

Leaching Behaviour of Air-Cooled Blast-Furnace Slag Under Intermittent and Continuous Wetting

Sofia Lidelöw

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SOFIA LIDELÖW

Department of Civil, Environmental and Natural Resources Engineering
Luleå University of Technology
SE-971 87 Luleå, Sweden

Printed by Universitetryckeriet, Luleå, 2011

ISSN: 1402-1536

ISBN 978-91-7439-237-1

Luleå 2011

www.ltu.se

Summary

Air-cooled blast-furnace slag is commonly utilised as a construction material in roads, fill and embankments. Materials used in such constructions do not remain continuously wetted, but is often subjected to cyclic wetting and drying under various exposure conditions. However, its leaching behaviour is often assessed based on tests performed under continuous wetting.

This work was conducted to evaluate the leaching behaviour of an air-cooled blast-furnace slag under intermittent and continuous wetting. Four different leaching tests were performed, including a static leaching test without leachant renewal and three dynamic leaching tests: a column leaching test with continuous flow of the leachant, a tank leaching test with sequential renewal of the leachant and an intermittent leaching test with periodical flow of leachant.

Leaching of the studied material under cyclic wetting and drying led to less alkaline and more oxidised eluates than leaching under continuously wetted conditions. The eluates are expected to maintain a mildly alkaline pH for long time periods during wetting, drying and oxidation of the material because the material has considerable acid neutralising potential.

The leaching of soluble elements such as Ca and S was lower under intermittent than under continuous flow of the leachant which could be due to the shorter contact time between the leachant and material, and the precipitation of secondary phases on the particle surfaces during intermittent leaching. During exposure of the BFS to cyclic wetting and drying, the leaching of these elements decreased and the speciation of S in the eluates shifted towards more oxidising forms.

The leached amounts of constituents were low in all performed tests, which indicate that the material was resistant to leaching under the conditions that were investigated here

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1 Introduction

Blast furnace slag (BFS) is a non-metallic material, consisting mainly of silicates and aluminosilicates of calcium and other basic elements produced simultaneously with iron in a blast furnace. The slag is formed as fluxing agents, mainly limestone, combine with e.g. silica and alumina compounds that would otherwise be incorporated into the molten iron. Depending on the cooling method applied, BFS is divided into two types: air-cooled and granulated BFS. The majority of air-cooled BFS is utilised as aggregates in unbound layers of roads, fill and embankments. Its strength and durability properties make it in many cases a sound alternative to rock materials. Using BFS also lower the environmental loads associated with the exploitation and processing of virgin raw materials (Lee and Park, 2005; Mroueh et al., 2001).

Materials used in constructions are often subjected to cyclic wetting and drying under various exposure conditions (e.g. variable relative humidity, temperature and atmospheric CO₂, O₂ etc.). However, many studies have investigated the leaching properties of BFS by means of laboratory leaching tests developed for characterisation of solid wastes (e.g. Bäverman, 1997; Fällman, 1997; Proctor et al., 2000; Tossavainen and Lind, 2008). These tests aim to predict leaching of inorganic constituents based on the assumptions that conditions will be saturated and that changes in leaching conditions will be relatively minor. BFS contain reactive minerals which under cyclic wetting and drying conditions can be expected to undergo transformations that may change their chemical and physical properties. Such processes are known to affect the leaching properties of other reactive materials such as cemented waste (Sanchez et al., 2002) and incineration ashes (Polettini and Pomi, 2004) by both changes in pH and constituent speciation. As a result of the prevalent O₂ depleted conditions in the blast furnace, BFS also contains reduced components that upon exposure to air may become more oxidised.

The research presented here was carried out to evaluate how continuous wetting and cyclic wetting and drying influences the leaching behaviour of an air-cooled BFS. The impact of intermittent wetting, drying and oxidation of the material was studied by comparison of long-term continuous leaching and leaching having interspersed periods of exposure to laboratory ambient conditions.

2 Material and methods

2.1 Material

The blast-furnace slag (BFS) used in this study originates from iron ore based production at the integrated steel plant in Luleå, Sweden. After tapping, the slag was cooled in air which mainly results in crystallised phases with a minor proportion of glassy phases. After cooling, the BFS had been crushed to a particle size of 0-31.5 mm and stockpiled outdoors for 1.5 year before the sample was collected. A 500 kg composite sample of BFS was taken to the laboratory and successively split into representative sub-samples using a riffle splitter.

2.2 Material characterisation

Total solids (TS) and bulk density were determined after drying at 105°C for 20h. Particle density and water absorption were determined by the pycnometer method.

X-ray diffraction (XRD) analyses were performed on pulverised (<50µm) material at room temperature, using a Siemens D5000 powder diffractometer with CuK α radiation (40kV, 40mA). Scanning was performed continuously between diffraction angles of 5 and 90° (2 θ) using a step size of 0.015° and a counting time of 5s per step. Scanning Electron Microscope (SEM) images were recorded using a Philips XL 30 instrument coupled with energy dispersive analysis of X-rays (EDX).

Chemical characteristics of the BFS were determined on material ground to <125µm using an agate ball mill. Total elemental composition was determined according to the modified EPA methods 200.7 (ICP-AES) and 200.8 (ICP-SFMS) by ALS Scandinavia, Luleå, Sweden. For the analysis of As, Cd Cu, Co, Hg, Ni, Pb, B, Sb, S, Se and Zn, the samples were digested in a microwave oven in teflon tubes with a mixture of 1:1 nitric acid/water (v/v). For the other elements, the samples were melted with LiBO₂ and dissolved using nitric acid. Element concentrations were determined using optical emission spectrometry with inductively coupled plasma (ICP-AES).

Reducing capacity was determined by redox titration according to NEN 7348 (NEN, 2006a). 2g material was allowed to react with an excess 0.1M Ce(IV)sulphate in 1M H₂SO₄ during 24h in an air-tight sealed vessel under N₂ atmosphere to oxidise the reducing components of the material. The oxidant demand (mol O₂ per gram solid material) was determined by back titration with 0.1M Fe(II)sulphate.

Neutralizing value (liming effect) was determined by titration to pH 4.8 according to EN 12945 (CEN, 2008). 0.5g material was dissolved in a specified quantity of 0.5M HCl. The excess of acid was determined by back titration with 0.25M NaOH.

Acid neutralisation capacity (ANC) was determined through parallel batch extractions with increasing additions of HNO₃. 10 g material was mixed with deionised water adjusted to specific pH with HNO₃, at an L/S (solid-to-liquid ratio) of 10 l kg⁻¹. The acid addition schedule was based on the buffering capacity of the material. The bottles were rotated end over end for 48 h. The pH was measured directly in the suspension. Measured pH values were plotted against the amount of acid added for each individual mixture.

2.3 Leaching behaviour tests

Four different leaching tests were used, including a static leaching test without leachant renewal and three dynamic leaching tests:

- Column leaching test with continuous flow of the leachant.
- Tank leaching test with sequential renewal of the leachant.
- Intermittent leaching test with periodical flow of leachant.

All tests were made under ambient conditions (20°C) and using deionised water as leachant. The intermittent test was performed on samples sieved into two different size fractions: <4 mm and <31.5 mm. The other tests were made only on the fraction sieved to <4 mm.

Static leaching test

Static leaching was studied by immersion of 50 g material in deionised water, at an L/S of 10 l/kg. The suspensions were placed in air-tight glass bottles and allowed to react with no agitation. Samples were extracted with a syringe for analyses of pH, Eh and electrical conductivity (EC) after 1, 2, 4, 8, 16, 36 and 64 days. Samples for elemental analyses were taken after 64 days.

Column leaching test

A column leaching test at an accumulated L/S of 2 l/kg was performed according to the up-flow percolation test CEN/TS 14405 (CEN, 2004). Deionised water was passed through the material in a vertical column with an internal diameter of 5 cm and a filling height of 31 cm. The total test duration was 6 days.

Tank leaching test

Based on the compacted granular leaching test NEN 7347 (NEN, 2006b), a tank leaching test was performed in order to distinguish between different leaching mechanisms (surface wash-off, dissolution and diffusion) upon immersion of the material in water. 1 kg of material were placed in a 4 cm layer on the bottom of a cylindrical plastic vessel (diameter 17 cm), covered with a 2-3 cm layer of glass marbles and saturated with deionised water. After 24h, deionised water was added to reach a level of 5 cm above the layer of glass marbles and the vessel was sealed. The free volume of water was changed eight times after specified time periods (0.25, 1, 2.25, 4, 9, 16, 32 and 64 days), yielding eight leaching fractions per test. Each leaching fraction was associated with an L/S of 0.55 l/kg. The volume of eluate collected was recorded and samples were extracted for analyses.

The evaluation of the leaching mechanisms was based on an arithmetical cumulative release of the inert elements Na and K. The measured cumulative release cannot be used since any deviations in one period affect the subsequent periods. The arithmetical cumulative release of a constituent per interval was calculated using:

$$\varepsilon_n = E_i^* \times \frac{\sqrt{t_i}}{\sqrt{t_i} - \sqrt{t_{i-1}}} \text{ for } n = 1 \text{ (where } i = N)$$

where: ε_n (mg/m) is the calculated release of a component for the n :th period
 E_i (mg/m) is the measured leaching of component in fraction i
 t_i, t_{i-1} (s) are replenishment times of fractions i and $i-1$

If the measured and calculated cumulative releases are equal, the release is controlled by diffusion (Chandler et al., 1997). To support and control the assessment of the leaching behaviour, regression analysis as described in the diffusion test standard NEN 7347 was used to calculate the slopes and standard deviations of the total (steps 2–7) and the subsections of the release plot (log release vs. log time) for the elements (start for steps 1–4, middle for steps 3–6, and end for steps 5–8). Diffusion-determined leaching behaviour is indicated by a slope of 0.5 ± 0.15 , dissolution leaching results in a slope of >0.65 and wash-off from the surface in a slope <0.35 .

Intermittent leaching test

Intermittent leaching tests were carried out to study the weathering and leaching over time under accelerated atmospheric conditions.

Two different shape (length×width×height) leaching cells were used in the experiment: 20×16×11 cm for the fraction <4 mm and 32×24×16 cm for the fraction <31.5 mm. The cells with <4 mm fraction were loaded with 1 kg of material and the cells with <31.5 mm fraction with 4 kg of material. The samples were placed on a geotextile overlaying a layer of glass marbles (Figure 1).

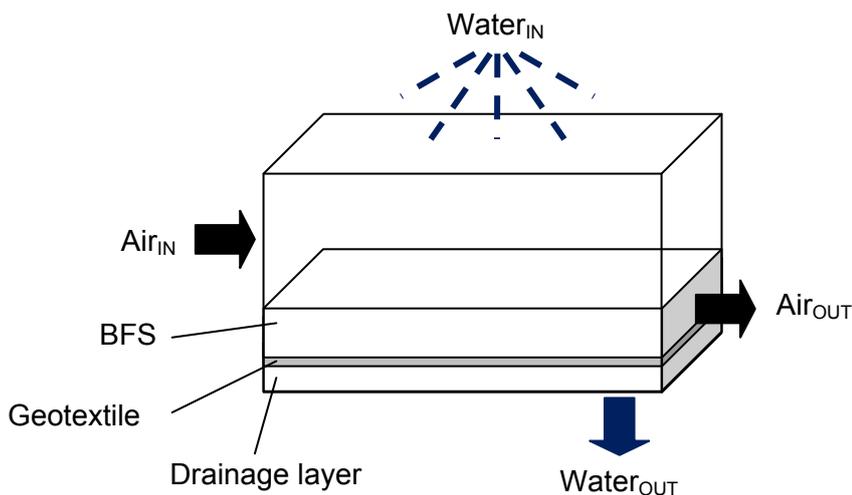


Figure 1 Experimental lay-out of cells used for the intermittent leaching tests.

The cells were subjected to a weekly aeration cycle with six days of dry air (supplied at 3.4 l/min) and flushed with 0.15 l/kg of deionised water on the final (7th) day of the cycle. This generated 0.1 l/kg of eluate per cycle. After the cells finished draining (1h or

less) the volume of eluate collected was recorded and samples were extracted for analyses. The tests were run for 20 leaching cycles, i.e. 140 days. After the tests were terminated the solid samples <4 mm were dried and characterised with regard to their mineralogical and chemical characteristics as described in section 2.2.

2.4 Chemical analyses

pH, redox potential and electrical conductivity were determined immediately after sampling on unfiltered samples. pH was measured using a 340/SET-1 pH meter with a SenTix 41 combined electrode (WTW, Germany). EC was determined using a 2-pole conductivity cell (CDC641T, radiometer, Denmark) connected to a CDM210 conductivity meter (Radiometer, Denmark). Redox potential was measured using an InLab gold-coated glass electrode connected to a PHM95 ion meter (Radiometer, Denmark). Measured redox potential values were adjusted to the standard hydrogen electrode.

Sulphate (SO_4^{2-}) was determined by segmented flow injection spectrophotometry with methylthymol blue after separation of interfering ions using a QuAAtro auto analyser (Bran+Luebbe, Germany). Thiosulphate ($\text{S}_2\text{O}_3^{2-}$) was determined by iodometric titration.

Dissolved fractions of elements were determined after filtration through 0.45 μm cellulose acetate syringe filters (Gema Medical, Spain) and acidification using 1 ml of HNO_3 for every 100 ml of sample. Prior to determination of total sulphur, the samples were stabilised with 10 ml H_2O_2 per 100 ml of sample to ensure complete oxidation of sulphur present in reduced and intermediate oxidation states. Such preparation also avoids any volatile sulphur species present in the samples to enter the ICP torch after nebulisation, which lead to the detection of a higher mass concentration of sulphur than actually present (Hwang et al., 2005; Raue et al., 1991). The samples were analyzed using ICP-AES by ALS Scandinavia, Luleå, Sweden. Analytical error was <15% for every element run.

2.5 Statistical analyses

The statistical significance of differences in means was determined (where appropriate) using Tukey's multiple comparison test or the two-sample t-test ($p < 0.05$).

3 Results

3.1 Physical characteristics

Basic physical characteristics of the BFS investigated here are given in Table 1.

Table 1 Physical characteristics of the BFS (n=3, ±SD).

	Unit	
Total solids (TS) (0-31.5 mm)	%	93.3 ±0.3
Bulk density (<4 mm; 0-31.5 mm)	ton/m	1.42 ±0.03; 1.33 ±0.04
Particle density (<4 mm; 4-31.5)	ton/m	2.84 ±0.03; 2.51 ±0.04
Water absorption (<4 mm; 4-31.5)	% dw	4.3 ±0.2; 4.7 ±0.5

The lower density of larger particle size fractions is indicative of the high porosity of the material. According to the particle size distribution (Figure 2), the BFS corresponded to relatively well-graded sandy gravel.

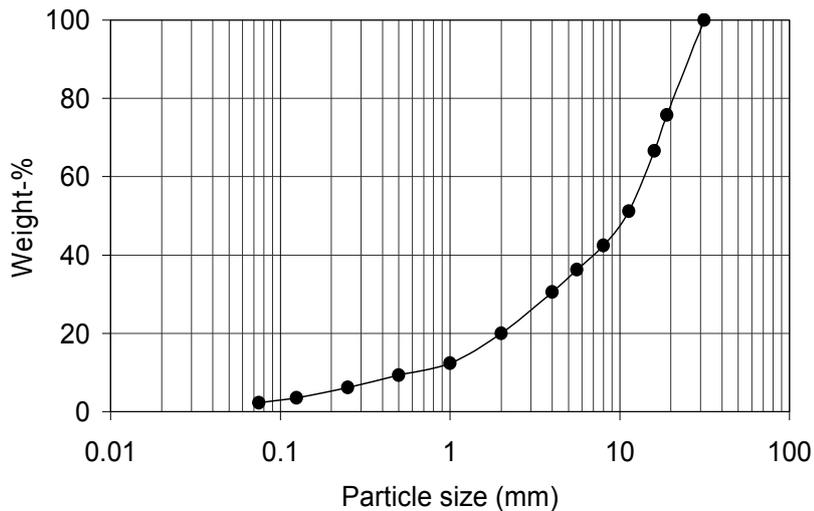


Figure 2 Particle size distribution of the original BFS with nominal size 0-31.5 mm.

3.2 Chemical characteristics and mineralogy

X-ray diffraction analysis was carried out to identify the crystalline solid phases for the studied BFS (Figure 3). Akermanite ($\text{Ca}_2\text{MgSi}_2\text{O}_7$) was identified to be the dominant phase, followed by monticellite (CaMgSiO_4) and some spinel. Additional mineral phases were present but could not be identified.

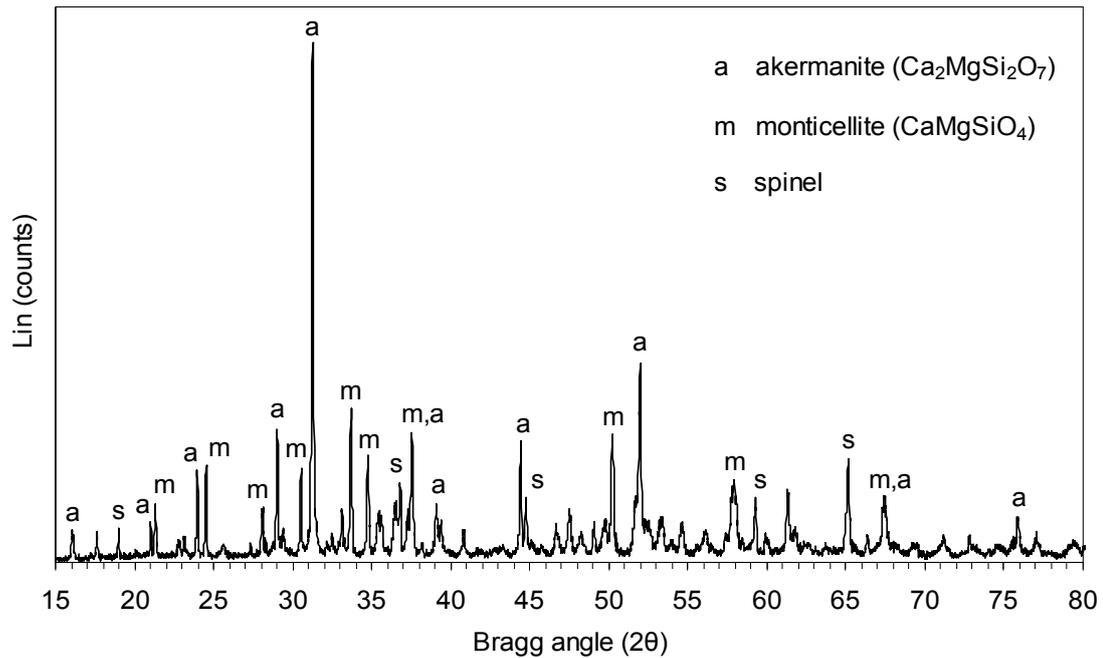


Figure 3 Particle XRD pattern of the studied BFS.

The chemical composition of the BFS under consideration and some of its characteristics are presented in Table 2. The BFS is mainly composed of Ca, Si, Mg and Al. In comparison with other blast-furnace slags from Europe and North America (Brämning and Wikström, 2002; Proctor et al., 2000; Reuter et al., 2004), the studied BFS contains higher amounts of Mg, but lower amounts of Ca. The results in Table 2 indicate that there are some differences between the composition of the bulk fraction <31.5 mm and the fraction <4 mm. Compared to the fraction <31.5 mm, the fraction <4 mm contains lower amounts of Ti, S and K and higher amounts of Na and Fe. The difference compared to the bulk fraction was larger for S (-18%) and Fe (49%) than for other elements ($\pm 5\%$).

The measured acid neutralising value and the 48h ANC test showed that the material has a high ANC and that much acid is required to neutralise the alkaline content (Table 2; Figure 4).

The measured reducing capacity showed that the material possesses reducing properties (Table 2).

Table 2 Chemical characteristics of the BFS before and after leaching in the intermittent leaching test (n=3, ±SD).

	Unleached (<31.5 mm)	Unleached (<4 mm)	Leached (<4 mm)
Chemical composition (% dw)			
Ca	23.0±0.2	22.8±0.1	22.8±0.04
Si	15.1±0.1	15.0±0.1	15.5±0.1
Mg	10.3±0.2	10.2±0.1	10.3±0.1
Al	6.26±0.2	6.26±0.03	6.46±0.1
Ti	1.44±0.01 ^a	1.40±0.01 ^a	1.40±0.00
S	1.04±0.05 ^a	0.86±0.02 ^{a,b}	0.69±0.02 ^b
K	0.60±0.01 ^a	0.58±0.01 ^{a,b}	0.54±0.01 ^b
Na	0.35±0.01 ^a	0.36±0.01 ^a	0.36±0.01
Fe	0.32±0.1 ^a	0.47±0.02 ^a	0.42±0.02
Mn	0.25±0.01	0.25±0.00	0.26±0.01
Ba	0.072±0.001 ^a	0.069±0.001 ^a	0.068±0.001
V	0.038±0.003 ^a	0.047±0.001 ^a	0.051±0.001
Neutralising value (% CaO)	52±2	n.a.	34±2
Reducing capacity (mmol O ₂ /kg)	186±3	n.a.	134±3

^a denotes significant difference between the fractions <31.5 and <4 mm (p<0.05).

^b denotes significant difference between unleached and leached material <4mm (p<0.05).

n.a. – not available

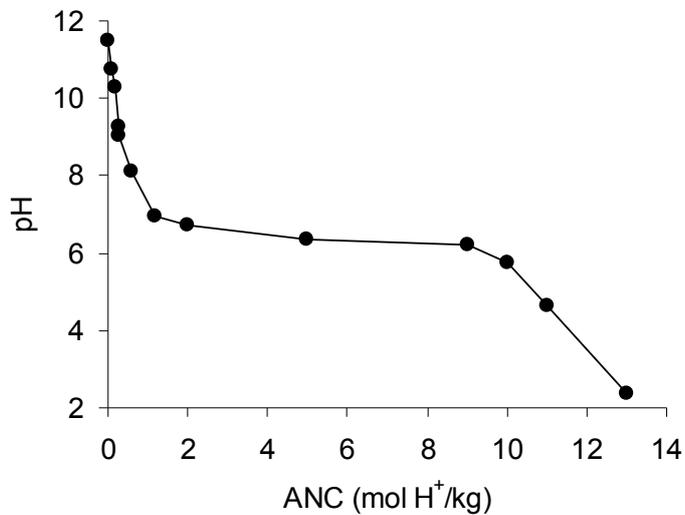


Figure 4 Acid neutralisation capacity, determined after 48h, of the studied BFS.

3.3 Leaching tests

Static leaching test

The developments of the pH and EC upon immersion of BFS in the static test at L/S 10 are shown in Figure 5. Both the pH and EC increased over time.

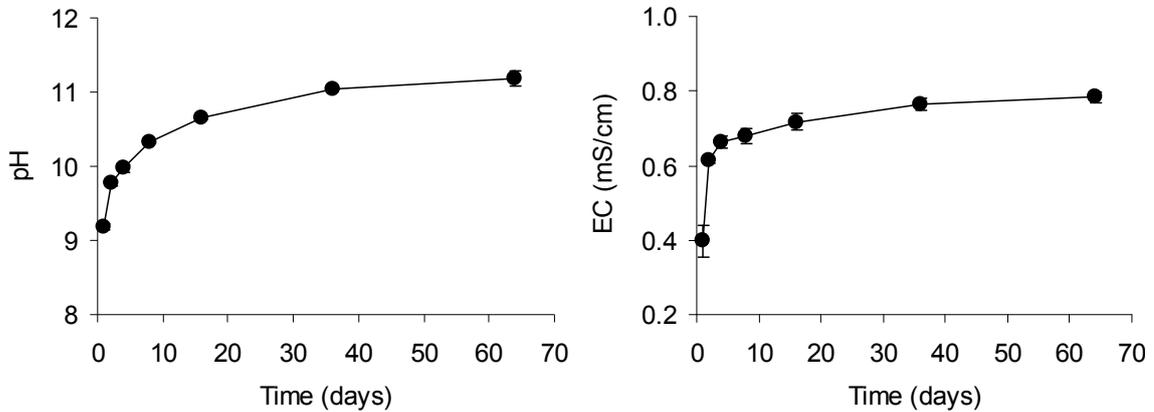


Figure 5 Developments of pH and EC in the static leaching test for BFS <4 mm at L/S 10 for 64 days (n=3, \pm SD).

The development of the measured Eh-values of the eluates is shown in Figure 6. The Eh-values have been placed in perspective by plotting the redox potential measured as a function of pH in comparison with oxidised, deionised H₂O (pH-adjusted using HNO₃ and NaOH). The Eh-values of the eluates were lower than the level observed in oxygenated water and decreased over time.

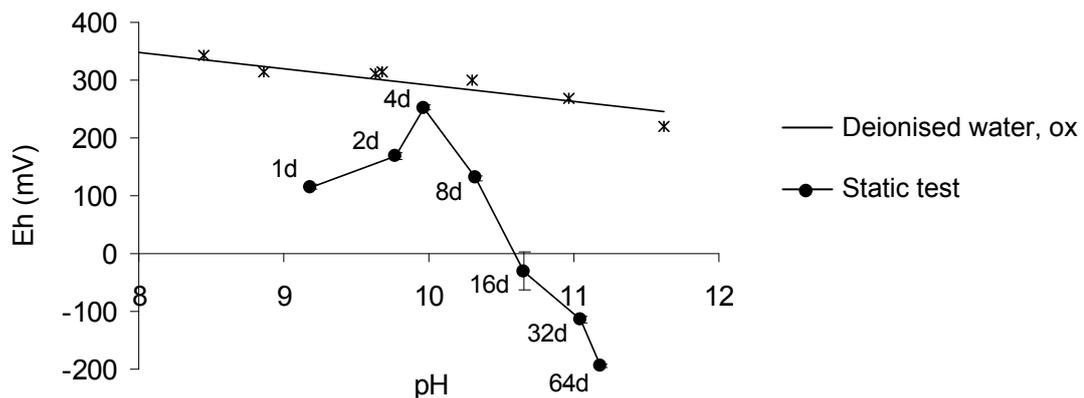


Figure 6 Relationship between Eh and pH of the eluates from the static leaching test for BFS <4 mm at L/S 10 in relation to oxidised deionised water. The data labels denote the leaching time.

The liquid phase was analysed after 64 days of reaction and found to contain mainly S (0.4%; of which 32% and 17% was in the form of $S_2O_3^{2-}$ -S respective SO_4^{2-} -S) and Ca (0.2%) followed by K and Na (Table 3).

Table 3 Chemical composition of eluates from the static leaching test for BFS <4 mm at L/S 10 after 64 days contact time (n=3, \pm SD).

Constituent	mg/kg
S _{tot}	3780 \pm 220
S ₂ O ₃ ²⁻ -S	1210 \pm 44
SO ₄ ²⁻ -S	630 \pm 41
Ca	2170 \pm 70
K	473 \pm 4
Na	143 \pm 2
Si	37 \pm 3
Mg	8.8 \pm 0.6
Mn	0.15 \pm 0.02
Fe	<0.2

Column leaching test

The leached amounts of S, Ca, K, Na and Mg at an accumulated L/S of 2 in the column leaching test were higher than for other elements (Table 4). Comparing the leached amounts with the composition of unleached BFS (Table 2), S (21%), K (9%) and Na (3%) presented higher leachability than other elements (<1%).

Table 4 Results of the column leaching test, the tank leaching test and the intermittent leaching test for BFS <4 mm at an accumulated L/S 2 (n=3, \pm SD).

	Column leaching test	Tank leaching test	Intermittent leaching test
pH	8.0 \pm 0.1	9.0 \pm 0.1	8.0 \pm 0.1
EC (mS/cm)	3.6 \pm 0.1	0.44 \pm 0.02	1.2 \pm 0.1
Eh (mV)	157 \pm 42	n.a.	432 \pm 1
Cumulative release of elements (mg/kg)			
S _{tot}	1821 \pm 83 ^{a,c}	341 \pm 31 ^{b,c}	1045 \pm 31 ^{a,b}
Ca	1488 \pm 53 ^{a,c}	204 \pm 26 ^{b,c}	647 \pm 21 ^{a,b}
K	503 \pm 24 ^{a,c}	87 \pm 9 ^{b,c}	371 \pm 12 ^{a,b}
Na	111 \pm 3 ^c	20 \pm 2 ^{b,c}	107 \pm 4 ^b
Mg	45 \pm 3 ^{a,c}	0.7 \pm 0.1 ^{b,c}	81 \pm 2 ^{a,b}
Si	n.a.	2 \pm 0.3 ^b	7.4 \pm 0.5 ^b
Mn	0.76 \pm 0.09 ^{a,c}	0.027 \pm 0.002 ^{b,c}	0.80 \pm 0.05 ^{a,b}
Fe	<0.008	<0.04	<0.04

^a denotes significant difference between intermittent and column leaching test (p<0.05).

^b denotes significant difference between intermittent and tank leaching test (p<0.05).

^c denotes significant difference between column and tank leaching test (p<0.05).

n.a. – not available

Tank leaching test

Figure 7 presents pH and EC values of various eluate fractions from the tank leaching test. After an initial reduction of 44%, the EC increased over eluate fractions. The pH remained fairly constant around 9 except for the last eluate fraction where the pH was higher (9.7).

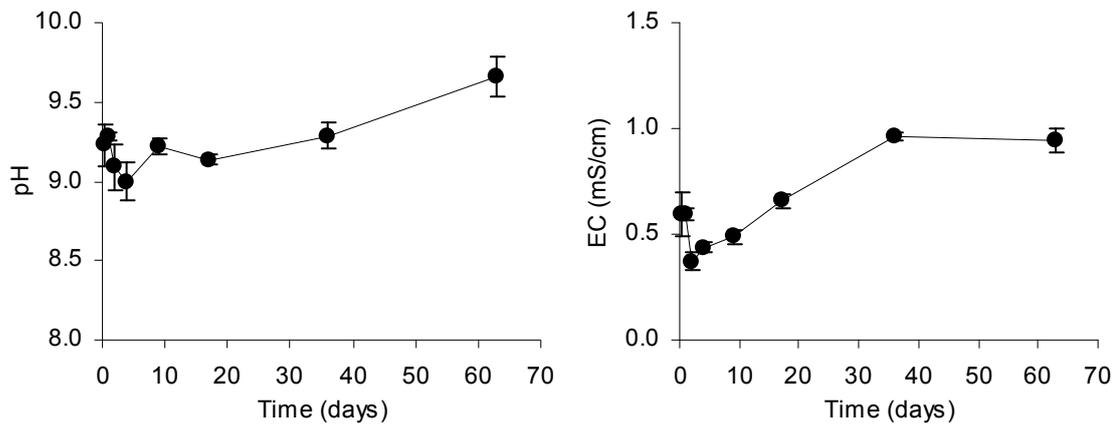


Figure 7 Developments of pH and EC in the tank leaching test on BFS <4 mm (n=3, ±SD).

The slopes of the release plots for K and Na versus time are given in Table 5.

Table 5 Slopes (k) of the total (steps 2-7) and partial subsections (start for steps 1-4, middle for steps 3-6, and end for steps 5-8) of the arithmetical cumulative release plot for K and Na of the tank leaching test on BFS <4 mm (n=3, ±SD).

Subsection	K	Na
2-7	0.52±0.04	0.45±0.05
1-4	0.31±0.10	0.20±0.04
3-6	0.45±0.03	0.43±0.04
5-8	0.66±0.03	0.69±0.04

The cumulative release of constituents from the tank leaching test at an accumulated L/S of 2, i.e. after the fourth leaching fraction, is given in Table 4. The leached amounts of S, Ca, K and Na were higher than for other elements. Comparing the leached amounts with the composition of unleached BFS (Table 2), S (3%) presented higher leachability than other elements (<1%).

Intermittent leaching test

The developments of pH, Eh and EC in eluates from intermittently leached BFS are presented in Figure 8.

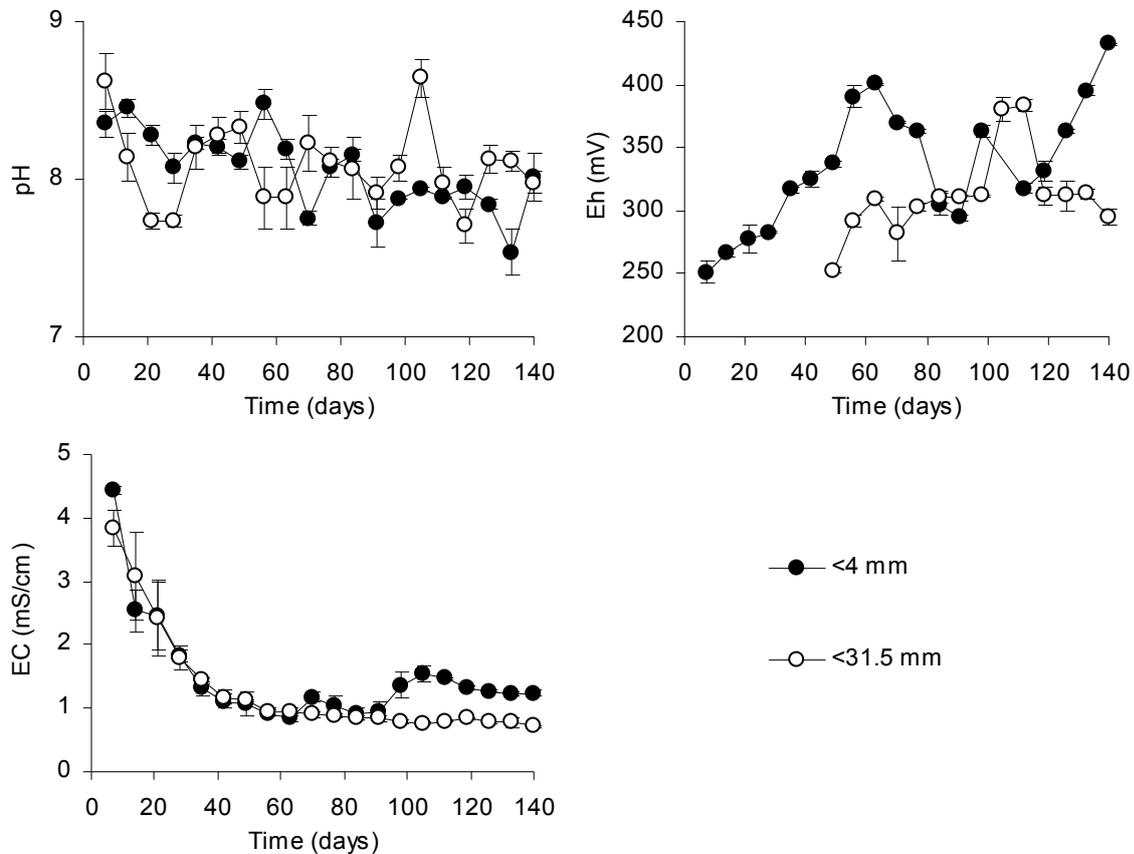


Figure 8 Developments of pH, Eh and EC in eluates from intermittently leached BFS (n=3, \pm SD).

The pH of the eluates varied between 7.5 and 8.6 without any clear temporal trends. The pH of eluates from the different particle size fractions was not significantly different. The EC of the eluates decreased over time. For the fraction <4 mm, the EC later increased but stabilised at around 1.2 mS/cm after 16 cycles. For the fraction <31.5 mm, the EC stabilised at a level of 0.6-0.8 mS/cm after about 10 cycles. The Eh of eluates from the fraction <4 mm increased by almost 200 mV without tendency to stabilise during the observation period. For the fraction <31.5 mm, Eh-values of the first six eluates were not measured but over time the eluate Eh seemed to stabilised around 300 mV.

Figures 9 and 10 show the amounts of Ca, K, Mg, Na, Si and S in the eluates from the intermittent leaching test. The amounts of these constituents in the initial eluates were significantly higher for the fraction <4 mm than the coarser particle size fraction. In the following eluates, the leached amounts of these elements from the fraction <4 mm were alternatively higher, similar or, in some cases, lower than from the coarser fractions, except for Mg which remained higher for the fraction <4 mm than the coarser fraction. The amounts of Ca, K, Na and S in the eluates decreased over time and then stabilised, while those of Mg and Si increased over time without showing any tendency to stabilise.

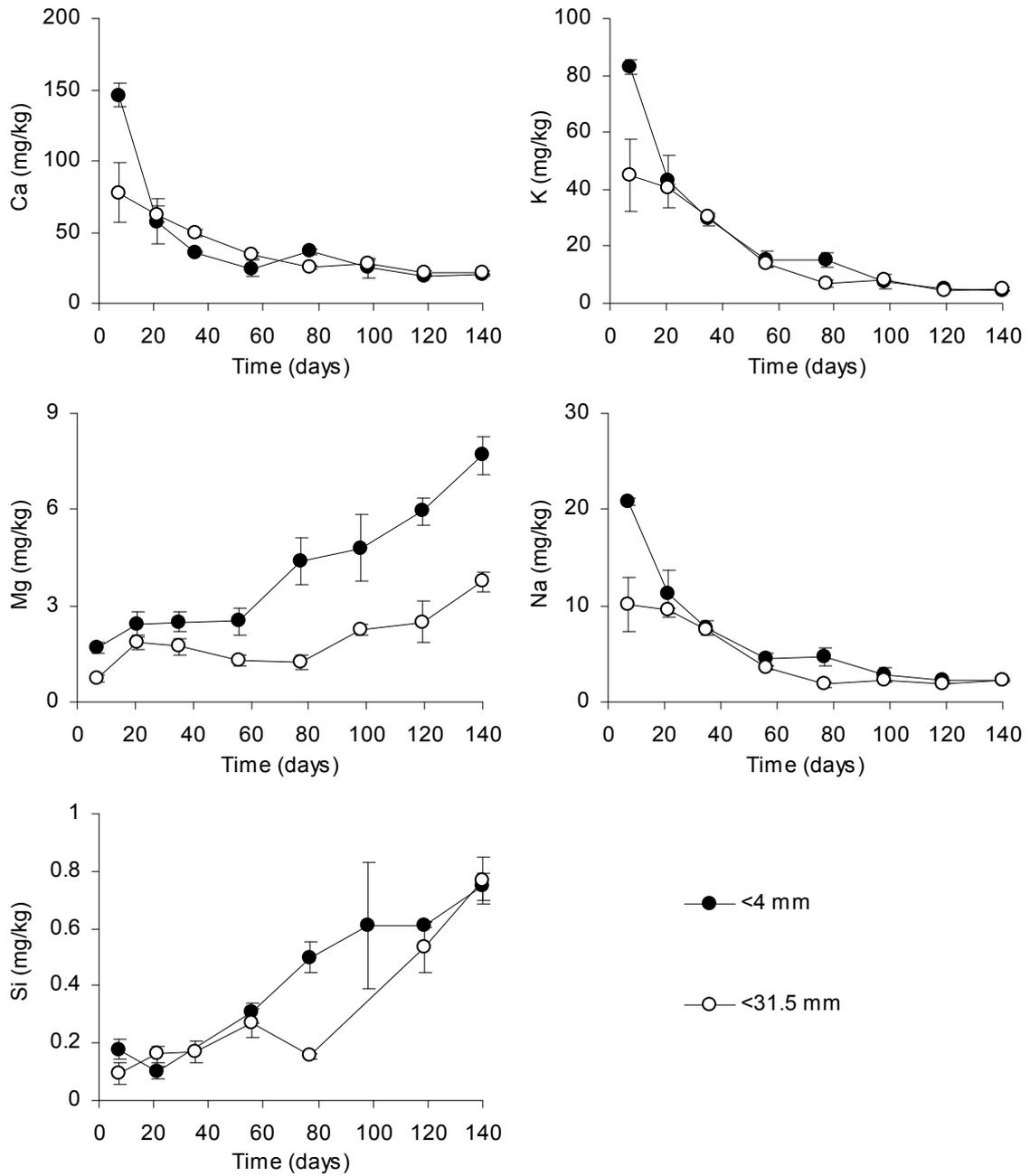


Figure 9 Changes in the amounts of Ca, K, Mg, Na and Si in the eluates from the intermittent leaching test (n=3, ±SD).

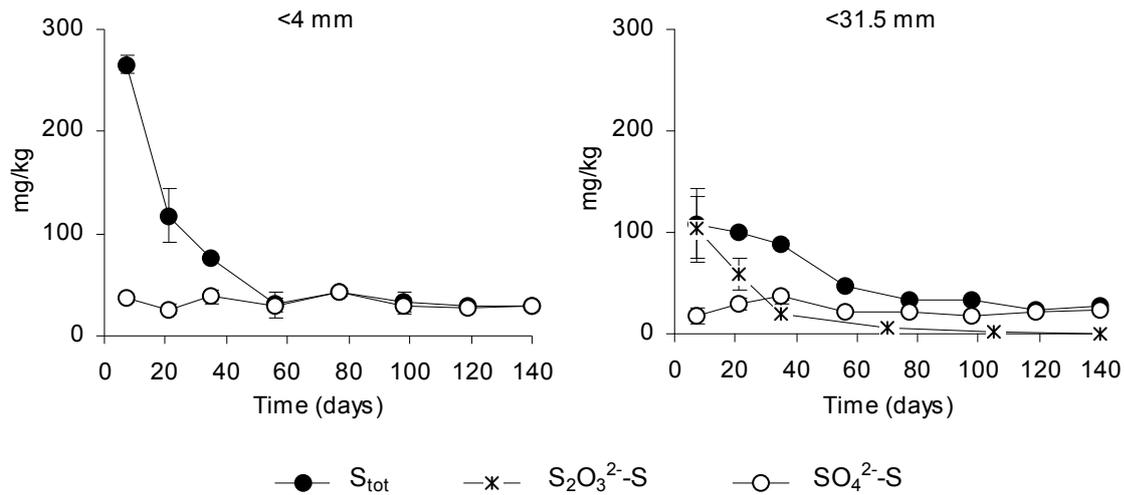


Figure 10 Changes in the amounts of different S species in the eluates from the intermittent leaching test (n=3, ±SD).

Initially, S₂O₃²⁻-S was the predominant S species measured from the fraction <31.5 mm (95% of total S) (Figure 10). Over time, the leached amounts of S₂O₃²⁻-S decreased to constitute about 2% of the total S in the final eluates of the BFS <31.5 mm. The amounts of SO₄²⁻-S remained relatively constant during the observation period. Initially, SO₄²⁻-S constituted about 14% and 16% of the S measured from the fractions <4 mm and <31.5 mm. Over time, SO₄²⁻-S became the predominant S species in the eluates. All S leached from the fraction <4 mm was in this form from the eleventh leaching cycle and onwards, whereas SO₄²⁻-S constituted 86% of the total S in the final eluates from the fraction <31.5 mm.

Table 4 summarises the results of the intermittent leaching tests, resulting in an accumulated L/S of 2, in terms of cumulative release from the fraction <4 mm. As for the column leaching test, the leached amounts of S, Ca, K, Na and Mg were higher than for other elements. Comparing the leached amounts with the total composition of unleached BFS (Table 2), S (12%), K (6%) and Na (3%) presented higher leachability than other elements (<1%).

After leaching in the intermittent test, the XRD pattern of the BFS showed no substantial changes (results not shown). The chemical composition was unaltered except that the contents of S and K were lower in the leached sample (Table 2). The reducing capacity and the neutralising value of the BFS decreased by 28 and 35%, respectively.

During the test, a white precipitate on the particle surfaces was observed to form. Analysis by SEM-EDS of surfaces of leached BFS revealed the presence of Ca-rich crystals and a smaller amount of a Ca- and S-rich phase (Figure 11).

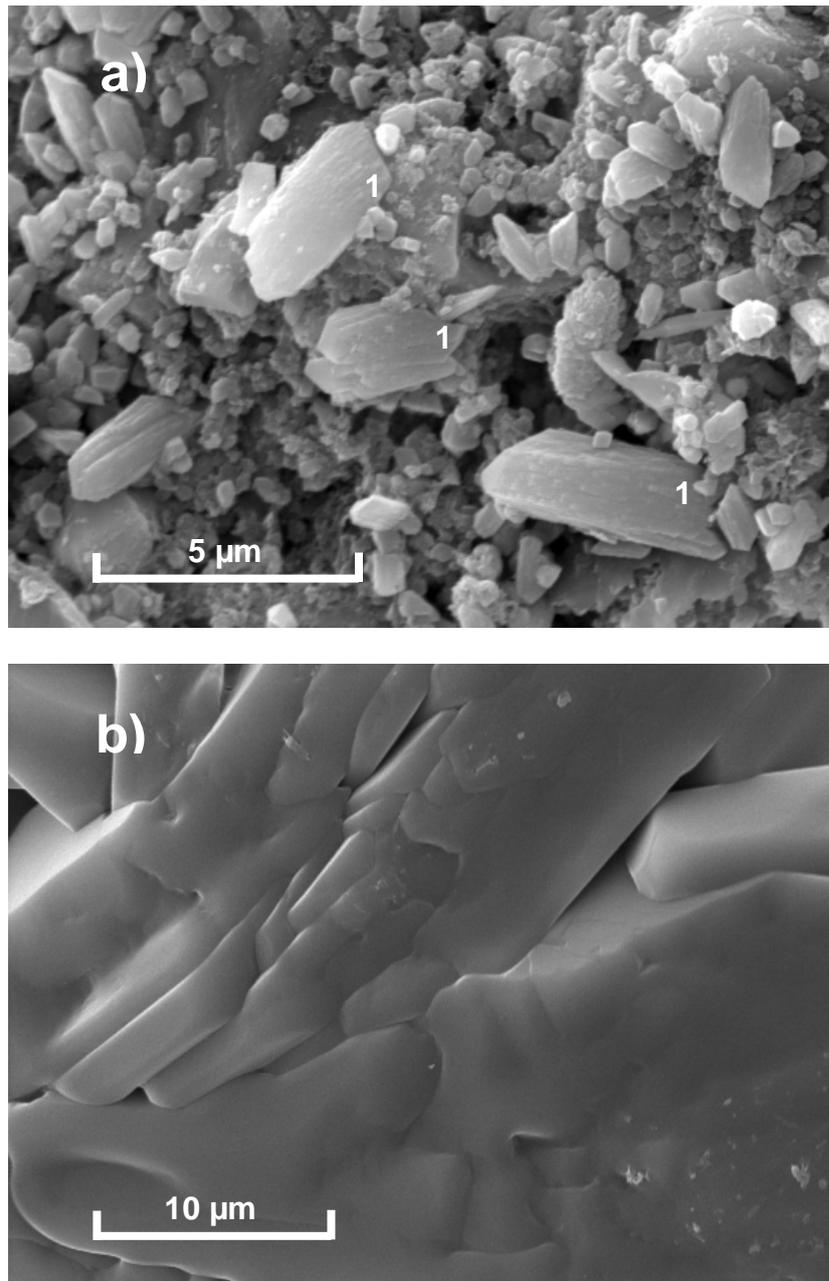


Figure 11 SEM images of surfaces of BFS particles after leaching in the intermittent leaching test: a) Ca-rich crystals (1) and b) a Ca- and S-rich phase.

4 Discussion

4.1 Leaching behaviour under continuous wetting

Upon immersion of the BFS in deionised water in the static test, the pH values for the liquid phase increased with time (Figure 5). Calcium silicates within the BFS such as akermanite are known to slowly release hydroxyl ions through incongruent hydrolysis reactions which rises solution pH (Dimitrova and Mehanjiev, 2000; Gao et al., 1995). Such reactions explain also the high acid buffering potential of the BFS indicated by its neutralising value (Table 2) and the results of the ANC test (Figure 4). The BFS can be expected to continue to react and buffer for time periods far extending the 48h testing time in the ANC test. Yan et al. (2000) found that the long term ANC of steel slags below pH 9 should be analysed for more than 500h and that a 24h test accounted for <60% of the available ANC, even with particle sizes <0.160 mm.

Although Eh readings should be viewed with caution, they allow a general characterisation of the redox status in a system and in this case showed that the BFS exhibit reducing properties (Figure 6). This is consistent with the consumption of O₂ measured in the redox capacity test (Table 2). The reducing properties of a material are largely determined by the presence of reduced forms of Fe, Mn and/or S, which may become available as a result of leaching. The leached amounts of elements in the static test (Table 3) show that the reducing capacity of the BFS is caused mainly by the presence of S species because Fe and Mn, which exhibit low leachability in neutral to alkaline environments, were present in low dissolved amounts in the eluates. S-species such as sulphides (S²⁻) and polysulphides (S_n²⁻) have been identified as the most important carriers for imposing reducing conditions in fluids in contact with BFS (Atkins and Glasser, 1992; van der Sloot et al., 1994).

An important factor affecting the extent and rate of constituent leaching is the latent pozzolanic reactions occurring during testing. Although air-cooled BFS is less reactive than granulated BFS, pozzolanic activity tests have shown it is hydraulically active (Mostafa et al., 2001). During the tank leaching test changes in release mechanisms occurred with increasing constituent release towards the end of the test. According to the slopes of the arithmetical cumulative release (Table 5), the inert elements Na and K demonstrated diffusion controlled leaching behaviour throughout most of the test (steps 2-7), with surface wash-out in the initial leaching intervals (steps 1-4). However, towards the end of the test (steps 5-8) the slopes of the arithmetically calculated release were in the range 0.66-0.69 suggesting that Na and K were released by dissolution. This illustrates that reactions took place without reaching equilibrium during the test, probably due to the relatively slow kinetics of the hydration reactions. As a consequence, it is not possible to determine whether diffusion or dissolution would eventually be the dominating release mechanism. Tossavainen and Lind (2008) investigated BFS with various glass contents in a similar 64 days leaching test and found that the testing time was not sufficient to fully account for the stabilising reactions of the pozzolanic minerals in the material.

Because of the reactivity of the material, the interpretation of results of leaching test on BFS in terms of absolute levels of pH, Eh and constituent release is not straightforward. Apart from the hydraulic reactivity the measured pH, Eh and constituents release are

also dependent on the L/S ratio, the leaching time, the leachant used, the access of atmospheric CO₂ and O₂ during leaching, etc.

4.2 Leaching behaviour under intermittent wetting

In the intermittent leaching test more oxidised and less alkaline conditions developed in the liquid phase (Figure 8) than during immersion of BFS in deionised water (Figure 5). This was expected due to the shorter liquid-to-solid contact times and greater exposure of the material to air in the intermittent leaching test. The pH of the eluates remained fairly constant over time (Figure 8) and the material possessed considerable acid neutralising potential both before and after exposure to cyclic wetting and drying in the intermittent test (Table 2). Eluates from the BFS can therefore be expected to maintain a mildly alkaline pH for long time periods during such conditions.

During the testing period, the Eh values increased (Figure 8) and the speciation of S in the eluates shifted towards more oxidising forms (Figure 10), which indicated that oxidation of the material occurred. Sulphur in BFS has been reported to occur as a form of sulphide which gradually transforms into stable sulphates upon contact with air during cooling and subsequent ageing (Roy, 2009; Watanabe et al., 1981). The lower reducing capacity of the BFS after leaching in the intermittent test (Table 2) was probably due to the combined effect of oxidation and leaching of available reducing agents.

In the intermittent leaching test, the EC and the amounts of e.g. Ca, K, Na and S in the eluates decreased (Figures 8 and 9), likely because of the initial dissolution of weathering products and adsorbed species at particle surfaces. At an L/S of about 1.5 (after about 100 days), the leaching was stabilised for these components and the system seemed to have reached steady state. At the same time the release of Mg and Si remained constant or increased, which may be attributed to weathering of Mg-Si bearing minerals. As Ca diffuses toward the surface of the particles, minerals such as akermanite and monticellite deplete in Ca and may then undergo transformations through which Mg and Si are released to solution.

The major elemental and mineralogical composition of the BFS after exposure to cyclic wetting and drying in the intermittent test practically did not change. This is indicative of relative resistance to leaching and chemical stability of the BFS under such conditions. Sulphur presented the highest leachability, in terms of percentages, among the discussed elements. However, the leached amount is small because of the low total content of this element in the material ($\leq 1\%$).

The cumulative releases of S and Ca were higher than for other elements in all performed tests. The leached amounts of these constituents in the intermittent leaching test were lower than in the column leaching test but they were higher than in the tank leaching test (Table 4). An accumulated L/S of 2 was reached in all three tests, but the leaching times and conditions were different. An L/S of 2 was reached after 140 days in the intermittent test with interspersed periods of drying, while it took 6 days in the column test with continuous water flow and 4 days in the tank leaching test with sequential renewal of leachant. Lowest leaching was expected in the tank test where the leached constituents are allowed to diffuse to the eluate without flushing of the voids of

the BFS. In addition, S and Ca precipitated in solid phases during the test which reduced the dissolved amounts of these constituents in the eluate. The lower leaching of S and Ca in the intermittent test than in the column test was probably due to a shorter contact time between the leachant and solid material in the intermittent test. In addition, during the drying phase, the material underwent ageing reactions which resulted in the precipitation of secondary minerals. It seems plausible that S- and Ca-rich phases precipitated on the surfaces (Figure 11), thereby reducing the leached amounts of these elements. The effects of such reactions are commonly not observed as most laboratory leaching tests are performed under saturated conditions, while under field conditions cyclic wetting and drying is frequently occurring. How naturally occurring processes such as biological activity and variations in water quality that the material is exposed to affect these reactions is a subject of future studies.

5 Conclusions

The studied air-cooled BFS showed different leaching behaviour under intermittent wetting and continuous leaching conditions. Leaching of the BFS under cyclic wetting and drying led to less alkaline and more oxidised eluates than leaching under saturated conditions.

The material possessed considerable acid neutralising potential. Eluates of the BFS are therefore expected to maintain a mildly alkaline pH for long time periods during wetting, drying and oxidation of the material.

S and Ca were leached in higher amounts than other elements in all performed leaching tests but the leached amounts were low. The leaching of S and Ca was lower under intermittent leaching conditions than under saturated leaching conditions with continuous water flow, probably due to the shorter contact time between the leachant and material and the precipitation of secondary phases rich in S and Ca on the particle surfaces. During exposure of the BFS to cyclic wetting and drying, the leaching of these elements decreased and the speciation of S in the eluates shifted towards more oxidising forms.

The major elemental and mineralogical composition of the BFS practically did not change after exposure to 140 days intermittent leaching up to L/S 2. This is indicative of its relative resistance to leaching and chemical stability under the conditions that were investigated here.

Acknowledgements

This work was financially supported by J Gust Richert Memorial Fund and European Union Structural Funds, Northern Sweden Soil Remediation Centre, ERDF Objective 2, Contract MCN IO No 43173.

The author thanks Ulla-Britt Uvemo and Désirée Nordmark for their assistance with chemical analyses, Silvia Diener for her help with XRD analyses and Ivan Carabante for his help with SEM analyses. For valuable comments on the manuscript, thanks are due to Henning Holmström, Lotta Lind, Pentti Lahtinen, Josef Mácsik, Staffan Rutqvist, Therese Stark and Anita Wedholm.

References

- Atkins, M. and Glasser, F.P. (1992). Application of portland cement-based materials to radioactive waste immobilization. *Waste Management* 12: 105-131.
- Brämning, M. and Wikström, J.-O. (2002). A blast furnace view on slags. *Scandinavian Journal of Metallurgy* 31: 88-99.
- Bäverman, C. (1997). Long-term leaching mechanisms of ashes and slags: Combining laboratory experiments with computer simulations. Doctoral thesis TRITA-KET R65. Stockholm: *Department of Chemical Engineering and Technology, Royal Institute of Technology*.
- Chandler, A.J., Eighmy, T.T., Hartlén, J., Hjelm, O., Kosson, D.S., Sawell, S.E., Van der Sloot, H.A. and Vehlow, J. (1997). *Municipal solid waste incinerator residues*. Amsterdam: Elsevier Science B.V.
- CEN (2004). Characterisation of waste – Leaching behaviour tests – Up-flow percolation test (under specified conditions), CEN/TS 14405. Brussels: *European Committee for Standardisation (CEN)*.
- CEN (2008). Liming materials - Determination of neutralizing value - Titrimetric methods, EN 12945. Brussels: *European Committee for Standardisation (CEN)*.
- Dimitrova, S.V. and Mehanjiev, D.R. (2000). Interaction of blast-furnace slag with heavy metal ions in water solutions. *Water Research* 34: 1957-1961.
- Fällman, A.-M. (1997). Characterisation of residues: Release of contaminants from slags and ashes. Doctoral thesis no. 486. Linköping: *Department of Physics and Measurement Technology Linköping University*.
- Gao, Y.-M., Sengupta, A.K. and Simpson, D. (1995). A new hybrid inorganic sorbent for heavy metals removal. *Water Research* 29: 2195-2205.
- Hwang, J.D., Horton, M. and Leong, D. (1992). The use of microwave digestion and ICP to determine elements in petroleum samples. *Journal of ASTM International* 2: 1-9.
- Lee, K.-M., Park, P.-J. (2005). Estimation of the environmental credit for the recycling of granulated blast furnace slag based on LCA. *Resources, Conservation and Recycling* 44: 139-151.
- Mostafa, N.Y., El-Hemaly, S.A.S., Al-Wakeel, E.I., El-Korashy, S.A. and Brown, P.W. (2001). Characterization and evaluation of the hydraulic activity of water-cooled slag and air-cooled slag. *Cement and Concrete Research* 31: 899-904.
- Mroueh, U.-M., Eskola, P. and Laine-Ylijoki, J. (2001). Life-cycle impacts of the use of industrial by-products in road and earth construction. *Waste Management* 21: 271-277.
- NEN (2006a). Leaching characteristics - Determination of the reducing character and the reducing capacity - Solid earthy and stony materials, NEN 7348. Delft: *Nederlands Normalisatie-instituut*.
- NEN (2006b). Leaching characteristics of solid earthy and stony building and waste materials - Leaching tests - Determination of the leaching of inorganic components from compacted granular materials, NEN 7347. Delft: *Nederlands Normalisatie-instituut*.
- Polettini, A. and Pomi, R. (2004). The leaching behavior of incinerator bottom ash as affected by accelerated ageing. *Journal of Hazardous Materials* 113: 209-215.
- Proctor, D.M., Fehling, K.A., Shay, E.C., Wittenborn, J.L., Green, J.J., Avent, C., Bigham, R.D., Connolly, M., Lee, B., Shepker, T.O. and Zak, M.A. (2000). Physical and chemical characteristics of blast furnace, basic oxygen furnace, and

- electric arc furnace steel industry slags. *Environmental Science and Technology* 34: 1576-1582.
- Raue, B., Brauch, H.J. and Frimmel, F.H. (1991). Determination of sulfate in natural waters by ICP/OES - comparative studies with ion chromatography. *Fresenius' Journal of Analytical Chemistry* 340: 395-398.
- Reuter, M., Xiao, Y. and Boin, U. (2004). Recycling and environmental issues of metallurgical slags and salt fluxes. *Proceedings of the VII International conference on molten slags and fluxes*, Cape Town, South Africa, January 25-28: pp. 349-356.
- Roy, A. (2009). Sulfur speciation in granulated blast furnace slag: An X-ray absorption spectroscopic investigation. *Cement and Concrete Research* 39: 659-663.
- Sanchez, F., Gervais, C., Garrabrants, A.C., Barna, R. and Kosson, D.S. (2002). Leaching of inorganic contaminants from cement-based waste materials as a result of carbonation during intermittent wetting. *Waste Management* 22: 249-260.
- Tossavainen, M. and Lind, L. (2008.) Leaching results of reactive materials. *Construction and Building Materials* 22: 566-572.
- van der Sloot, H.A., Hoede, D. and Comans, R.N.J. (1994). The influence of reducing properties on leaching of elements from waste materials and construction materials. *Proceedings of the International Conference on Environmental Implications of Construction Materials and Technology Developments*, WASCON '94, Maastrich, The Netherlands, 1-3 June: pp. 483-490.
- Watanabe, T., Hashiguchi, Y. and Sato, H. (1981). Determination of the chemical states of sulfur in blast furnace slags by chemical shift (X-ray excitation). *Transactions of the Iron and Steel Institute of Japan* 21: 173-177.
- Yan, J., Moreno, L. and Neretnieks, I. (2000). Long-term acid neutralizing capacity of steel slag. *Waste Management* 20: 217-223.