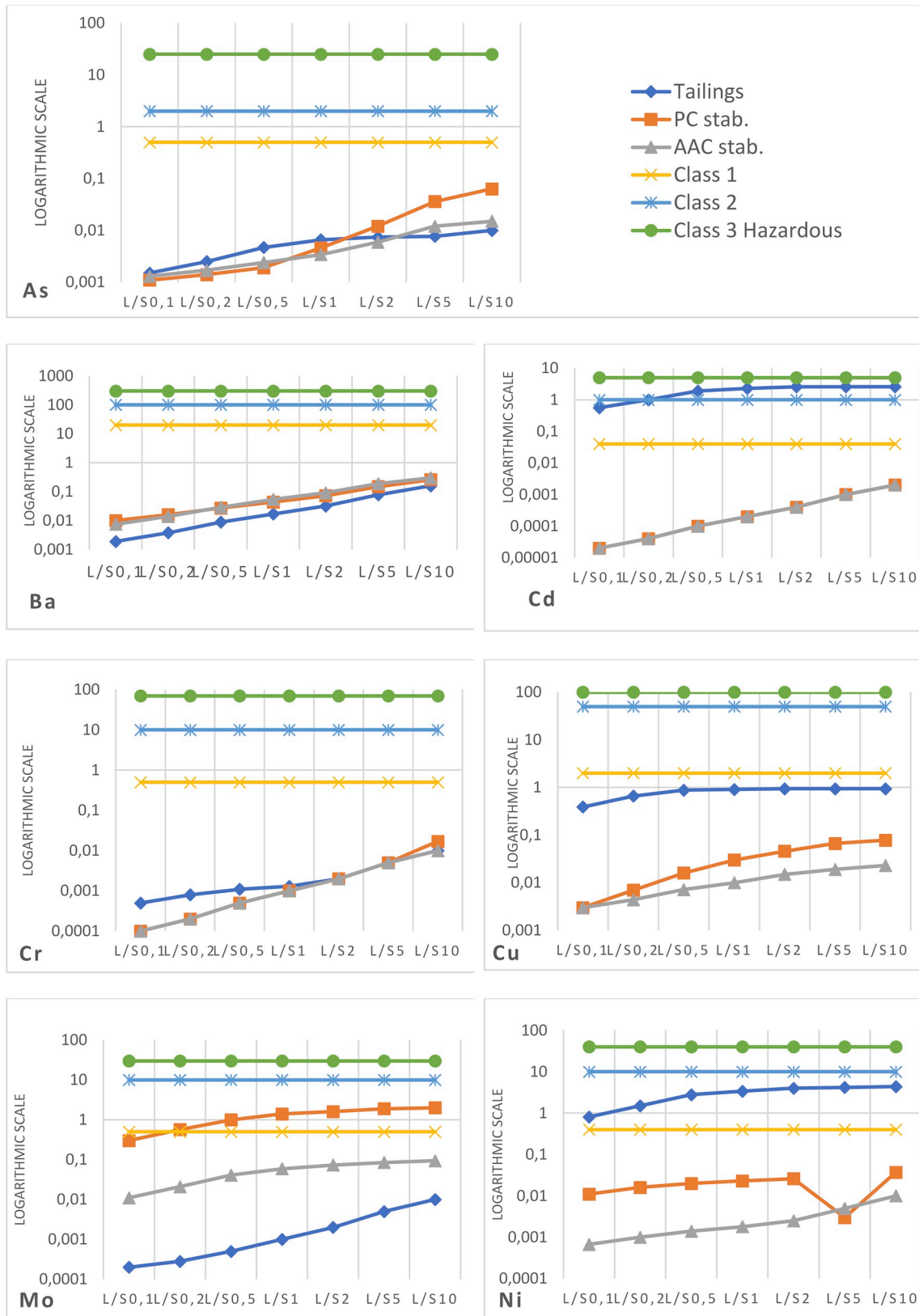


Fig. 7. Leaching (mg/kg) of As, Ba, Cd, Cr, Cu, Mo, and Ni.

As, Cr, Cu, Mo, Ni, Pb, Se, Zn, Cl, and SO<sub>4</sub> better than PC (Table 4). This is supported by the findings of Jin and Al-Tabbaa (2014) on the efficiency of MgO-GGBFS to immobilize Pb and Zn. The main reason for this good immobilization was the hydrotalcite formed and the good pH

buffering capacity of the binder. On the other hand, PC can have low efficiency when it comes to immobilizing As (Jin, Wang, & Al-Tabbaa, 2016). According to the same study, MgO-bearing binders can effectively decrease the leaching of Cu and Ni. These results support the



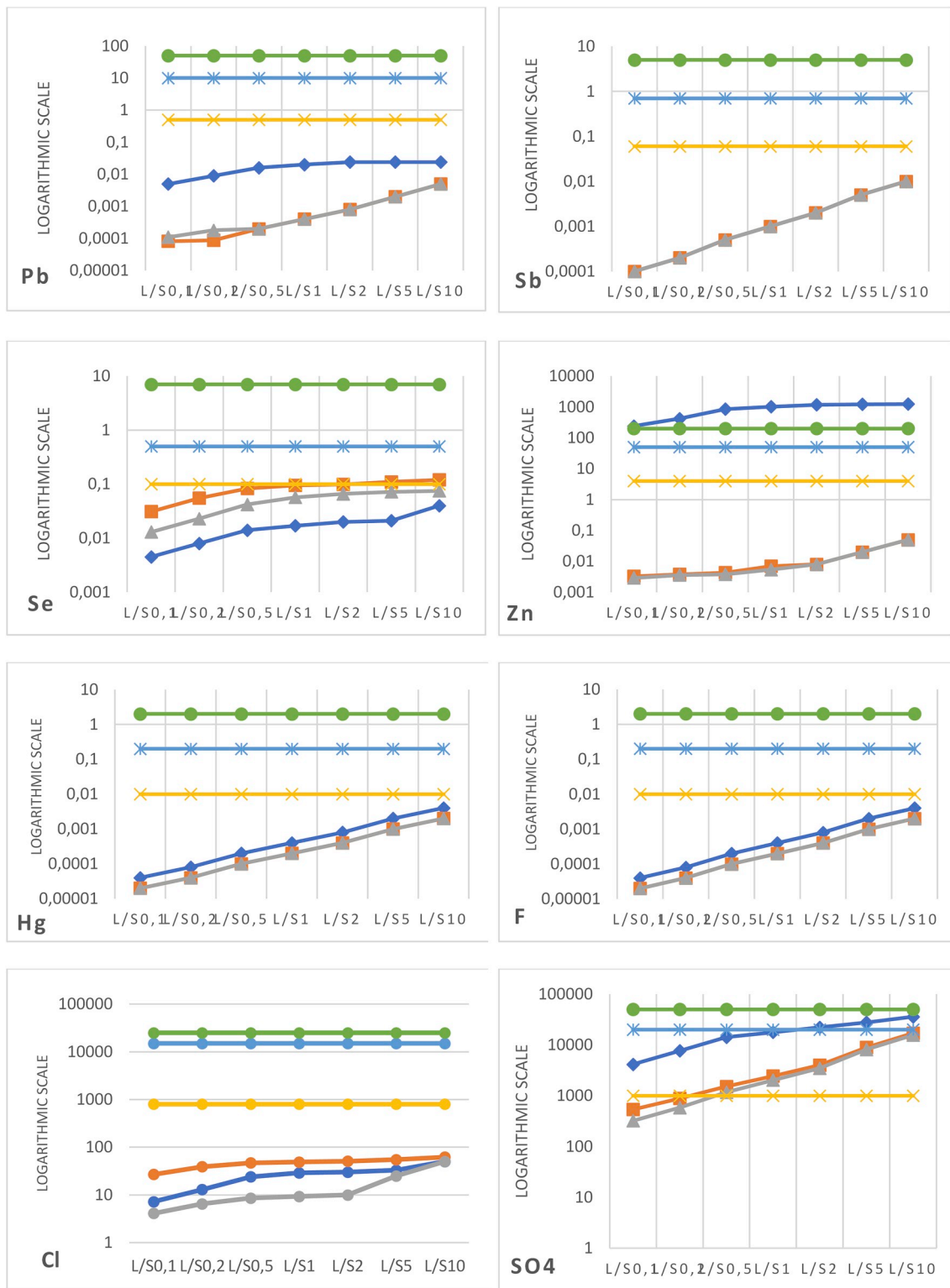


Fig. 8. Leaching (mg/kg) of Pb, Sb, Se, Zn, Hg, F, Cl and SO<sub>4</sub>.

studies of Garcia et al. (2004) on the efficiency of low-grade MgO to immobilize Pb, Zn, and Ni in flue-dust contaminated soil. The main reason for low solubility was MgO which precipitates as brucite Mg(OH)<sub>2</sub>. Comparing the diffusion results between monolithic and crushed samples, the efficiency of AAC stabilization is higher for monolithic samples, indicating a strong positive impact of lower hydraulic conductivity. In addition, LCA shows clear environmental benefits of AAC over PC as a binder.

Considering the second goal, b) on the efficiency of AAC and PC as stabilization agents for tailings, Table 4 summarizes the leaching results. According to the results, both binders were effective in the stabilization of Cd, Cu, Ni, Pb, Zn, Hg, and SO<sub>4</sub>. AAC was more efficient than PC concerning the stabilization of As, Cr, Cu, Mo, Ni, Se, Cl, and SO<sub>4</sub>. It can be concluded that the use of 10% of binder AAC met all the criteria of Class 1 for inert storage, except with regards to SO<sub>4</sub>. From this perspective, the result of this study is good. According to some

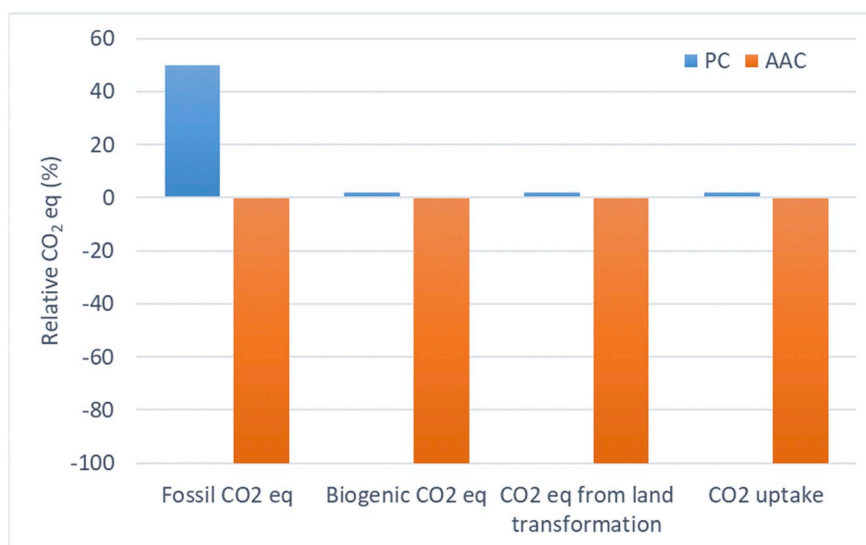


Fig. 9. Life cycle assessment defined as the greenhouse gas protocol for CO<sub>2</sub> equivalent for fossil, biogenic and from the land transformation, and as CO<sub>2</sub> uptake. AAC = alkali activated composite and PC = Portland cement.

Table 4  
Relative differences between the three diffusion test methods.

	As	Ba	Cd	Co	Cr	Cu	Hg	Mo	Ni
Crushed fract. 8/PC	1.201	27.191	0.009	0.154	0.070	3.884	0.016	79.169	1.117
Crushed fract. 8/AAC	0.687	30.795	0.008	0.192	0.048	2.013	0.016	4.201	0.218
a) relation PC/AAC	<b>1.75</b>	<b>0.88</b>	<b>1.15</b>	<b>0.80</b>	<b>1.46</b>	<b>1.93</b>	<b>1.00</b>	<b>18.85</b>	<b>5.13</b>
Monolithic fract. 8/PC	3.173	63.635	0.040	0.475	0.790	3.673	0.080	85.295	0.965
Monolithic fract. 8/AAC	1.575	61.319	0.040	0.420	0.405	1.793	0.092	2.102	0.250
b) relation PC/AAC	<b>2.02</b>	<b>1.04</b>	<b>1.00</b>	<b>1.13</b>	<b>1.95</b>	<b>2.05</b>	<b>0.87</b>	<b>40.59</b>	<b>3.87</b>
L/S10 PC	0.063	0.260	0.002	0.004	0.017	0.078	0.002	2	0.037
L/S10 AAC	0.015	0.3	0.002	0.004	0.010	0.023	0.002	0.094	0.010
c) relation PC/AAC	<b>4.20</b>	<b>0.87</b>	<b>1.00</b>	<b>1.00</b>	<b>1.70</b>	<b>3.39</b>	<b>1.00</b>	<b>21.28</b>	<b>3.70</b>

	Pb	Sb	Se	Sn	V	Zn	Cl	F	SO4
Crushed fract. 8/PC	0.035	26.368	5.781	0.048	0.864	15.823	4830	440	288000
Crushed fract. 8/AAC	0.016	26.775	3.061	0.101	4.765	5.423	2240	440	246000
a) relation PC/AAC	<b>2.19</b>	<b>0.98</b>	<b>1.89</b>	<b>0.47</b>	<b>0.18</b>	<b>2.92</b>	<b>2.16</b>	<b>1.00</b>	<b>1.17</b>
Monolithic fract. 8/PC	0.080	0.823	6.270	0.200	1.832	5.005	9680	2000	539000
Monolithic fract. 8/AAC	0.080	0.333	3.288	0.630	10.048	1.277	9680	2000	330000
b) relation PC/AAC	<b>1.00</b>	<b>2.47</b>	<b>1.91</b>	<b>0.32</b>	<b>0.18</b>	<b>3.92</b>	<b>1.00</b>	<b>1.00</b>	<b>1.63</b>
L/S10 PC	0.005	0.01	0.12	0.01	0.062	0.05	62	5	17100
L/S10 AAC	0.005	0.01	0.075	0.01	0.34	0.05	50	5	15700
c) relation PC/AAC	<b>1.00</b>	<b>1.00</b>	<b>1.60</b>	<b>1.00</b>	<b>0.18</b>	<b>1.00</b>	<b>1.24</b>	<b>1.00</b>	<b>1.09</b>

Table 5  
Relative differences between PC and ACC stabilized tailings and tailings.

	As	Ba	Cd	Cr	Cu	Mo	Ni	Pb	Sb	Se	Zn	Hg	F	Cl	SO4
Tailings	0.01	0.16	<b>2.6</b>	0.01	<b>0.94</b>	0.01	<b>4.4</b>	<b>0.024</b>	0.01	0.04	<b>1240</b>	<b>0.004</b>	5	<b>50</b>	<b>35900</b>
PC stab.	0.063	0.26	0.002	0.017	0.078	2.0	0.037	0.005	0.01	0.12	0.05	0.002	5	62	17100
PC rel.	<b>0.16</b>	<b>0.62</b>	<b>1300</b>	<b>0.59</b>	<b>12.05</b>	<b>0</b>	<b>119</b>	<b>4.80</b>	<b>1.00</b>	<b>0.33</b>	<b>24800</b>	<b>2.00</b>	<b>1.00</b>	<b>0.81</b>	<b>2.10</b>
AAC stab.	0.015	0.30	0.002	0.01	0.023	0.094	0.01	0.005	0.01	0.075	0.05	0.002	5	50	15700
ACC rel.	<b>0.67</b>	<b>0.53</b>	<b>1300</b>	<b>1.00</b>	<b>40.87</b>	<b>0.11</b>	<b>440</b>	<b>4.80</b>	<b>1.00</b>	<b>0.53</b>	<b>24800</b>	<b>2.00</b>	<b>1.00</b>	<b>1.00</b>	<b>2.29</b>

earlier research, 20% dosage was required to immobilize the metals when using GGBFS and CEMI (Kogbara et al., 2014). In CEMI, Cu and Pb are absorbed in the calcium silicate hydrate (C–S–H) gel, while Cd, Ni, and Zn precipitate as hydroxides (Gineys, Aouad, & Damidot, 2010). C–S–H is also the main product of alkali-activated slag (Yip, Lukey, & van Deventer, 2005). However, it should be noted that the tailings material used in the analysis of plain tailings was from a different sample batch than the tailings used in the stabilized samples, which may cause some variation in the diffusion results. Low hydraulic

conductivity, good compressive strength, and good freeze-thaw resistance indicate the good performance of both binders in sulfidic conditions. The hydraulic conductivity threshold of 10<sup>-9</sup> m/s is achieved with AAC, but not with tailings alone or when using PC as the binder. The PC used in the studies was blended cement containing GGBFS as an additive, which may have had a beneficial effect leading to relatively good performance when compared to the results achieved with AAC.

Regarding the third goal, c) on the reliability of different diffusion

**Table 6**

Descriptive statistics of the three diffusion test results. Results with the lowest variety have been underlined and the result with the highest variety has been highlighted.

	As	Ba	Cd	Co	Cr	Cu	Hg	Mo	Ni
Mean	2.65	0.93	1.05	0.98	1.71	2.46	0.96	26.90	4.23
Stand. Error	0.78	0.05	0.05	0.10	0.14	0.47	0.04	6.88	0.45
Median	2.02	0.88	1.00	1.00	1.70	2.05	1.00	21.28	3.87
Stand. Deviation	1.35	0.09	0.09	0.16	0.24	0.81	0.07	11.91	0.78
Sample Variance	1.81	0.01	0.01	0.03	0.06	0.66	0.01	141.92	0.61
Range	2.45	0.17	0.15	0.33	0.49	1.46	0.13	21.74	1.43
Conf. Level (95.0%)	3.34	0.23	0.22	0.41	0.60	2.02	0.18	29.59	1.93

	Ni	Pb	Sb	Se	Sn	V	Zn	Cl	F	SO <sub>4</sub>
Mean	4.23	1.40	1.49	1.80	0.60	0.18	2.61	1.47	1.00	1.30
Stand. Error	0.45	0.40	0.49	0.10	0.21	0.00	0.86	0.35	0.00	0.17
Median	3.87	1.00	1.00	1.89	0.47	0.18	2.92	1.24	1.00	1.17
Stand. Deviation	0.78	0.69	0.85	0.17	0.36	0.00	1.48	0.61	0.00	0.29
Sample Variance	0.61	0.48	0.73	0.03	0.13	0.00	2.20	0.37	0.00	0.09
Range	1.43	1.19	1.49	0.31	0.68	0.00	2.92	1.16	0.00	0.54
Conf. Level (95.0%)	1.93	1.71	2.12	0.43	0.89	0.00	3.69	1.52	0.00	0.73

test methods, Table 3 above shows the differences as relative values for each test. According to the ANOVA: Two-Factor Without Replication, the difference between the test method results was not significant (P-value 0.37). However, it is obvious that the difference between leaching values between the substances was significant.

The descriptive statistical analysis in Table 6 indicates that the results for the three diffusion methods were most reliable with Ba, Cd, Hg, V, and F. Variability was highest in the results of Mo, in terms of standard error, standard deviation, sample variance, range and confidence level (95.0%) value.

## 5. Conclusions

A range of laboratory tests was conducted in order to analyze the differences between binders and the impact of stabilization. Special focus was placed on the analysis of diffusion leaching, because the main goal of tailing protection is to prevent the oxidation of sulfide minerals.

This work indicates that there are more ecological and technically better stabilization binder alternatives than the conventionally used PC. Accordingly, MgO activated GGBFS can be a useful alternative to PC with equal or higher technical performance in terms of compressive strength, hydraulic conductivity, and encapsulation efficiency, in addition to lower greenhouse gas emissions.

This study shows that stabilization may be a good solution for reducing hydraulic conductivity and preventing the leaching of harmful substances; hydraulic conductivity is one of the main criteria stated by authorities for the performance of tailing cover materials. In areas where low-cost cover materials are not available stabilization is an alternative. In addition, physical stabilization is an option for enhancing the structural safety of tailing dams.

## Conflicts of interest

None declared.

## Ethical statement

Authors state that the research was conducted according to ethical standards.

## Funding body

European Regional Development Fund (ERDF).

## Acknowledgement

This work was supported by the European Regional Development Fund, Kajaani University of Applied Sciences, Tapojärvi Ltd, Kainuun Voima Ltd, Juuan Dolomiittikalkki Ltd, Kajaanin Romu Ltd, Solid Liner Ltd, and K.H. Renlund's Foundation.

## References

- Al-Tabbaa, A., Barker, P., & Evans, C. W. (2011). Soil mix technology for land remediation: Recent innovations. *Proceedings of the Institution of Civil Engineers – Ground Improvement*, 164(3), 127–137. <https://doi.org/10.1680/grim.2011.164.3.127>.
- Azam, S., & Li, Q. (2010). Tailings dam failures: A review of the last one hundred years. *Geotechnical News*, 28(4), 50–53.
- Bruce, D. A. (2001). Practitioner's guide to the deep mixing method. *Proceedings of the Institution of Civil Engineers – Ground Improvement*, 5(3), 95–100. <https://doi.org/10.1680/grim.2001.5.3.95>.
- Cihangir, F., Erikkid, B., Kesimal, A., Turan, A., & Devenci, H. (2012). Utilisation of alkali-activated blast furnace slag in paste backfill of high-sulphide mill tailings: Effect of binder type and dosage. *Minerals Engineering*, 30, 33–43. <https://doi.org/10.1016/j.mineng.2012.01.009>.
- Desogus, P., Manca, P. P., Orru, G., & Zucca, A. (2013). Stabilization–solidification treatment of mine tailings using Portland cement, potassium dihydrogen phosphate and ferric chloride hexahydrate. *Minerals Engineering*, 45, 47–54. <https://doi.org/10.1016/j.mineng.2013.01.003>.
- Edraki, M., Baumgart, T., Manlapig, E., Bradshaw, D., Franks, M., & Moran, C. J. (2014). Designing mine tailings for better environmental, social and economic outcomes: A review of alternative approaches. *Journal of Cleaner Production*, 84, 411–420. <https://doi.org/10.1016/j.jclepro.2014.04.079>.
- Environment Agency (2006). *Guidance for waste destined for disposals in landfills, version 2, interpretation of the waste acceptance requirements of the landfill (England and Wales) regulations (as amended)*. Bristol: Environment Agency.
- Garcia, M. A., Chimenos, J. M., Fernandez, A. I., Miralles, L., Segarra, M., & Espiell, F. (2004). Low-grade MgO used to stabilize heavy metals in highly contaminated soils. *Chemosphere*, 56(5), 481–491. <https://doi.org/10.1016/j.chemosphere.2004.04.005>.
- Gineys, N., Aouad, G., & Damidot, D. (2010). Managing trace elements in Portland cement – Part I: Interactions between cement paste and heavy metals added during mixing as soluble salts. *Cement and Concrete Composites*, 32(8), 563–570. <https://doi.org/10.1016/j.cemconcomp.2010.06.002>.
- Gu, K., Jin, F., Al-Tabbaa, A., Shi, B., & Liu, J. (2014). Mechanical and hydration properties of ground granulated blast furnace slag pastes activated with MgO–CaO mixtures. *Construction and Building Materials*, 69, 101–108. <https://doi.org/10.1016/j.conbuildmat.2014.07.032>.
- Gu, K., Jin, F., Al-Tabbaa, A., Shi, B., Liu, C., & Gao, L. (2015). Incorporation of reactive magnesia and quicklime in sustainable binders for soil stabilization. *Engineering Geology*, 195, 53–62. <https://doi.org/10.1016/j.enggeo.2015.05.025>.
- Jin, F. (2014). *Characterisation and performance of reactive MgO-based cements (PhD thesis)* UK: University of Cambridge.
- Jin, F., Abdollahzadeh, A., & Al-Tabbaa, A. (2013). *Effect of different MgO on the hydration of MgO-activated granulated ground blast furnace slag paste. Proceedings of 3rd International Conference on Sustainable Construction Materials and Technologies*. Japan: Kyoto Research Park, Kyoto.
- Jin, F., & Al-Tabbaa, A. (2014). Evaluation of novel reactive MgO activated slag binder for the immobilisation of lead and zinc. *Chemosphere*, 117, 285–294. <https://doi.org/10.1016/j.chemosphere.2014.07.027>.
- Jin, F., Gu, K., & Al-Tabbaa, A. (2015). Strength and hydration properties of reactive MgO-activated ground granulated blastfurnace slag paste. *Cement and Concrete*

- Composites*, 57, 8–16. <https://doi.org/10.1016/j.cemconcomp.2014.10.007>.
- Jin, F., Wang, F., & Al-Tabbaa, A. (2016). Three-year performance of in-situ solidified/stabilised soil using novel MgO-bearing binders. *Chemosphere*, 144, 681–688. <https://doi.org/10.1016/j.chemosphere.2015.09.046>.
- Kogbara, R. B., Al-Tabbaa, A., & Stegemann, J. A. (2014). Comparisons of operating envelopes for contaminated soil stabilised/solidified with different cementitious binders. *Environmental Science and Pollution Research*, 21(5), 3395–3414. <https://doi.org/10.1007/s11356-013-2276-7>.
- Lange, L. C., Hills, C. D., & Poole, A. B. (1995). Preliminary investigation into the effects of carbonation on cement-solidified hazardous wastes. *Environmental Science and Technology*, 30(1), 25–30. <https://pubs.acs.org/doi/abs/10.1021/es940702m>.
- Mäkelä, E., Wahlström, M., Pihlajaniemi, M., & Mroueh, U.-M. (1998). Kivihiiilivoimaloiden rikinpoistotuotteet ja lentotuhka maarakentamisessa. *Jatkokutkimus.VTT Tiedotteita 1952*, 1–64. Espoo: VTT. (in Finnish). Retrieved April 4th, 2018 Month Day, Year from <http://www.inf.vtt.fi/pdf/>.
- Manjunatha, L. S., & Sunil, B. M. (2013). Stabilization/solidification of iron ore mine tailings using cement, lime and fly ash. *International Journal of Renewable Energy Technology*, 02(12), 625–636. <https://doi.org/10.15623/ijret.2013.0212107>.
- Mudd, G. M., & Boger, D. V. (2013). The ever growing case for paste and thickened tailings – towards more sustainable mine waste management. *The AusIMM Bulletin*, 2, 56–59.
- Nehdi, M., & Mindess, S. (1999). A quantitative approach to predicting the performance of blended cements. *Concrete Science and Engineering*, 1, 205–214.
- Nehdi, M., & Tariq, A. (2007). Stabilization of sulphidic mine tailings for prevention of metal release and acid drainage using cementitious materials: A review. *Journal of Environmental Engineering and Science*, 6(4), 423–435. <https://doi.org/10.1139/s06-060>.
- Obuzor, G. N., Kinuthia, J. M., & Robinson, R. B. (2012). Soil stabilisation with lime-activated- GGBS – a mitigation to flooding effects on road structural layers/embankments constructed on floodplains. *Engineering Geology*, 151, 112–119. <https://doi.org/10.1016/j.enggeo.2012.09.010>.
- Sarkkinen, M., Tuomikoski, S., Kujala, K., Kempainen, K., & Gehör, S. (2017). Replacement of Portland cement in Portland blast-furnace slag cement for cold-agglomerated briquetting. *Proceedings of the fifth international slag valorisation symposium* (pp. 1–4). Leuven: Faculteit Ingenieurswetenschappen KU Leuven.
- Seco, A., Miqueleiz, L., Prieto, E., Marcelino, S., García, B., & Urmeneta, P. (2017). Sulfate soils stabilization with magnesium-based binders. *Applied Clay Science*, 135, 457–464. <https://doi.org/10.1016/j.clay.2016.10.033>.
- Tariq, A., & Yanful, E. K. (2013). A review of binders used in cemented paste tailings for underground and surface disposal practices. *Journal of Environmental Management*, 131, 138–149. <https://doi.org/10.1016/j.jenvman.2013.09.039>.
- Tresintsi, S., Simeonidis, K., Katsikini, M., Paloura, E. C., Bantsis, G., & Mitrakas, M. (2014). A novel approach for arsenic adsorbents regeneration using MgO. *Journal of Hazardous Materials*, 265, 217–225. <https://doi.org/10.1016/j.jhazmat.2013.12.003>.
- Wang, C., Harbottle, D., Liu, Q., & Xu, Z. (2014). Current state of fine mineral tailings treatment: A critical review on theory and practice. *Minerals Engineering*, 58, 113–131. <https://doi.org/10.1016/j.mineng.2014.01.018>.
- Xie, X., Tian, W., Wang, Y., & Zhan, G. X. (2009). The safety analysis of current situation and management countermeasure on tailing reservoir in China. *Journal of Safety Science and Technology*, 5(2), 5–9.
- Yi, Y., Gu, L., Liu, S., & Jin, F. (2016a). Magnesia reactivity on activating efficacy for ground granulated blastfurnace slag for soft clay stabilization. *Applied Clay Science*, 126, 57–62. <https://doi.org/10.1016/j.clay.2016.02.033>.
- Yi, Y., Li, C., Liu, S. Y., & Al-Tabbaa, A. (2014a). Resistance of MgO-GGBS and CS-GGBS stabilised marine soft clays to sodium sulfate attack. *Géotechnique*, 64(8), 673–679. <https://doi.org/10.1680/geot.14.T.012>.
- Yi, Y., Liska, M., & Al-Tabbaa, A. (2014b). Properties of two model soils stabilized with different blends and contents of GGBS, MgO, lime, and PC. *Journal of Materials in Civil Engineering*, 26(2), 267–274.
- Yi, Y., Liska, M., Jin, F., & Al-Tabbaa, A. (2016b). Mechanism of reactive magnesia – ground granulated blastfurnace slag (GGBS) soil stabilization. *Canadian Geotechnical Journal*, 53(5), 773–782. <https://doi.org/10.1139/cgj-2015-0183>.
- Yip, C. K., Lukey, G. C., & van Deventer, J. S. J. (2005). The coexistence of geopolymeric gel and calcium silicate hydrate at the early stage of alkaline activation. *Cement and Concrete Research*, 35(9), 1688–1697. <https://doi.org/10.1016/j.cemconres.2004.10.042>.