

Geopolymers as active capping materials for in situ remediation of metal(loid)-contaminated lake sediments

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Abstract

Metal(loid) contamination in sediments is a widespread environmental issue. Sediments act normally as metal(loid) sinks, but if chemical conditions (such as pH or redox potential) change, they can become sources of secondary pollution. Consequently, various strategies for both *in* and *ex situ* remediation of contaminated sediments have been developed. One promising method is active capping, which involves the injection of adsorbents as a layer on the sediment surface or the mixing of adsorbents within the sediment. Adsorbents decrease the bioavailability of metal(loid)s. In the present work, the suitability of **alkali-activated** blast-furnace-slag, metakaolin geopolymer, and exfoliated vermiculite were evaluated for *in situ* stabilization of two metal(loid)-contaminated lake sediments through laboratory-scale experiments. The results indicated that adsorbent

amendments had metal(loid)-specific performance: [alkali-activated](#) blast-furnace slag was suitable for Al, Cu, Fe, and Ni; metakaolin geopolymer for Cu, Cr (total), and Fe; and vermiculite for Al and Zn. None of the materials could stabilize Ba, Sr, or Ti. Furthermore, the amendments performed differently in two different lake sediments, implying that the effectiveness of the amendments needs to be confirmed on a case-by-case basis.

Keywords: active capping; [alkali-activation](#); geopolymer; remediation; sediment; vermiculite

1. Introduction

Metal and metalloid contamination in soils and sediments is a widespread environmental issue (Klavinš et al., 2000). Some metal(loid)s can be potentially toxic for flora and fauna if they exceed certain threshold levels, and since they are non-biodegradable, they accumulate in the food chain. Mining activities, especially from unsustainably closed mines (González-Fernández et al., 2018), and accidentally released un-treated effluents or tailings (Cagnin et al., 2017; Saup et al., 2017) represent a major point source of metal(loid) contamination to water bodies and thus affect sediments in the long term (Jain and Das, 2017).

In aquatic systems, metal(loid)s can occur as dissolved, colloids, suspensions, or adsorbed in sediments. In fact, when conditions are favorable, sediments can bind to more than 99% of aqueous metal(loid)s (Salomons and Stigliani, 2012). Sediments therefore act as important sinks. However, changes in chemical conditions (i.e., pH value or reduction-oxidation potential) can result in partial re-dissolution of the bound metal(loid)s, and thus, sediments can act also as secondary sources of pollution (Simpson et al., 2000; Zoumis et al., 2001). In addition, hydrological factors affect the dynamics of metal(loid) stability in the sediments; for instance, bioturbation caused by benthic organisms, advection, diffusion, or underflows can result in metal(loid) re-suspension (Jacobs and Förstner, 2001).

Natural processes are frequently inadequate to cope with elevated metal(loid) loading, and there is therefore a need for remediation measures. In *ex situ* treatment, contaminated sediment is dredged and treated off-site using different techniques (Mulligan et al., 2001). However, dredging is costly and causes significant disturbance to benthic fauna and the whole ecosystem (Rasheed and Balchand, 2007). *In situ* treatment, on the other hand, is a less disruptive method. It involves injection of either inert materials (such as sand, clay, or crushed stone on geotextiles) or active capping materials (adsorbent) on the sediment surface or mixing of these materials within the sediment (Koschorreck et al., 2007; Mohan et al., 2000; Palermo et al., 1998; Zhang et al., 2016). The aim of passive and active capping is to decrease the metal bioavailability either by physically isolating the sediment from the overlying water or binding metal(loid)s with physical and/or chemical interactions, respectively (Koschorreck et al., 2007; Mohan et al., 2000; Palermo et al., 1998; Zhang et al., 2016). The modelling of metal(loid), methyl mercury, and cyanide release from active capping has demonstrated that the method is effective for at least 100 years (Viana et al., 2008). Active capping materials have several advantages over inert caps: a thinner layer is typically required, and thus, less disturbance is caused to benthic fauna; adsorbents can be introduced as a permeable granule bed, which does not form a hydraulic barrier for water flow; and the costs can be lower compared to dredging (Ghosh et al., 2011; Jacobs and Förstner, 2001; Zhang et al., 2016). However, passive capping is a more mature technology (Azcue et al., 1998), whereas, only a few pilot-scale experiments have been reported in the scientific literature with active capping (Knox et al., 2012). Nevertheless, a commercially available application method for active capping materials has been developed, called reactive core mat, in which an adsorbent is placed between permeable geotextiles (Meric et al., 2013).

Active capping materials for metal(loid) stabilization include commercial ion exchange resins, zeolites, activated carbons (with or without chemical modification), activated alumina, apatite, barite, bentonite, chitosan, red mud, organoclay, titanosilicate, and thiol-modified mesoporous support (Knox et al., 2012; Kwon et al., 2010). Several of these materials are still in the early research stage, have only modest efficiency, or represent too high costs for widespread use. One

novel option could be geopolymers (or alkali-activated materials), which are mesoporous amorphous aluminosilicates with ion-exchange properties. They have been recently studied for a number of potential environmental applications as adsorbents/ion exchangers (Luukkonen et al., 2016; Luukkonen et al., 2017b; Runtti et al., 2016; Alzboon et al., 2011; Al-Harashsheh et al., 2015), photocatalysts (Gasca-Tirado et al., 2012; Li et al., 2016; Zhang and Liu, 2013), pH buffers (Novais et al., 2016; Novais et al., 2017), membrane and filter materials (Ge et al., 2015; Xu et al., 2015), and for stabilization of hazardous wastes (Asavapisit and Chotklang, 2004). Furthermore, geopolymers can be prepared from several industrial by-products with a simple, up-scalable, and low-energy process.

In this study, sediment samples were collected from two lakes. Both lakes are affected by mine waters and contain a significant amount of anthropogenic-origin metal(loid)s in their sediments, and thus, the motivation for this work was to evaluate a potentially cost-effective remediation method for mine water-impacted sediments. A laboratory-scale *in situ* treatment was conducted using three adsorbent amendments: [alkali-activated](#) blast-furnace-slag, metakaolin geopolymer, and vermiculite. Geopolymers ([or alkali-activated materials](#)) were selected as they have not been studied for *in situ* sediment remediation but they have indicated potential as adsorbents.

Metakaolin and blast furnace slag represent low and high-calcium raw materials, respectively, and thus their reaction products are different. Metakaolin forms three-dimensional and highly interconnected aluminosilicate framework (sodium-aluminum-silicate hydrate gel or N-A-S-H in the cement chemist notation), whereas blast-furnace slag forms structures resembling tobermorite, $\text{Ca}_5\text{Si}_6\text{O}_{16}(\text{OH})_2 \cdot n\text{H}_2\text{O}$ (calcium-aluminum-silicate-hydrate gel or C-A-S-H). Vermiculite, however, has already been proved to be a potential *in situ* sediment remediation material with *Pseudomonas putida* biofilm (Ferronato et al., 2016) and to be effective in decreasing metal bioavailability from soils to plants (Malandrino et al., 2011). Thus, it was selected as a reference. The effect of amendment additions were evaluated by a sequential leaching test, indicating the bioavailability of metal(loid)s, and compared to a blank sample (sediment without adsorbent amendment).

2. Materials and methods

2.1 Employed adsorbents

The preparation of geopolymers was based on previous optimization experiments (Luukkonen et al., 2017a) and it is briefly summarized below.

Alkali-activated blast furnace slag (BFS-GP) was prepared by alkali activation of ground-granulated blast-furnace slag (obtained from Finnsementti, Finland; d_{50} value 10.8 μm). The alkali activator consisted of 8 M NaOH (analytical grade, VWR Chemicals) and sodium silicate solution (technical grade, VWR Chemicals, molar ratio $\text{SiO}_2/\text{Na}_2\text{O} \approx 3.5$) mixed in a weight ratio of 1.2. The solution was allowed to stand overnight before use. The alkali activator was mixed with the blast-furnace slag in a weight ratio of 0.77 for 15 min using a top-mounted mixer.. The paste was allowed to cure in a plastic bag (at 100% relative humidity) and room temperature (22 °C) for three days. The obtained monolith was crushed and sieved to particle sizes of 1–4 mm before use. BFS-GP had the following theoretical molar composition (assuming complete reaction): $\text{SiO}_2/\text{Al}_2\text{O}_3 = 13.03$, $\text{Na}_2\text{O}/\text{SiO}_2 = 0.27$, $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3 = 3.57$, and $\text{CaO}/\text{SiO}_2 = 0.56$. Water/solid weight ratio was 0.44.

The metakaolin geopolymer (MK-GP) was prepared of metakaolin (obtained from Aquaminerals Finland Ltd, Finland) and the alkali activator, which was a mixture of 12 M NaOH and sodium silicate solution ($\text{SiO}_2/\text{Na}_2\text{O} \approx 3.5$). Metakaolin and alkali activator were mixed in a weight ratio of 1.2. The solution was allowed to stand overnight before use. Alkali activator and metakaolin were mixed in a weight ratio of 1.0 for 15 min using a top-mounted mixer. The paste was allowed to cure for three days in a plastic bag (at 100% relative humidity) and was crushed and sieved to particle sizes of 1–4 mm. MK-GP had the following theoretical molar composition: $\text{SiO}_2/\text{Al}_2\text{O}_3 = 2.86$, $\text{Na}_2\text{O}/\text{SiO}_2 = 0.28$, and $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3 = 0.79$. Water to solid weight ratio was 0.48.

Vermiculite (VER) was obtained from the Palabora mining company (South Africa). It was exfoliated at 450°C for 1 h before use. The particle size distribution was $d_{97} = 687 \mu\text{m}$, $d_{50} = 402 \mu\text{m}$, and $d_{10} = 255 \mu\text{m}$ (determined using Hosokawa alpine Air Jet Sieve e200 LS).

2.2 Adsorbent characterization methods

The mineralogical composition of adsorbents was determined with powder X-ray diffraction (XRD) using a PanAnalytical Xpert Pro diffractometer (Co K α radiations generated at 40 kV and 40 mA). Patterns were collected from 5° to 80° 2 θ using a scan time of 1.25 s per 0.02° 2 θ . Samples were prepared by dispensing a finely ground specimen with ethanol onto a glass plate and allowing the ethanol to vaporize before measurement. Diffractograms were interpreted using the Highscore software (version 3.0) and Chrystallography Open Database 2013 version.

The elemental composition of adsorbents was determined by dissolving samples in a mixture of nitric and hydrochloric acids, according to the EPA 3051 method (EPA, 2007), and then analyzing the solution using an optical emission spectrometer (Thermo Electron IRIS Intrepid II XDL Duo), according to the SFS-EN ISO 11885 standard (Finnish Standard Association, 2009). Silicon concentration was determined using X-ray fluorescence (XRF) spectrometer (PanAnalytical Minipal 4).

2.3 Sediment and water samples

Sediment samples were collected from Lake Pyhäjärvi (N63, 7102°, E25, 9844°, mean depth 8.9 m) and Lake Kivijärvi (N63, 9199°, E27, 9306°, mean depth 6.6 m) using a Limnos sampler. Locations of these two lakes and places where samples were collected is shown in Figure 1. Sediment samples had total solids of 5.6 g/L (Kivijärvi) and 14.6 g/L (Pyhäjärvi). Samples were stored in a glass bottle at +5°C in the dark until experiments [to minimize chemical changes](#). Water samples were also collected from the same locations at the upper part of the hypolimnion (mixolimnion in the case of Lake Kivijärvi, which is currently permanently stratified), that is, approximately 4 m at Kivijärvi and 3 m at Pyhäjärvi. Water and sediment samples were characterized according to the EPA 3051A method ([microwave-assisted HNO₃ leach with ICP-OES/MS determination](#)) (EPA, 2007) and the SFS-EN ISO 11885 standard (Finnish Standard

Association, 2009). ICP-MS (inductively coupled plasma mass spectrometry) method is used according standard SFS-EN ISO 17294-2:2016 (Finnish Standard Association, 2016). Carbon and nitrogen in sediment samples were determined with a carbon analyzer and C/N analyzer, respectively.

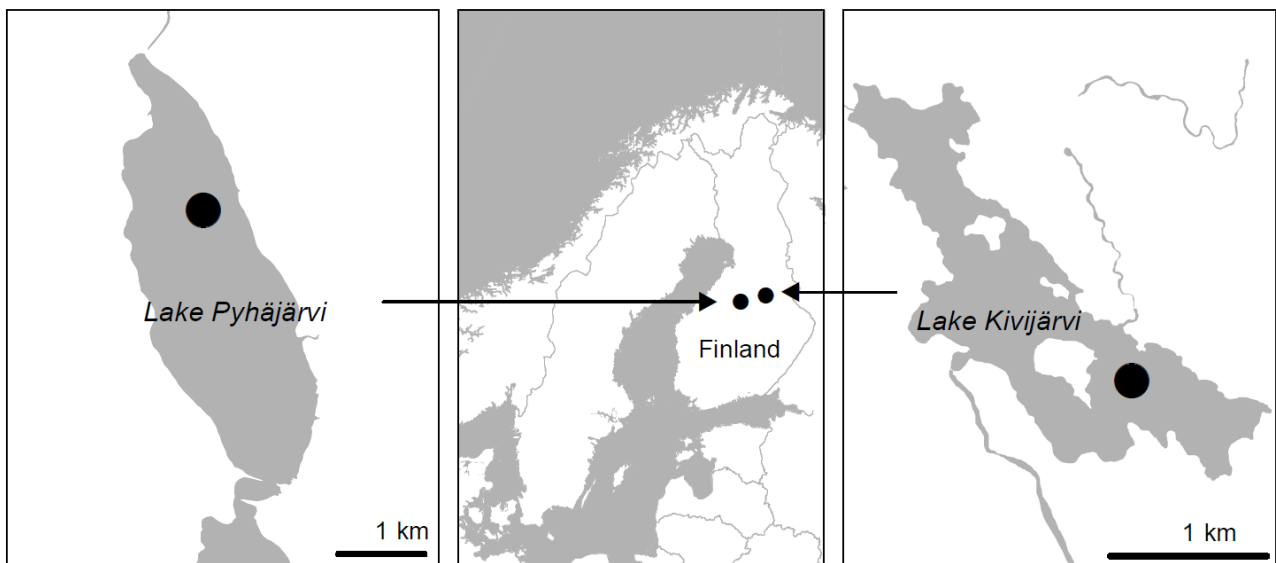


Figure 1. Locations of Lake Kivijärvi and Lake Pyhäjärvi.

2.4 Stabilization experiments and sequential leaching

Laboratory-scale *in-situ* metal stabilization experiments were performed by dosing adsorbents to sediments (2.2%, 4.4%, or 8.7% as weight of adsorbent per volume of sediment), mixed, kept at +4°C in the dark undisturbed for two weeks. Thereafter, the samples, were evaporated at 105°C. To evaluate the success of stabilization, a three-step sequential leaching test (Rauret et al., 1999) was applied to the adsorbent-treated sediment samples and blank (untreated) sample. The procedure is shown in Figure 2. In the first step, 0.5 g of the dried sediment was added to a 50 ml centrifuge tube followed by the addition of 20 mL of 0.11 M acetic acid and shaking overnight with a mechanical end-over-end shaker. The supernatant (S1) was separated by centrifugation (20 min)

and analyzed using an optical emission spectrometer (Thermo Electron IRIS Intrepid II XDL Duo), according to the SFS-EN ISO 11885 standard (Finnish Standard Association, 2009). The solid residue was washed with 10 mL of distilled water, shaken for 15 min, and separated by centrifuging (20 min). In the second step, 20 mL of freshly prepared 0.5 M hydroxylammonium chloride solution was added to the solid residue from the first step, and the mixture was shaken overnight. After shaking, the solid residue was separated by centrifugation (20 min), and the supernatant (S2) was again analyzed. The solid residue was washed with 10 mL of distilled water (15 min shaking) and centrifuged (20 min). In the third step, 5 mL of 8.8 M (30%, w/w) hydrogen peroxide was added to the solid residue from the second step in small amounts. Vessels were covered softly and allowed to react at room temperature for 1 h with occasional shaking. The leaching was continued at 85 °C (in a water bath) for 1 h, and then, the solution was evaporated to 1.5 mL volume. Another 5 mL of 8.8 M hydrogen peroxide was added, and the volume was allowed to evaporate to 0.5 mL. After cooling to room temperature, 25 mL of 1 M ammonium acetate solution was added, and mixtures were shaken overnight. The supernatant (S3) was separated by centrifugation (20 min), and the solids were washed with 10 mL of distilled water, shaken for 15 min, and centrifuged (20 min). The final solids (S4) were dissolved according to the EPA 3051 method (EPA, 2007) and analyzed according to the SFS-EN ISO 11885 standard (Finnish Standard Association, 2009).

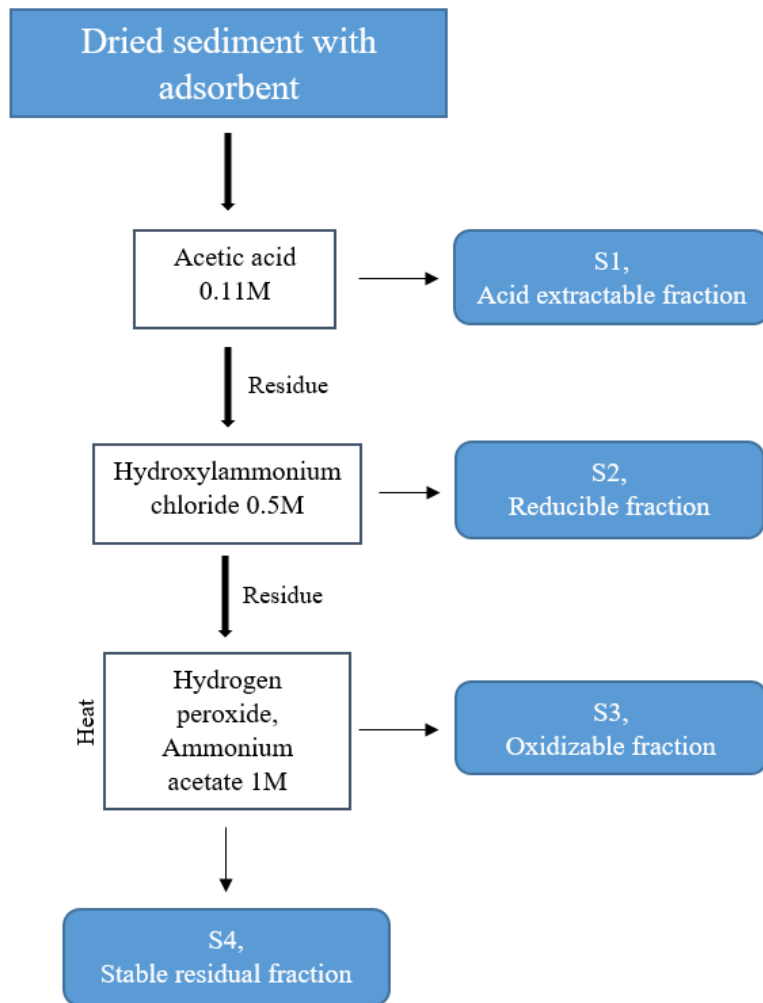


Figure 2. Sequential leaching procedure for the treated contaminated lake sediments.

3. Results and discussion

3.1 Adsorbent characterization

The elemental compositions of the geopolymer raw materials and vermiculite (Table 1) were determined to evaluate the possible leaching of metal(loid)s out of the adsorbents. The main elements in metakaolin (ideal stoichiometry $Al_2Si_2O_7$) are aluminum and silicon with iron, potassium, magnesium, calcium, sulfur, and titanium contained likely in minor impurity phases. Blast-furnace slag contains mainly calcium, aluminum, silicon, and magnesium, and its structure is usually described as a mixture of poorly crystalline phases such as gehlenite ($Ca_2Al[AlSiO_7]$),

akermanite ($\text{Ca}_2\text{Mg}[\text{Si}_2\text{O}_7]$), and depolymerized glasses (Li et al., 2011). In addition, the amount of sulfur, iron, potassium, sodium, and manganese are relatively high. Vermiculite has an ideal stoichiometry of $(\text{Mg}^{+2}, \text{Fe}^{+2}, \text{Fe}^{+3})_3[(\text{Al}, \text{Si})_4\text{O}_{10}](\text{OH})_2 \cdot 4\text{H}_2\text{O}$, and accordingly, the main elements are magnesium, iron, potassium, aluminum, calcium, and silicon. In addition, there are varying trace amounts of potentially toxic elements in all adsorbents, e.g., barium, beryllium, chromium, nickel, lead, tin, and zinc. The largest amount of potentially toxic elements is encountered in the vermiculite as it can adsorb them from the soils from the location it has been excavated (Sipos et al., 2008). The stability of these potentially hazardous elements in adsorbent materials is a potential obstruction for their use, and this is discussed in the section presenting the results of leaching experiments.

Table 1. Elemental composition of metakaolin, blast-furnace slag, and vermiculite.

Element	Metakaolin [mg/kg]	Blast-furnace slag [mg/kg]	Vermiculite [mg/kg]
Al	175000	50000	48300
Si	248200	127100	167900
Ca	360	287000	9670
Fe	12200	5250	54700
K	17700	5790	43800
Mg	6080	48700	129000
S	350	14400	71
Ti	230	6010	4050
B	18	67	0
Ba	100	550	510
Be	10	4,6	1,4
Cr	28	46	230
Mn	130	2770	400

Na	360	5000	340
Ni	28	1,2	150
P	420	0	1950
Pb	35	0	3,9
V	8,9	410	18
Zn	59	0	72
Sn	54	0	0

The XRD analysis results of the adsorbents are shown in Figure 3. The diffractogram of MK-GP indicates that quartz (SiO_2) and muscovite ($\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{F},\text{OH})_2$) are present in addition to an amorphous material (hump between $25\text{--}40^\circ 2\theta$). The amorphous content of the metakaolin-based geopolymer is described as sodium-aluminum-silicate-hydrate gel (N-A-S-H in the cement chemistry notation), the structure of which has been described schematically by some authors (Barbosa et al., 2000; García-Lodeiro et al., 2010; Rowles et al., 2007). The charge-balancing sodium cations in the N-A-S-H gel can be exchanged to other cations, which gives rise to applications as an adsorbent/ion exchanger (O'Connor et al., 2010). The vermiculite sample contains phlogopite and biotite of which vermiculite is a weathering product (Kogel, 2006). However, no vermiculite itself was identified from the diffractogram. BFS-GP contains only faujasite-type zeolite phase as a well-crystallized phase: other phases are amorphous or poorly crystalline, as indicated by the amorphous halo at approximately $30\text{--}40^\circ 2\theta$. The structure of the alkali-activated blast-furnace slag is described as tobermorite-like calcium-sodium-aluminum-silicate-hydrate gel (C-(N)-A-S-H in cement chemistry notation) (Bernal et al., 2014). Similarly to MK-GP, BFS-GP exhibits a structure that has a net negative charge, which is balanced by cations. It sometimes also contains layered double hydroxides, such as hydrotalcite, as [secondary](#) reaction products, which explains the potential for anion exchange (Luukkonen et al., 2016).

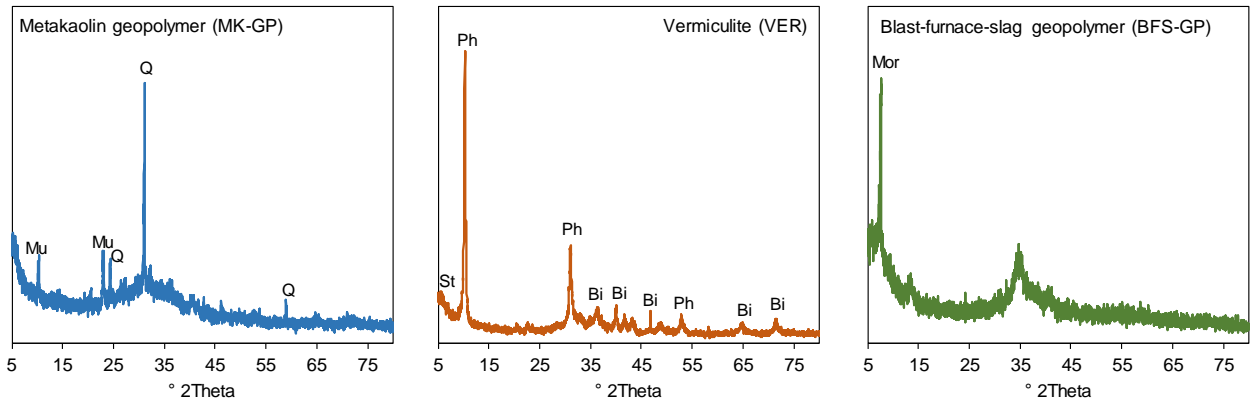


Figure 3. The diffractograms of adsorbents: Mu = muscovite ($\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{F},\text{OH})_2$), Q = quartz (SiO_2), St = stilbite ($\text{NaCa}_4(\text{Si}_{27}\text{Al}_9)\text{O}_{72}\cdot 28(\text{H}_2\text{O})$), Ph = phlogopite ($\text{KMg}_3(\text{AlSi}_3\text{O}_{10})(\text{F},\text{OH})_2$), Bi = biotite ($\text{K}(\text{Mg},\text{Fe})_3(\text{AlSi}_3\text{O}_{10})(\text{F},\text{OH})_2$), and Fau = faujasite ($(\text{Na}_2,\text{Ca},\text{Mg})_{3.5}[\text{Al}_7\text{Si}_{17}\text{O}_{48}]\cdot 32(\text{H}_2\text{O})$).

3.2 Metal(loid) contamination in the studied lakes

Lake Pyhäjärvi has been exposed to loading from the Pyhäsalmi mine since 1962. In 2006, the thickness of the contaminated sediments varied between 15 and 20 cm within the accumulation zone (Mäkinen and Lerssi, 2007). The most notable mining-related increases in metal concentrations are found for Cu, Zn, and S (146 mg/kg, 481 mg/kg, and 0.6%, respectively). These concentrations are approximately five times higher than the background.

Lake Kivijärvi is located SE from the Talvivaara mine of Terrafame Ltd. and has received mine water loading since 2009. Especially gypsum pond accident in 2012 caused significant loading of metals from the mine site (Kauppi et al. 2013). The thickness of the contaminated sediment layer was 1–2 cm in Lake Kivijärvi in 2015–2016 (Leppänen et al., 2017). Contamination is most evident in the concentrations of Ni, Zn, and S (638 mg/kg, 682 mg/kg, and 3.8 %), which are several times higher than the local background concentrations. High concentrations of Fe, Mn, and Na at the sediment surface are also typical for Lake Kivijärvi as a consequence of using NaOH to increase pH in the process. In addition, high concentrations of Ca are found in both Lake Pyhäjärvi and Lake Kivijärvi sediments owing to the liming of the effluent waters. The drainage basin of Lake

Kivijärvi consists partly of black shale rocks and therefore also natural background values of metals are relatively high (Loukola-Ruskeeniemi et al. 1998).

The average concentrations for the contaminated sediment sections in Lake Pyhäjärvi and Lake Kivijärvi sediments are shown in Table 2. The 0–20 cm sediment sample from Lake Pyhäjärvi (Junttiselkä basin) corresponds well to the contaminated sediment section, while the 0–2 cm section from Lake Kivijärvi may contain some pre-contamination material. The water quality of the hypolimnia of these lakes in 2016 is presented in Table 3.

Based on these results, the following metal(loid)s were selected to be tested in stabilization experiments: for Lake Kivijärvi sediments - Al, Fe, Ti, Cr, Cu, Zn, Ni, As, Sr, Cd, Ba, and U; and for Lake Pyhäjärvi sediments - Al, Zn, Cu and Cr.

Table 2. Average concentrations for the contaminated sediment sections.

		Lake Kivijärvi	Lake Pyhäjärvi
As	mg/kg	5	13
Cd	mg/kg	2	0
Co	mg/kg	21	18
Cr	mg/kg	17	60
Cu	mg/kg	41	146
Mo	mg/kg	2	1
Ni	mg/kg	638	26
Pb	mg/kg	28	30
Th	mg/kg	3	8
U	mg/kg	10	3
V	mg/kg	51	70
Zn	mg/kg	682	481

Al	mg/kg	11050	29361
Ba	mg/kg	195	145
Ca	mg/kg	10150	11412
Fe	mg/kg	81800	51239
K	mg/kg	834	5221
Mg	mg/kg	5615	8067
Mn	mg/kg	2855	444
Na	mg/kg	17500	454
P	mg/kg	2525	1641
S	mg/kg	37850	6127
Ti	mg/kg	386	1096
C	%	19	7
N	%	2	1

Table 3. Water quality of the hypolimnia of Lake Kivijärvi and Lake Pyhäjärvi (Junttiselkä basin) in the late winter 2016.

		Lake Kivijärvi	Lake Pyhäjärvi
Al	µg/l	285	210
As	µg/l	0.29	3.29
B	µg/l	14.3	< 10
Ba	µg/l	33.7	28.9
Be	µg/l	< 0.5	< 0.5
Bi	µg/l	< 5	< 5
Cd	µg/l	< 0.2	0.24
Co	µg/l	3.79	4.13
Cr	µg/l	1.02	< 1

Cu	µg/l	< 5	< 5
Li	µg/l	141	8.71
Mn	µg/l	41400	1680
Mo	µg/l	< 0.2	< 0.2
Ni	µg/l	< 5	< 5
P	µg/l	401	340
Pb	µg/l	< 1	< 1
Rb	µg/l	23.3	4.29
Sb	µg/l	< 10	< 10
Se	µg/l	< 0.5	< 0.5
Sr	µg/l	294	127
Th	µg/l	< 10	< 10
Tl	µg/l	< 0.2	< 0.2
U	µg/l	1.84	0.17
V	µg/l	4.24	3.67
Zn	µg/l	< 5	40.6
Ca	mg/l	204	106
Fe	mg/l	74	35
K	mg/l	25	3
Mg	mg/l	205	6
Na	mg/l	2660	7
S	mg/l	2080	75

3.3 *In situ* remediation results

The variation in the sediment pH as a function of adsorbent dose after two-week contact time is shown in Figure 4. The speciation of several studied metal(loid)s is strongly affected by pH: many cations precipitate as hydroxides and oxyanions deprotonate as pH increases over certain

threshold values. Among the studied amendments, BFS-GP caused the most striking increase in pH: from the initial pH of approximately 6 up to 12. This is because of the residual alkalinity present in the geopolymer structure. From this point of view, the materials differ from each other. MK-GP increased pH up to two units while vermiculite caused less than one unit increase. However, the results in Figure 4 most likely exaggerated the pH increase compared to the actual environmental conditions since the sediments were still and isolated during the experiment. In actual conditions of lakes, the overlaying water column would cause some dilution and mixing.

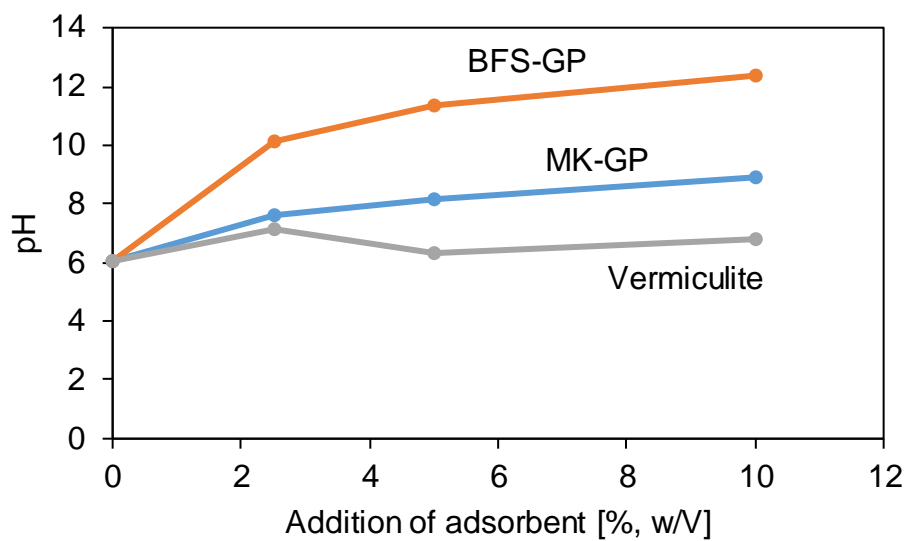


Figure 4. pH of sediment as a function of adsorbent amendment (in %, w/V).

The results of the stabilization experiments [after two week contact time](#) are shown in Figure 5 as a ratio of C/C_0 for each of the sequential leaching test phases (S1, S2, S3, or S4). C and C_0 refer to the concentration of the metal(loid) with and without adsorbent amendment, respectively. In the sequential leaching test, S1 is the acid-extractable fraction, S2 is the reducible fraction, S3 is the oxidizable fraction, and S4 is the stable residual fraction. Subsequently, in phases S1 to S3, values $C/C_0 < 1$ indicate that the adsorbent amendment has successfully decreased metal(loid) bioavailability and values $C/C_0 > 1$ indicate that the adsorbent amendment has increased

metal(loid) release compared to the blank. In the S4 phase, the result $C/C_0 > 1$ indicates the enhanced accumulation of metal(loid) in the stable fraction compared to the blank sample.

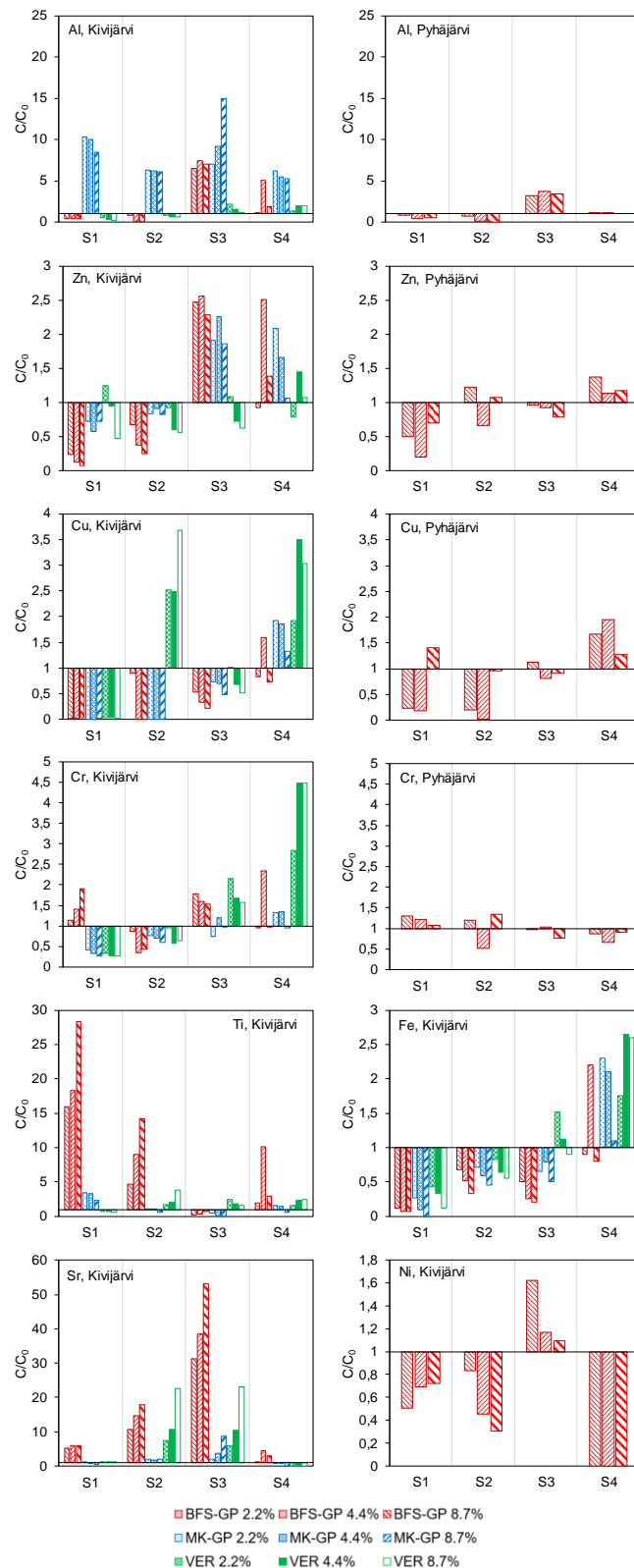


Figure 5. Results of the sequential leaching experiments [after two week contact time](#). S1 is the acid-extractable fraction, S2 is the reducible fraction, S3 is the oxidizable fraction, and S4 is the residual fraction. C/C_0 is the ratio of the concentration in the specific phase (S1, S2, S3, or S4) to concentration in unamended sediment.

Aqueous soluble aluminum occurs as Al^{3+} . Aluminum is not acutely toxic to humans, but for instance, a link between Alzheimer disease and aluminum intake is suspected (Gupta et al., 2005). The provisional tolerable weekly intake value for aluminum is 0.9 mg/L (World Health Organization, 2015). However, aluminum is usually sparingly soluble at typical pH encountered in natural aqueous environments: the precipitation of $Al(OH)_3$ occurs already at $pH > 4$, but at $pH > 11$, soluble $Al(OH)_4^-$ becomes the predominant species (Schweitzer and Pesterfield, 2010). The results of BFS-GP indicated enhanced binding of aluminum at acid-extraction (S1) and reduction (S2) phases compared to the blank. In the S3 (oxidizable fraction), however, there was a release of aluminum compared to the blank. Finally, in the S4 (residual) fraction, BFS-GP results indicated accumulation of aluminum in the stable residual fraction. MK-GP, on the hand, released aluminum significantly compared to the blank in the S1–S3 phases, possibly due to partial solubilization of the aluminosilicate structure of MK-GP. With vermiculite, there was a minor stabilizing effect observable in S1 and S2, a slight release of Al in S3, and, again, a minor accumulation of Al in the stable S4 fraction. Interestingly, the dose of adsorbent had no clear trend on the aluminum stabilization results, which is likely due to the effect of pH: all adsorbents increased pH clearly over the $Al(OH)_3$ precipitation value independent of dose. BFS-GP was tested with both lake sediments, and it performed similarly.

Zinc is present in the aqueous environment as soluble Zn^{2+} at $pH < 6.5$, precipitated $Zn(OH)_2$ at $pH 6.5–12.5$, and then again soluble $Zn(OH)_4^{2-}$ at $pH > 13$ (Schweitzer and Pesterfield, 2010). There are no health-based guideline values for zinc in drinking water, although concentrations above 3 mg/L cause unpleasant color and taste (World Health Organization, 1996). In the Lake Kivijärvi samples, all adsorbents decreased zinc availability compared to the blank with certain dosing

amounts in the acid-extraction (S1) and reduction (S2) stages. During the oxidative leaching (S3), however, BFS-GP and MK-GP released zinc while vermiculite was still able to keep zinc bounded. In fact, vermiculite (without exfoliation) has previously indicated promising adsorption efficiency towards zinc at pH > 7 (Abollino et al., 2008). Strikingly different results were obtained for Lake Pyhäjärvi, where BFS-GP was also able to bind Zn at oxidative conditions (S3). These results suggest that other water chemistry parameters (such as the presence of ligands) might affect the efficiency of the adsorbent amendments. Results of the stable fraction (S4) indicate that all adsorbents have accumulated zinc compared to the blank. Results of Lake Pyhäjärvi indicate also that 4.4% is the optimum dose for BFS-GP treatment of this sediment (decreased dissolution of Zn in S1–S3 and increased accumulation in S4).

Copper has the most stable oxidation state at +2 and thus occurs as soluble Cu^{2+} when pH is below approximately 5 (Schweitzer and Pesterfield, 2010). The WHO has a guideline value of 2 mg/L for copper in drinking water (World Health Organization, 2015). BFS-GP and MK-GP can reduce copper availability effectively in S1, S2, and S3 leaching stages, while vermiculite releases copper in reducing conditions (S2). Vermiculite has been shown to be effective for copper adsorption at pH > 7 (Abollino et al., 2008; Vijayaraghavan and Raja, 2015). All adsorbents have accumulated copper to the stable fraction, which can be seen from the results of phase S4. However, the lowest and highest BFS-GP doses have resulted in a decreased accumulation of copper to the stable phase (S4). The results of the samples from Pyhäjärvi show that a BFS-GP dose of 4.4% results in decreased dissolution in phases S1–S3 and increased accumulation to stable phase (S4), while with other doses, there is inconsistency. For a *Chironomus* genus specimen (a robust widespread genus of nonbiting midges that can be found around the world also in harsh and oxygen lacking conditions like in stratificated lakes) detrimental effects can be seen in concentrations of 89.2 mg/kg meaning that utilizing geopolymers could have an effect on the survival possibilities of the benthos in Lake Pyhäjärvi (Roman et.al., 2007).

Aqueous chromium is most commonly present at oxidations states +3 or +6, that is, as cationic Cr^{3+} or as chromate oxyanions (for instance, CrO_4^{2-}), respectively (Schweitzer and Pesterfield,

2010). Trivalent chromium is the predominant form in natural waters, while the significantly toxic hexavalent chromium originates usually from industrial loading. WHO has a provisional guideline value of 0.05 mg/L (total chromium) for drinking water (World Health Organization, 1996).

Cr(III) precipitates as Cr_2O_3 or $\text{Cr}(\text{OH})_3$ when pH is above approximately 4, while Cr(VI) stays soluble and deprotonates as pH increases (Schweitzer and Pesterfield, 2010). The speciation of chromium was not performed for the collected samples, and thus, the results are interpreted as total chromium. Only BFS-GP was able to decrease chromium solubility in the acid-extraction (S1) stage. In reducing conditions (S2), however, all adsorbents released chromium compared to the blank. In oxidative conditions (S3), BFS-GP and vermiculite were able to decrease availability. Finally, the accumulation of chromium to stable fraction (S4) was noticed with all adsorbents although there was some inconsistency in the results. It should be noted that MK-GP and vermiculite can adsorb only cations, whereas BFS-GP also has anion exchange properties as demonstrated previously (Luukkonen et al., 2016).

Dissolved titanium is typically present in aqueous environments at the oxidation state +4, for instance, as non-ionic $\text{Ti}(\text{OH})_4$. However, it is more frequently present in the insoluble form (e.g., TiO_2), and as such, it is highly stable and poses no environmental or health risks (Schweitzer and Pesterfield, 2010). According to results in Figure 5, BFS-GP releases titanium in the acid-extraction (S1) and reduction (S2) stages but reduced titanium release in the oxidative extraction phase (S3) compared to the blank. As can be seen from Table 1, there is approximately 0.6% Ti in the blast-furnace slag. MK-GP also releases minor amount of Ti in the S1 and S2 extraction stages and stabilizes Ti compared to the blank in the S3 phase. Vermiculite has C/C_0 of approximately 1 in the S1 extraction stage (i.e., no effect), but significant release of Ti takes place in S2 and S3. In the S4 (residual) fraction, MK-GP and vermiculite indicate higher Ti content compared to the blank.

Iron is an essential nutritional element, which can be present at +2 or +3 oxidation stages. When reducing conditions prevail, Fe^{2+} stays soluble up to pH approximately 6 (Schweitzer and Pesterfield, 2010). However, Fe^{2+} is easily oxidized to Fe^{3+} , which precipitates as hydroxides at pH of approximately 3 (Schweitzer and Pesterfield, 2010). BFS-GP and MK-GP bind iron effectively at

stages S1 to S3, and enhanced accumulation to sediment dry matter is observed for all adsorbents.

Strontium occurs as soluble Sr^{2+} up to pH of approximately 14 and then precipitates as $\text{Sr}(\text{OH})_2$ (Schweitzer and Pesterfield, 2010). Strontium is not currently regulated in drinking water although concentration above 4 mg/L can cause detrimental health (O'Donnell et al., 2016). Strontium has synthetic radioactive isotopes, such as ^{90}Sr (half-life 28.9 years), which are associated with certain cancers (Guillén et al., 2010). Stabilization of strontium was not effective with any of the studied adsorbents and, in fact, they released strontium during all extraction stages compared to the blank.

Nickel is present in aqueous environments as soluble Ni^{2+} at pH less than 8, as precipitated hydroxide ($\text{Ni}(\text{OH})_2$) between pH 8–14, and as soluble HNiO_2^- at pH higher than 14 (Schweitzer and Pesterfield, 2010). The guideline value for nickel in drinking water is 70 $\mu\text{g}/\text{L}$ (World Health Organization, 2005). The typical symptom from nickel exposure is allergic contact dermatitis.

Nickel is also carcinogenic although the risk from oral exposure is unclear (IARC, 1990).

Stabilization of nickel was studied with BFS-GP from Lake Kivijärvi sediment, and it was successful in S1 and S2 extraction stages. However, in the S3 stage (oxidative extraction), nickel was less stable with BFS-GP compared to the blank without adsorbent. Finally, in the residue (S4) stage, there was no accumulation of nickel observable compared to the blank. . For one *Chironomus* genus specimen detrimental effects can be seen in concentrations of 538 mg/kg meaning that utilizing geopolymers could have an effect on the survival possibilities of the benthos in Lake Kivijärvi (Karsten et. al., 2011).

In addition to the abovementioned metal(loid)s, uranium, cadmium, and arsenic were also analyzed but the concentrations were extremely small ($\ll 10 \mu\text{g}/\text{L}$ in all extraction stages), and thus, their results are not shown. Regarding barium, all adsorbents exhibited a significant release especially in the acid-extraction stage (S1) but also during the reduction (S2) and oxidation (S3) stages.

The suitability of adsorbent materials for each of the studied metal(loid)s can be summarized using Table 4.

Table 4. Summary of the metal(loid) stabilization results.

Metal(loid)	The most suitable adsorbent	Remarks
Al	Vermiculite, BFS-GP	Not effective at oxidative conditions
Zn	Vermiculite, BFS-GP	Inconsistent results with BFS-GP at oxidative conditions
Ni	BFS-GP	Not effective at oxidative conditions
Cu	BFS-GP, MK-GP	-
Cr (total)	MK-GP	Dose 2.2% was the optimum
Fe (total)	BFS-GP, MK-GP	-
Ti	None	None of the studied adsorbents was able to withstand all conditions consistently
Sr	None	All adsorbents released strontium
Ba	None	All adsorbents released barium

4. Conclusions

The suitability of metakaolin geopolymer, alkali-activated blast-furnace-slag, and exfoliated vermiculite were studied for the *in situ* stabilization (i.e., active gapping) of potentially toxic metal(loid)s in lake sediments. Sediment samples were collected from two Finnish lakes, which have been subjected to metal(loid) loading from human activities. The suitability was evaluated by a sequential leaching test of amendment-containing sediments compared to a blank sample (without amendment). The aim of the study was to observe the technical feasibility of these novel amendments to be used in the remediation of lakes instead of dredging. Studied metal(loid)s were Al, Zn, Ni, Cu, Cr, Ti, Fe, Sr, and Ba. In addition, As, Cd, and U were also studied, but their concentrations were too low to observe the stabilization effect of the adsorbents.

Following conclusions can be made:

- Blast-furnace-slag geopolymer proved to be the most versatile of the studied adsorbents as it could stabilize Al, Zn, Ni, Cu, and Fe simultaneously. However, it was not always effective at oxidative conditions of the leaching test. One possible reason for the better adsorption capacity is tobermorite, which is shown to have good adsorption properties. In addition, it likely adds Ca to the pore waters of the sediment, reducing metal toxicity.
- Vermiculite could be used for Al and Zn
- Metakaolin geopolymer was effective for stabilizing Cu and Fe.
- The observed performance was difference between the two studied lakes, which implies that other water chemistry parameters also have an effect on the adsorbent amendment efficiency.
- Thus, the efficiency of active capping needs to be determined case specifically.

As a final word, it can be concluded that the results demonstrated the preliminary suitability of geopolymers as active capping materials of metal(loid)-contaminated lake sediment and possibly in improving the living conditions of benthos in comparison to more invasive remediation methods.

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