

## Comparison of immobilisation of air pollution control residues with cement and with silica

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### Abstract

Cement as agent for immobilising Pb from air pollution control residues is compared with the use of different silica-containing materials. The DIN 38414-S4 leaching test was used to control Pb leachability and to compare obtained Pb leachate concentrations with the landfill limit of 2 mg/l for Pb. Firstly, one scrubber residues was treated with cement and micro-silica. With cement, the Pb leachability could be reduced with a factor ranging from 3 to 50 depending on the type and amount of cement used and depending on the curing time. The landfill limit of 2 mg/l was, however, never attained. From all tested silica-containing additives, aerosil could reduce the initial Pb leaching (101.3 mg/l) to below the detection limit at a dosage of 0.13 g aerosil/g residue. Second best and an economically preferable silica-containing additive was micro-silica: a reduction from 101.3 to 0.7 mg/l was observed at a dosage of 0.4 g micro-silica/g residue. The formation of Ca-silicates was found to be responsible for the decreased Pb leachability.

To generalise the findings, the Pb leachability of five cement-treated and five micro-silica-treated air pollution control residues were compared. For three scrubber residues, 2–20 times lower Pb leachate concentrations were measured for micro-silica-treated samples (cured for 5 weeks) than cement-treated samples. For a fly ash and a boiler ash the difference was, respectively, 48 and 17 times.

pH-dependent leaching tests showed that at pH = 2.5, Pb leaching is 250 times lower for the micro-silica-treated residue than for the cement-treated residue and almost seven times lower at pH 12.4.

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### 1. Introduction

Incineration of municipal solid waste produces approximately 200 kg of bottom ash and 40 kg of air pollution control residues per ton of incinerated waste. Recycling options are available for bottom ash, but for air pollution control residues these are scarce and are in most countries not considered as good environmental waste-saving management practices. Landfilling is typically the final option. Although multi-layers of PE-liners and clay layer prevent contamination of the groundwater around the landfill, it is still necessary to prevent leaching of contaminants from the residue itself. This not only eliminates the need for intensive landfill percolate treatment, but also reduces the risks for groundwater contamination if containment would fail.

Cement is most commonly used for immobilisation. Without such treatment, it may seem irresponsible to limit the landfill after-care period to several decades as information on long term performance of PE-liners and clay layers is lacking, and it is expected that liners will ultimately fail [1].

The use of cement for heavy metal immobilisation is justified because of the physical and chemical entrapment of pollutants in the cement matrix [2,3]. Due to the formation of a monolithic block, water flow is restricted to a minimal amount of pores and leaching of pollutants is hampered due to the reduced contact area with water. Upon breakdown of the physical structure, contact area and consequently also leaching, increase. The resistance to breakdown depends on the amount of cement in the cement/residue mixture. In general, the ratio of cement to residue is kept as low as possible to save landfill space and to minimise costs: a cement/residue ratio of 0.1–0.4 is common. With residues containing large amounts of soluble salts, no high strengths develop, so that preservation of the monolithical structure

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cannot be guaranteed. Fortunately, heavy metal leaching also significantly decreases due to chemical interaction with cement constituents. Two heavy metal hosts were identified in hydrated cement-based waste forms: ettringite ( $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{CaSO}_4\cdot 32\text{H}_2\text{O}$ ) and calcium silicate hydrate (C–S–H) [4,5]. For ettringite, it is generally accepted that chemical substitution of Ca by divalent metals (Zn, Pb, etc.) takes place, but it is not clear whether in real systems the mineral ettringite contributes to the overall decreased heavy metal mobility. C–S–H, the main component of hydrated cement, is formed upon hydration of tri- and di-calcium silicate ( $\text{C}_3\text{S}$ ,  $\text{C}_2\text{S}$ ), the main cement clinker minerals. As host for heavy metals in real cement-based waste systems, C–S–H finds more support than ettringite although the binding mechanism was still not determined univocally. Different mechanisms were observed for different metals and for different concentrations [6–10].

pH remains an important controlling parameter for heavy metal leaching [11,12]. The leachate pH of cement-based solidified/stabilised residues is high due to high concentrations of  $\text{Ca}(\text{OH})_2$  [13,14]. Amphoteric metals such as Pb and Zn have an increased solubility at elevated pH. Therefore, it would be interesting if, in addition to the incorporation of heavy metals in C–S–H or ettringite, also the pH could be decreased to minimise leaching of amphoteric metals [15]. C–S–H cannot only be produced by hydrating cement, but also from reaction of Ca with pozzolanic silica [3,16–18]. Boiler ash, fly ash and scrubber residue can act as source for Ca. Aerosil, micro-silica, waterglass, alumino-silicate, bottom ash and glass, can act as source for silica. In this way, in contrast to cement addition, no alkaline additive is used and the residual alkalinity of the residue is partly consumed for the dissolution of silica.

The objective of this work was to look for silica-containing materials for use as additive for treatment of air pollution control residues so that Pb leachability is decreased and Pb leaching is below the Flemish and German landfill limit of 2 mg/l. Aerosil, micro-silica, waterglass, alumino-silicate, bottom ash and glass were used and compared with different types of cement for the immobilisation of a lime-based scrubber residue. Pb leachability was tested by leaching following the DIN 38414-S4 extraction protocol (DIN 38414-S4 [19]). The study was limited to chemical immobilisation by decreasing the size of leached solids to below 1 mm.

Cement used for immobilisation generally contains finely ground blast furnace slag or fly ash from electric power plants, to partly replace clinker in the cement blend. Firstly, it was investigated whether lower Pb leaching could be obtained with cement containing more clinker and thus containing higher concentrations of  $\text{C}_3\text{S}$  and  $\text{C}_2\text{S}$  than the blast furnace or fly ash-based types of cement, so that more CSH can be formed upon hydration. Unfortunately, the lead leaching limit of 2 mg/l was never attained.

Secondly, different silica-containing materials were tested. In this study, micro-silica appeared the best option for

large-scale immobilisation. The Pb landfill limit of 2 mg/l could be attained. The immobilisation with micro-silica was therefore more extensively studied and was compared with cement immobilisation for several air pollution control residues (three scrubber residues, one fly ash and one boiler ash). The developed strengths for some cement- and micro-silica-treated samples were measured in laboratory environment and in humid conditions. pH-dependent leaching was used to indicate that the decreased Pb leachability by adding micro-silica was not only due to a decrease in pH.

## 2. Materials and methods

### 2.1. Immobilisation with different types of cement

Clinker material and seven different standard types of cement all obtained from the same producer, but produced from different raw materials were compared: CEM I 42.5, CEM I 52.5, CEM II 32.5, CEM III/A 32.5, CEM III/B 32.5, CEM III/B 42.5, CEM III/C 32.5. The different types of cement differ in the applied raw materials in the cement mixture and in particle size: CEM I type cement only consists of clinker and a small amount of gypsum; CEM II type cement contains in addition to a minimum of 65% of clinker also other pozzolanic materials such as fly ash from electric power plants and small amounts of blast furnace slag; CEM III type cement contains more than 36, 66 or 81% of blast furnace slag for CEM III A, CEM III B and CEM III C, respectively. The increasing compressive strength identification of 32.5, 42.5 and 52.5 N/mm<sup>2</sup> is correlated with a decrease in particle size.

To 20 g of a scrubber residue (dry weight >99.9%) 0, 2, 4, 6 and 8 g of the different types of cement was added along with a minimal amount of water to prepare a paste. The ratios of additive (cement) to residue correspond to 0, 0.1, 0.2, 0.3, and 0.4, respectively, and are indicated in this way on the abscissa of the graphs. Residue and additive (cement) were mixed before the addition of water. For each residue–cement combination two series of samples (pastes) were prepared. One series was leached after 1 week of curing; the second series was leached after 5 weeks of curing. Curing induced hardening of samples. Cured pastes were ground to sizes smaller than 1 mm before leaching following the DIN 38414-S4 leaching protocol, which is a batch leach test (distilled water at L/S = 10, 24 h). Part of the leachate was filtered through a 0.45 μm membrane filters. Diluted leachate samples were acidified with nitric acid to a concentration of 2 vol.% before analysis.

### 2.2. Immobilisation with different silica-containing materials

The different silica-containing materials used are pyrogenic silica (Aerosil), micro-silica, waterglass, alumino-silicate, bottom ash and glass.

Pyrogenic silica consists of very small, highly amorphous particles formed as a result of the gas phase synthesis ( $\text{SiCl}_4 + \text{O}_2 \rightarrow \text{SiO}_2 + 2\text{Cl}_2$ ). The pyrogenic silica (aerosil) used had a surface area of  $300 \text{ m}^2/\text{g}$  and a mean particle size of 7 nm.

Micro-silica, also called condensed silica fume, is a residue from the production of ferro silicon alloys in an electric arc furnace and contains 90–94 wt.% of  $\text{SiO}_2$ . The off gasses of the electric arc furnace contain  $\text{SiO}$ , which, in contact with oxygen, is oxidised to  $\text{SiO}_2$  and condenses into spherical particles of pure and amorphous  $\text{SiO}_2$  (average particle size from 0.1 to  $0.5 \mu\text{m}$ , more than 10 times larger than aerosil particles; specific surface area between 20 and  $30 \text{ m}^2/\text{g}$ ). It is mostly sold in densified form, which is much easier to handle in immobilisation technology than the undensified or slurried products. Micro-silica is used as filler in combination with cement for its high pozzolanic activity, in high strength concrete and in concrete with low permeability. Upon hydration of  $\text{C}_3\text{S}$  and  $\text{C}_2\text{S}$  of cement,  $\text{C-S-H}$  and  $\text{Ca}(\text{OH})_2$  are formed. The amorphous  $\text{SiO}_2$  from micro-silica reacts with this  $\text{Ca}(\text{OH})_2$  to produce more  $\text{C-S-H}$  which is responsible for the strength development [17].

Solid sodium silicate ( $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ ) and liquid water-glass with 27.8%  $\text{SiO}_2$  and a  $\text{SiO}_2/\text{Na}_2\text{O}$  ratio of 3.22 were used as sources of soluble silica. Solid sodium silicate and liquid water-glass was obtained from Fluka.

Some waste products such as a powdered aluminium-silicate catalytic support with 50%  $\text{SiO}_2$  and 42%  $\text{Al}_2\text{O}_3$ , the fine fraction of a bottom ash from a municipal waste incinerator, and waste glass were tested after grinding to particle sizes of  $15 \mu\text{m}$ .

Bentonite and perlite were also used in immobilisation experiments. Bentonite is composed of montmorillonite clay and is a result of 100 million years of alteration reactions from volcanic ash. Bentonite is used as clay lining to prevent contamination of groundwater from landfills [20]. The use is based on the swelling capacity due to water uptake between clay layers. Next to this swelling effect, bentonite has a cation exchange capacity (CEC) above 1 meq/g, which makes it a very good adsorbent for numerous pollutants [21].

Perlite is a naturally occurring glassy siliceous rock containing approximately 10% of water. Upon heating above  $870^\circ\text{C}$  lightweight expanded perlite is produced. Expanded perlite is a relatively cheap material with widespread use, e.g. in the construction industry, as filler and in horticulture. Because of its low price and its alumino-silicate nature, expanded perlite also finds its way in the environmental market as adsorbent for varying pollutants or as filler to improve the stability of sludge [22–24]. It differs from bentonite by its amorphous structure and lower aluminium content. Because of its amorphous structure, perlite has pozzolanic properties [25]. In the experiments of this study, powdered perlite was used.

As for cement, 20 g of residue is combined with amounts ranging from 0 to at least 10 g of silica-containing ma-

terial (additive). Samples were prepared by mixing the silica-containing material and residue in a plastic cup. Water was added in amounts ranging from 10 to 15 ml depending on the required dosage for total wetting and the formation of a paste. Samples were leached after 5 weeks curing following the DIN 38414-S4 leaching protocol.

### 2.3. Immobilisation of different air pollution control residues

For immobilisation experiment in which different types of cement and different siliceous materials were compared as additive, always the same air pollution control residue was used. It was a scrubber residue, further called SR1, from a plant with a flue gas cleaning system including, semi-dry lime injection, activated carbon injection and a fabric filter. The sample was taken from a silo and stored in a 101 air-tight container. In addition to SR1, immobilisation of Pb from in total five different air pollution control residues was studied to generalise whether with micro-silica lower Pb leaching can be obtained than with cement. The selection was based on the main waste types produced by municipal solid waste incinerators in Belgium. SR2 was also a scrubber residue from an installation with a boiler, an electrostatic precipitator, semi-dry lime injection, activated carbon injection and a fabric filter. Electrostatic precipitator residues and scrubber residues retained on the fabric filter are stored separately. The sample was taken from the baghouse silos and stored in a 101 air-tight container. SR3 was a scrubber residue from an installation with a boiler, a semi-dry lime injection, an electrostatic precipitator, activated carbon injection and a fabric filter. The sample was taken from the electrostatic precipitator silos and stored in an air-tight container. FA 4 was the electrostatic precipitator fly ash produced by the same plant where SR2 is produced. BA was a boiler ash produced by the plant where also SR1 is produced.

Today, some of the air pollution control systems described were already changed; addition of a wet flue gas cleaning system at the end of the flue gas track and in some cases the installations of a catalytic  $\text{deNO}_x$  system. These changes are not supposed to alter the residues studied as they were installed after the dust collection systems.

With all five residues, four series of samples were prepared: two series (1 week and 5 weeks curing) with cement and two series with micro-silica. CEM I 52.5 was used because with this type of cement the best leaching results were obtained. Again 20 g of residue was combined with amounts ranging from 0 to 10 g of additive to obtain dosages ranging from 0 to  $0.5 \text{ g additive/g residue}$ . The amount of water was kept to a minimum but total wetting and a homogeneous paste had to be obtained. All subsequent steps were similar as described for samples prepared with different types of cements or with different silica-containing materials.

#### 2.4. Leaching test

The untreated residues and the immobilised samples were leached according to the German DIN 38414-S4 leaching test. This test is used in Flanders, Wallonia and Germany to evaluate the leachability of heavy metals and to compare leaching results with landfill acceptance criteria. It is a batch-leaching test with only one extraction step: the sample is shaken for 24 h with distilled water ( $L/S = 10$ ), at the pH determined by the residue itself. Particle size should be smaller than 10 mm. In principle,  $L/S = 10$  should be based on the total mass leached: residue plus additive. Therefore, when the amount of additive per gram of residue is increased, the amount of water per gram of residue during leaching would also increase. By doing so, metals leached out of the residue during DIN 38414-S4 leaching, will be more diluted when more additive is added in the S/S sample. To allow better comparison of experimental data without inclusion of the above-mentioned dilution effect, the  $L/S = 10$  in this experiment was based on the actual amount of residue in the immobilised sample, rather than on the sum of residue and additive. To avoid that diffusion controlled metal leaching, particles were ground to sizes below 1 mm instead of only below 10 mm.

#### 2.5. pH-dependent leaching

Next to the DIN 38414-S4 leaching results, also pH-dependent leaching was performed to compare the Pb immobilisation efficiency of a cement-treated and a micro-silica-treated residue. The test was only done for one scrubber residue (SR1). Cement-treated samples were prepared by adding 0.4 g cement/g residue and micro-silica-treated samples were prepared by adding 0.2 g micro-silica/g residue. Samples were leached during 24 h at  $L/S = 10$  with distilled water acidified with  $HNO_3$ . The pH was measured at the end of the leaching test.

#### 2.6. Measurements

The DIN 38414-S4 leachates were filtered through a  $0.45 \mu\text{m}$  membrane filter. After 200-fold dilution and addition of nitric acid to a concentration of 2 vol.%, samples were measured by ICP-MS (VG, PlasmaQuad 2 Plus). Total concentrations were measured after destruction of the residue in Teflon crucibles with  $HNO_3$ ,  $HClO_4$  and HF. Chloride in the leachate was measured by titration with by  $AgNO_3$ , using endpoint detection by the formation of  $Ag_2CrO_4$ .

X-ray diffractograms of a powdered sample were taken with a Philips PW 1130/90 diffractometer working with a Co X-ray source at 30 kV and 20 mA.

Compressive strengths of the immobilised scrubber residues SR1, SR2 and the boiler ash BA were measured with a Schenck RM-TP 100/0.6 press. Samples were prepared in metal moulds and sawn in rectangular shape of

4 cm  $\times$  4 cm and 2 cm high. Samples were pressed perpendicularly to the 4 cm  $\times$  4 cm surfaces.

### 3. Results and discussion

#### 3.1. Total concentrations and leachate concentrations of air pollution control residues

Table 1 shows total concentrations of major elements and heavy metals in five different air pollution control residues from MSW incineration. The three lime-based scrubber residues (SR1, SR2 and SR3) contained, of course, as a result of the lime injection higher concentrations of calcium than the fly ash (FA) and the boiler ash (BA). Zn and Pb were for all air pollution control residues the heavy metals that occurred in the highest concentration. For all five residues the Zn concentration exceeded the Pb concentration. The % total dissolvable solids (%TDS) was around 20% for the three scrubber residues, 9% for the fly ash and only 2% for the boiler ash.

Table 2 shows the concentrations of major elements and heavy metals in DIN 38414-S4 leachates of the five residues. Pb was clearly the element of most concern, with leachate concentrations significantly exceeding the Flemish (Vlarem II [26]) and German (TA-Abfall [27]) leaching limit of 2 mg/l. The high Pb concentrations were due to the high pH of the leachates, at which Pb dissolves as  $Pb(OH)_3^-$  or  $Pb(OH)_4^{2-}$ . For BA (boiler ash) the Pb leachate concentration was lower (5.5 mg/l) than for the other residues, although a pH of 12.4 was attained. This lower concentration was attributed to the lower Pb content of this residue and probably also to a different lead speciation compared to the main lead speciation in scrubber residues and fly ash. The different residues did not exceed the 10 mg/l leaching limit for Zn.

Table 1

Total content (mg/g) of major elements and heavy metals of different air pollution control residues

	Scrubber residue			Fly ash	Boiler ash
	SR1	SR2	SR3		
Ca	348.8	287.3	262.7	156.6	161.8
Na	19.2	24.6	21.8	31.0	10.7
K	25.3	20.0	22.0	36.6	8.0
Zn	6.49	7.76	12.28	11.45	4.55
Al	4.5	5.5	8.63	50.7	52.5
Mg	5.0	3.6	5.4	12.8	13.2
Pb	3.05	4.60	4.84	6.22	1.40
Cu	0.55	0.50	0.43	0.84	0.42
Ni	0.05	0.01	0.06	0.10	0.15
Cr	0.08	0.10	0.12	0.13	0.18
Cd	0.12	0.20	0.17	0.24	0.03
%TDS <sup>a</sup>	18.8	22.9	21.2	9.2	2.0

<sup>a</sup> Percentage of total dissolved solids, dissolved during 24 h leaching in DW water at  $L/S = 10$ .

Table 2

DIN 38414-S4 leachate concentrations (mg/l) of major elements, heavy metals and pH of different air pollution control residues

	Scrubber residue			Fly ash	Boiler ash	Limit values
	SR1	SR2	SR3			
Ca	8420	9560	8260	2720	1640	
Na	2530	2160	2990	2320	790	
K	2280	2040	2760	3010	610	
Zn	5.6	8.2	5.5	3.4	3.7	10
Al	0.1	<0.1	1.4	<0.1	0.2	
Mg	1.2	0.8	1.7	1.6	0.7	
Pb	103.1	116.6	97.8	172.7	5.5	2
Cu	0.3	0.1	0.2	0.1	0.2	10
Ni	0.1	0.2	< 0.1	0.1	0.2	2
Cr	0.1	0.4	0.1	0.6	0.4	0.5
Cd	<0.1	<0.1	<0.1	<0.1	<0.1	0.5
Cl <sup>-</sup>	16700	20920	19250	1490	2200	
pH	12.49	12.38	12.25	12.48	12.43	

The limit values of the Flemish and German landfill acceptance criteria are indicated in column 7.

The pH of 12.3–12.5 in the leachate of the scrubber residues (SR1, SR2 and SR3) was in accordance with that of a saturated  $\text{Ca}(\text{OH})_2$  solution. Fig. 1 gives powder XRD diffractograms of the scrubber residues, the fly ash and the boiler ash. The diffractograms show that still not neutralised crystalline portlandite ( $\text{Ca}(\text{OH})_2$ ) was present in the scrubber residues. The neutralisation products  $\text{CaOHCl}$  and anhydrite ( $\text{CaSO}_4$ ) could also be identified based on the XRD diffractograms.  $\text{CaCl}_2$ , which is probably more amorphous, was only identified with SEM-EDX. The higher  $\text{CaCl}_2$  and/or  $\text{CaOHCl}$  concentrations in scrubber residues resulted in higher calcium concentrations in the leachates of these residues compared to fly ash and boiler ash. The calcium concentration by far exceeded the equilibrium concentration of a saturated  $\text{Ca}(\text{OH})_2$  solution ( $[\text{Ca}^{2+}] \sim 400 \text{ mg/l}$  for an ionic strength of  $I = 0$ ;  $[\text{Ca}^{2+}] \sim 1000 \text{ mg/l}$  for  $I = 1$ ). The measured pH in these solutes with high electrolyte concentrations was not only controlled by the high content of  $\text{Ca}(\text{OH})_2$  but also by the ionic strength and by the presence of Ca containing minerals such as  $\text{CaCl}_2$ ,  $\text{CaOHCl}$ ,  $\text{CaSO}_4$  and the formation of calcium silicate. Therefore, pH slightly

varied from the theoretical pH of a saturated  $\text{Ca}(\text{OH})_2$  solution. The lower pH of the leachate of SR3 was attributed to the lower content of  $\text{Ca}(\text{OH})_2$  in comparison with SR1 and SR2 and to a higher ionic strength of the leachate. The XRD diffractogram of SR3 shows lower intensities for  $\text{Ca}(\text{OH})_2$  than for the SR1 and SR2. The acid dose to obtain a  $\text{pH} = 7$  in a leachate of SR3 was  $6.2 \text{ mol H}^+/\text{kg}$  residue (acid neutralisation capacity or ANC). For SR1 and SR2 this was 9.1 and  $6.8 \text{ mol H}^+/\text{kg}$  residue, respectively.

The pH of 12.5 for the leachates of the fly ash and the boiler ash could not be explained from the XRD diffractograms because no diffractions of alkaline products were detected (Fig. 1). The leachate pH of 12.5 for both residues was in accordance with a saturated  $\text{Ca}(\text{OH})_2$  solution. But no portlandite or other alkaline products could be identified; XRD diffractograms indicated quartz as main component. Based on ANC measurements ( $4.0$  and  $3.6 \text{ mol H}^+/\text{kg}$  residue for FA and BA, respectively), relatively low concentrations compared to the scrubber residues of possibly amorphous alkaline oxides dissolved upon leaching and an

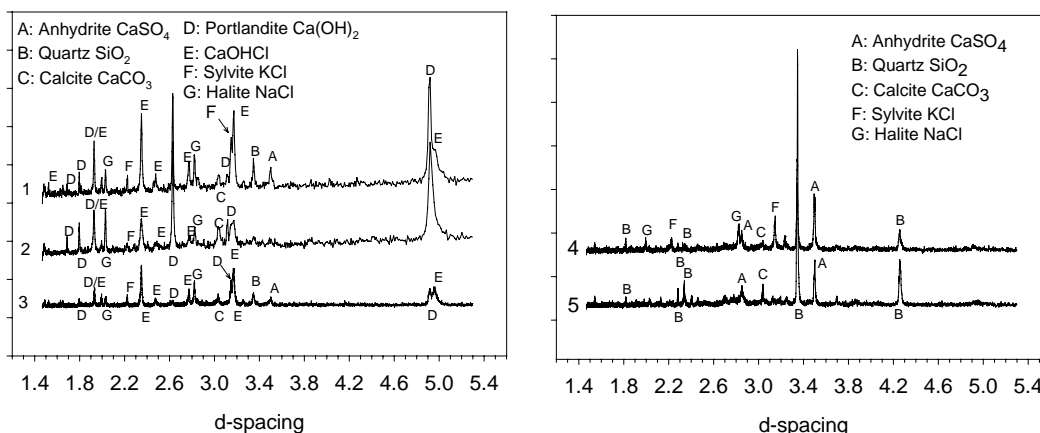


Fig. 1. Powder XRD diffractograms of three scrubber residues SR1 (1), SR2 (2), SR3 (3) (left graph), fly ash FA (4) and boiler ash BA (5) (right graph).



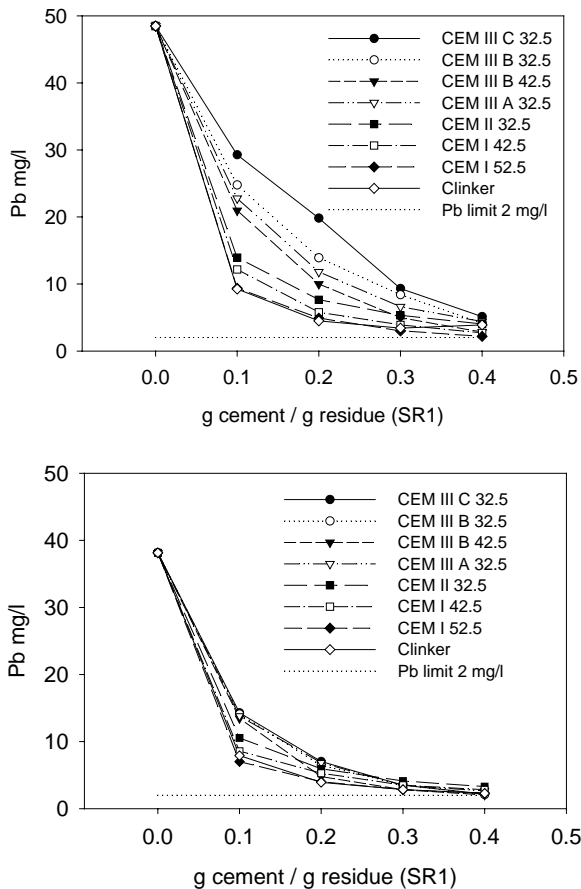


Fig. 2. Pb concentrations in the leachates (DIN 38414-S4) (mg/l) of scrubber residue SR1 immobilised with different types of cement, leached after 1 week of curing (top), and after 5 weeks of curing (bottom).

over-saturated  $\text{Ca}(\text{OH})_2$  solution was formed delivering a pH around 12.5.

The lower Zn leachability around pH 12.5 than the leachability of Pb was already observed for different residues [11]. The low solubility of Zn in these residue leachates was attributed to the formation of  $\text{CaZn}_2(\text{OH})_6 \cdot 2\text{H}_2\text{O}$  precipitation in an alkaline Ca-rich environments [8,10]. At a pH above 13.0 the Zn leachability became more pronounced.

### 3.2. Immobilisation with different types of cement

Samples of SR1 immobilised with nine different types of cement (eight commercial cements and pure clinker) were leached after 1 and 5 weeks curing. Only the leaching values for Pb are discussed here because the leachate concentrations of the other heavy metals (e.g. Zn) were below the limit of the Flemish and German landfill acceptance criteria (Table 2, column 7).

The Pb leachate concentrations of SR1-treated with the different types of cement are shown in Fig. 2 for leaching after 1 and 5 weeks of curing. The Pb leachability decreased when more cement was used in the immobilisation mixture. The Pb leachate concentration decreased with a factor

ranging from 3 to 50 compared with the Pb leachate concentration of the untreated residue. The decrease depended on the amount of cement used, on the type of cement used and on the curing time. The Pb limit of 2 mg/l was however not reached.

After 1 week curing (Fig. 2, top) and for cement dosages of 0.1, 0.2 and 0.3 g cement/g residue, a clear difference in effectiveness existed between the different types of cement and between cement with different particle size. Effectiveness decreased in the order clinker > CEM I > CEM II > CEM III. The curves in Fig. 2 for CEM I cements are below the curves for CEM II and below the curves for CEM III cement. Amongst the three blast furnace cements (CEM III 32.5 types) effectiveness increased with the content of clinker in the cement. At a dosage of 0.3 g cement/g residue, CEM III/A 32.5 was most effective with a Pb leachate concentration of 6.6 mg/l compared to 8.4 mg/l for CEM III/B 32.5 and 9.3 mg/l for CEM III/C 32.5. The types of cements ground to smaller particle sizes (higher compressive strength identification) were more effective than those with larger particle sizes. At a dosage of 0.3 g cement/g residue, CEM III/B 42.5 (5.0 mg/l) was more effective than CEM III/B 32.5 (8.4 mg/l) and CEM I 52.5 (3.0 mg/l) was more effective than CEM I 42.5 (3.9 mg/l). All these differences were less pronounced at a dosage of 0.4 g cement/g residue. At this dosage, particle size seemed more important than cement constituents. The lowest Pb leachate concentrations were obtained with CEM I 52.5 (2.2 mg/l) followed by CEM I 42.5 (2.7 mg/l) and CEM III 42.5 (2.8 mg/l). For CEM 32.5 cements, values ranged from 4.0 to 5.1 mg/l.

Also after 5 weeks of curing (Fig. 2, bottom), all these differences were less pronounced even at lower dosages of 0.2 g cement/g residue and negligible when 0.4 g cement/g residue was used. Although addition of 0.1–0.4 g cement (CEM I 52.5) per gram of residue lowered the leachability of Pb after 5 weeks curing with a factor of 5–20 in comparison to a sample that was only cured with water (0 g cement/g residue), the limit for Pb (2 mg/l as indicated by the straight lines in Fig. 2) was not reached. The pH of the leachate of cement-treated residues remained between 12.2 and 12.4 for all mixes due the high amount of  $\text{Ca}(\text{OH})_2$  in the residue and in cement. Cement increases the acid neutralisation capacity because upon hydration of  $\text{C}_3\text{S}$  and  $\text{C}_2\text{S}$  and to form C–S–H also  $\text{Ca}(\text{OH})_2$  is formed [17]. An important advantage of cement is the low price which can be lower than € 120/t depending on the type of cement.

### 3.3. Comparison of different silica-containing materials

Metal silicates are known to be slightly soluble and their formation was the basis of several immobilisation formulations in the past [3]. In this study, silicates were used to form C–S–H-like structures in which metals are retained by covalent bonding. Different siliceous materials were compared for their Pb immobilisation efficiency of scrubber residue

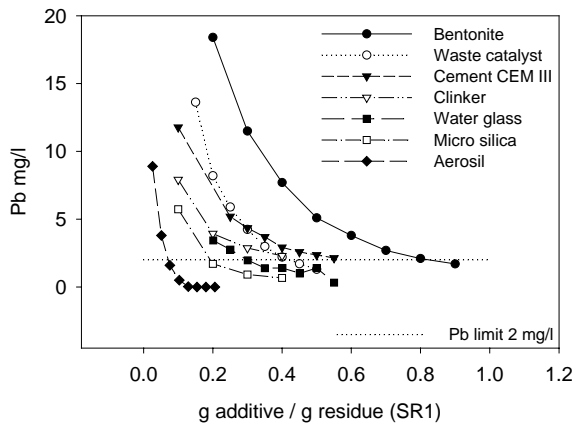


Fig. 3. Pb concentrations in the leachates (DIN 38414-S4) (mg/l) of scrubber residue (SR1) immobilised with different silica-containing materials after 5 weeks of curing.

SR1; Pb leachate concentrations of treated samples leached after 5 weeks curing are shown in Fig. 3.

### 3.3.1. Aerosil and micro-silica used as additive for immobilisation

The best results were obtained with pyrogenic silica such as aerosil. At a dosage of 0.08 g aerosil/g residue, a Pb leachate concentration of 1.6 mg/l, lower than the landfill limit of 2 mg/l, was attained. Pb leachate concentrations lower than 0.1 mg/l were measured at dosages above 0.1 g aerosil/g. The silica dissolves in the alkaline environment of the mixture of residue, silica and water and reacts with Ca from the residue to form calcium silicate hydrates [28]. Pb can be incorporated in the C–S–H structure. The low Pb leachate concentration was also due to a decrease in pH from 12.3 at dosages of 0.03, 0.05 and 0.08 g/g to 10.4 at a dosage of 0.2 g aerosil/g residue.

To investigate whether upon using aerosil, Pb precipitated due to the formation of simple Pb-silicate or whether calcium was involved in the precipitation, an experiment was set up in which 4.4 g of aerosil and variable amounts of  $\text{CaCl}_2$  ranging from 0 to 6 g were stirred in 200 ml of a solution containing 300 mg/l of Pb. For all tests, the pH was kept between 13.5 and 14, controlled by adding NaOH. Concentrations of Pb and Si are shown in Fig. 4. The more Ca was added, the less Si and Pb remained in solution. The upper curve in the graph gives Pb concentrations for a reference test in which increased amounts of Ca were added to 200 ml solutions of 300 mg/l Pb. No aerosil or other silica-containing material was added. The reference test shows that the concentration of Pb in solution decreased from 300 down to 230 mg/l when 1.6 g Ca was added. This decrease in Pb leaching could be due to co-precipitation with  $\text{Ca}(\text{OH})_2$ , formed upon reaction of  $\text{CaCl}_2$  with NaOH. The decrease could also be attributed to the formation and precipitation of  $\text{CaPb}_2(\text{OH})_6$  or  $\text{CaPb}(\text{OH})_4$  related products in alkaline environment. Although no data about the formation of these minerals is available, it would be similar to the formation

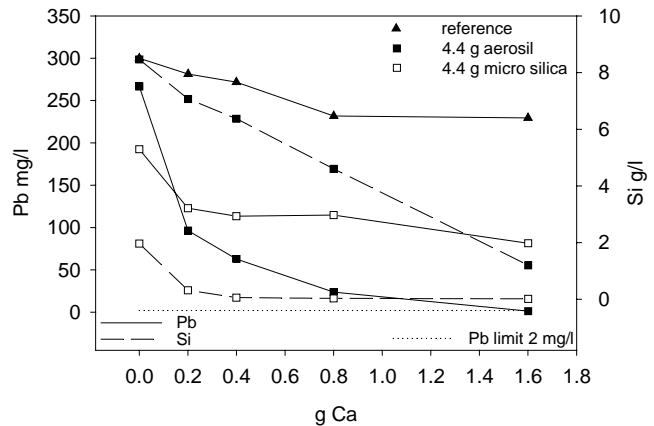


Fig. 4. Pb concentrations (solid lines) (mg/l) and Si concentrations (dashed lines) (g/l) in function of the added amount of  $\text{CaCl}_2$  as Ca (g) to 200 ml MilliQ water containing 300 mg/l Pb and 4.4 g aerosil or 4.4 g micro-silica: blank test (triangles), test with 4.4 g aerosil (filled squares) and test with 4.4 g micro-silica (open squares). The dotted line is the 2 mg/l Pb leaching limit.

of  $\text{CaZn}_2(\text{OH})_6$  [8,10]. When 4.4 g aerosil and 1.6 g Ca was added to the 300 mg/l Pb solution, the Pb concentration decreased to 1.2 mg/l. At that point, 1.2 g/l Si was measured in the solution, the Ca concentration was approximately 20 mg/l and pH was 13.5. The Pb concentration of 1.2 mg/l was significantly lower than the 230 mg/l (1.6 g Ca added) of the reference test and than the 265 mg/l of the point on the curve where no Ca was added to the aerosil suspension. It was the combination of Ca and aerosil that made Pb become less soluble.

The concentration of 1.2 mg/l Pb found for the combination of 4.4 g aerosil and 1.6 g Ca is however higher than the above reported low Pb leachate concentrations (Pb concentrations lower than 0.1 mg/l) of scrubber residue SR1 treated with aerosil. Therefore, tests were done in which scrubber residue SR1 was treated with aerosil and leached without curing. Results are shown in Fig. 5 indicated: “with-

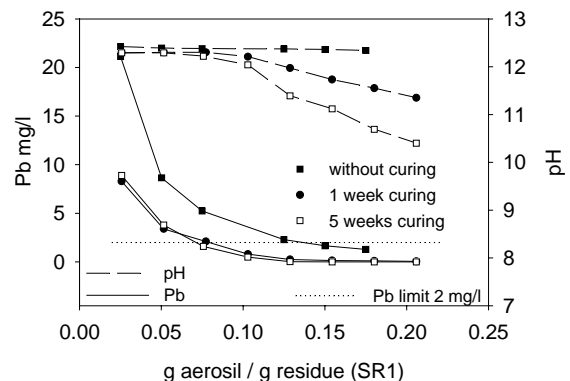


Fig. 5. Pb leachate concentrations (DIN 38414-S4) (mg/l) (solid lines) and pH (dashed lines) of a scrubber residue (SR1) leached in presence of aerosil (without curing) and Pb leachate concentrations of a scrubber residue (SR1) immobilised with aerosil and leached after 1 and 5 weeks of curing time. The dotted line is the 2 mg/l Pb leaching limit.

out curing". At almost 0.2 g aerosil/g residue (this corresponds with 4 g aerosil in suspension) a Pb concentration of 1.3 mg/l was measured, almost equal to the 1.2 mg/l mentioned above. If, before leaching, the mixture of SR1 and aerosil was cured, lower Pb concentrations were found. Thus curing of aerosil-treated samples decreased Pb leachability. Also shown in Fig. 5 is the decrease in pH as a consequence of curing. Above an aerosil dosage of 0.1 g/g, a pH decrease of the leachate down to 11.4 after 1 week curing and down to 10.4 after 5 weeks curing was measured. This pH decrease is supposed to be responsible for an additional decrease in Pb leachate concentration. At an aerosil dosage of 0.2 g/g residue, the Pb concentration in the leachate after 5 weeks curing was decreased to lower than 0.1 mg/l. It still has to be confirmed that the pH decrease after curing is due to the reaction of acid SiO<sub>2</sub> with Ca(OH)<sub>2</sub> but if it would only be due to carbonation we would also have observed this decrease for other additives. This was not the case.

Based on its immobilisation efficiency, aerosil can be considered as the ultimate silica source but it is too expensive for use in immobilisation technology. Interesting characteristics of aerosil are the high solubility in an alkaline environment and its acidity that reduces pH. The high solubility at elevated pH can be seen in Fig. 4, which shows that almost all Si (8.4 g/l) was in solution when no Ca<sup>2+</sup> was added (10 g/l corresponds with total dissolution).

The second best silica-containing additive based on the reduction in Pb leachate concentration was micro-silica (Fig. 3). A Pb concentration of 0.7 mg/l was measured at a dosage of 0.4 g micro-silica/g residue. The same experiment as done with aerosil to control whether or not Ca was involved in the decreased Pb leachability, was conducted for micro-silica. Again different amounts of CaCl<sub>2</sub> and 4.4 g micro-silica were added to 200 ml solutions of 300 mg/l Pb. Measured Pb and Si concentrations in solution after 24 h equilibration are shown in Fig. 4. The solubility of micro-silica was much lower than that of aerosil. When no Ca<sup>2+</sup> was added only 2.0 g/l Si was in solution (10 g/l corresponds with complete dissolution) instead of 8.3 g/l when aerosil was used. At this point only 190 mg/l Pb was measured in solution, which is lower than the 265 mg/l measured in case aerosil was used. It seems that an important part of Pb is retained on the micro-silica grains (300 mg/l Pb was the initial concentration). The decrease in Pb concentration upon addition of CaCl<sub>2</sub>·2H<sub>2</sub>O was not as extreme as with aerosil. A Pb concentration of 81 mg/l was attained at a Ca dosage of 1.6 g. The amount of Si in solution was probably too low to form enough C–S–H to trap all Pb. At a dosage of 0.4 g Ca, the Si concentration in solution was decreased to 55 mg/l (cf. lower curve in Fig. 4). Whereas, when that amount of Ca was added to aerosil, still 6 g/l of Si was in solution.

The same test to see the effect of curing as described for aerosil and SR1 in Fig. 5 was carried out with micro-silica (not shown here). Also here, after curing, Pb leachate concentrations decreased to 3.1 mg/l after 1 week curing and 0.7 mg/l after 5 weeks curing.

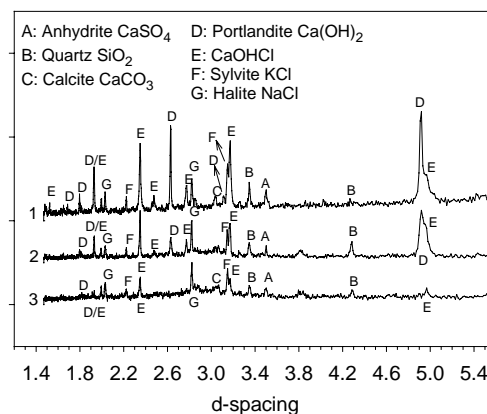


Fig. 6. Powder XRD diffractogram of untreated residue SR1 (1), SR1-treated with 0.1 g/g micro-silica (2) and SR1-treated with 0.2 g/g micro-silica (3).

Although it was supposed that Ca(OH)<sub>2</sub> would react with silica, no C–S–H could be observed in powder XRD diffractograms; probably the formed C–S–H had no crystalline structure. The diffractograms shown in Fig. 6 of cured samples of micro-silica-treated SR1 show decreasing intensities for portlandite (Ca(OH)<sub>2</sub>: main peaks at *d*-spacing 4.92 and 2.63) and CaOHCl (main peaks at *d*-spacing 2.35 and 3.17) when treated with increasing amounts of micro-silica.

### 3.3.2. Other silica-containing materials used as additive for immobilisation

Fig. 3 shows that with waterglass, Pb leachate concentrations of 0.3 mg/l were measured at dosage of 0.55 g waterglass/g residue. At a dosage of 0.4 g/g, the Pb concentration was 1.4 mg/l. Lower Pb leachate concentrations can be attained than with cement but leachate concentrations remained above those obtained with micro-silica (test limited to dosage of 0.4 g/g). Waterglass and also solid sodium silicate were already shown earlier to be interesting products for the immobilisation of different types of waste [3]. A pH decrease would be welcome for treatment of highly alkaline wastes, as this would decrease Pb and Zn leaching at lower dosages of additive. With waterglass and solid sodium silicate such a pH decrease is not obtained, but on the contrary, due to the high content of NaOH pH increases up to 13.0.

With bentonite, an alumino-silicate, a decrease in leachate concentration down to 1.7 mg/l could be attained but 0.9 g of bentonite per gram of residue was necessary to reach this value. The leachate pH was ca. 12.4. Alumino-silicates are negatively charged which make them very attractive for adsorbing positively charged pollutants. The negative charge density increases in alkaline environment. At elevated pH amphoteric metals such as Pb and Zn form negatively charged complexes (e.g. Pb(OH)<sub>4</sub><sup>2-</sup> and Zn(OH)<sub>4</sub><sup>2-</sup>) so that adsorption of these elements is not expected to take place. It is therefore not clear which mechanism was responsible for the observed decrease in Pb leachate concentration.



The results obtained with perlite are not shown: after 1 week of curing and at a dosage of 0.3 g/g, the Pb leachate concentration was 45 mg/l, comparable to the value obtained when only water is added (48.5 mg/l). No decrease in Pb concentration was observed when increasing the amount of perlite in the immobilisation recipe from 0 to 0.3 g/g.

Ideal waste management practice is to carry out immobilisation by combining waste products. A waste catalyst from a petrochemical cracking plant was used in this study and interesting results were obtained. Waste catalyst of 0.45 g was needed per gram of residue to reach the Pb leaching limit of 2 mg/l. A Pb concentration of 1.3 mg/l was attained at a dosage of 0.5 g/g and after 5 weeks curing. Not shown but also tested are different sized glass and MSW bottom ash fractions (all ground down to 15 µm). Although some effect on Pb leachability could be observed, leachability decreased much less than with the other tested silica-containing materials. At a dosage of 0.4 glass/g residue or 0.5 g bottom ash and after 5 weeks curing, Pb leachate concentrations ranged

from 35 to 23 mg/l for glass and from 35 to 10 mg/l for bottom ash. The Pb leachate concentration could further be decreased to 5 mg/l at a dosage of 1 g bottom ash/g residue.

Micro-silica may be considered as the best silica-containing material for use as additive for Pb immobilisation taking an acceptable dosage (0.4 g/g) and an acceptable price (€ 150/t) in to account. The material can be easily stored and handled which is not always the case for water-glass. The price of waterglass is similar (€ 120–150/t) to that of micro-silica.

### 3.4. Comparison of immobilisation with micro-silica and with cement

In order to make a general assessment of the use of micro-silica for Pb immobilisation, five different air pollution control residues were immobilised with micro-silica. The different residues were three lime-based scrubber residues (SR1, SR2 and SR3), one fly ash and one bottom ash. Pb

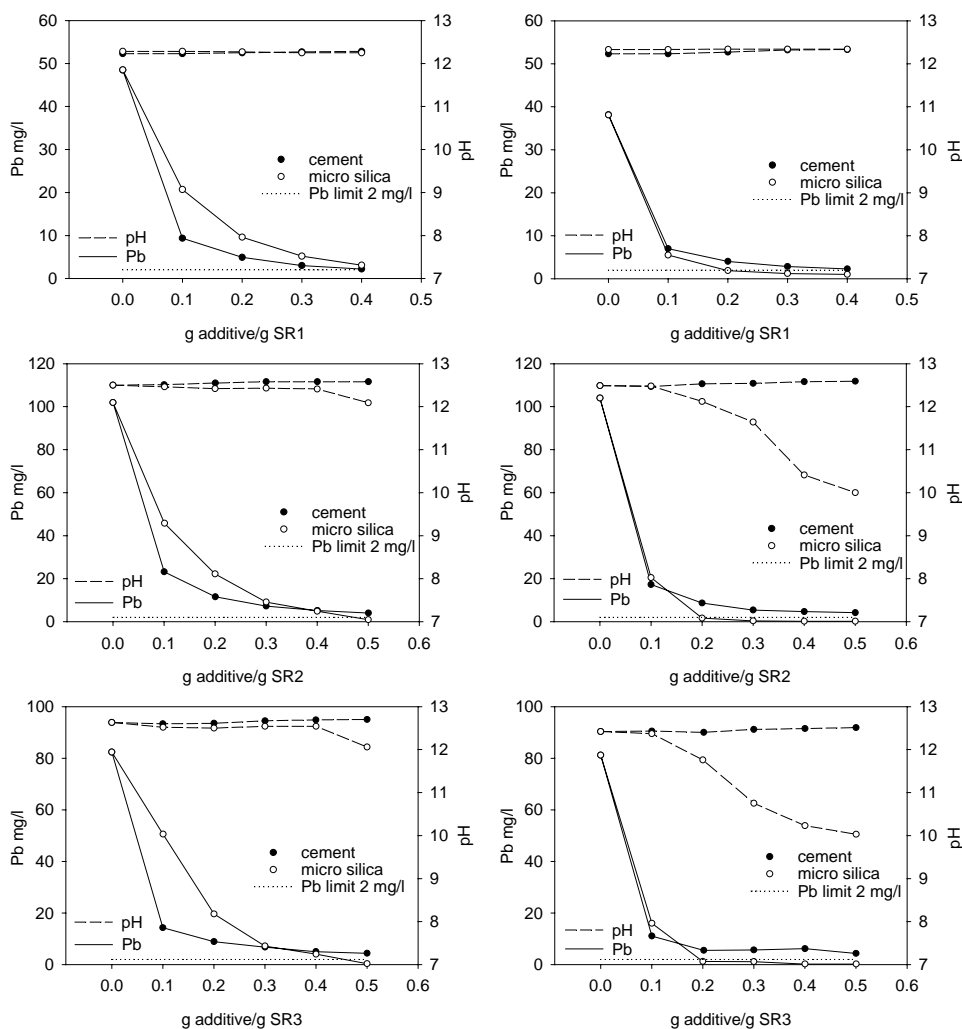


Fig. 7. Pb concentration in the leachate (solid lines) (mg/l) and pH of the leachate (dashed lines) of DIN 38414-S4 leaching of three lime-based scrubber residues (SR1, SR2 and SR3) immobilised with cement and with micro-silica and leached after 1 week of curing (left) and leached after 5 weeks of curing (right). The dotted lines correspond with the 2 mg/l Pb leaching limit.

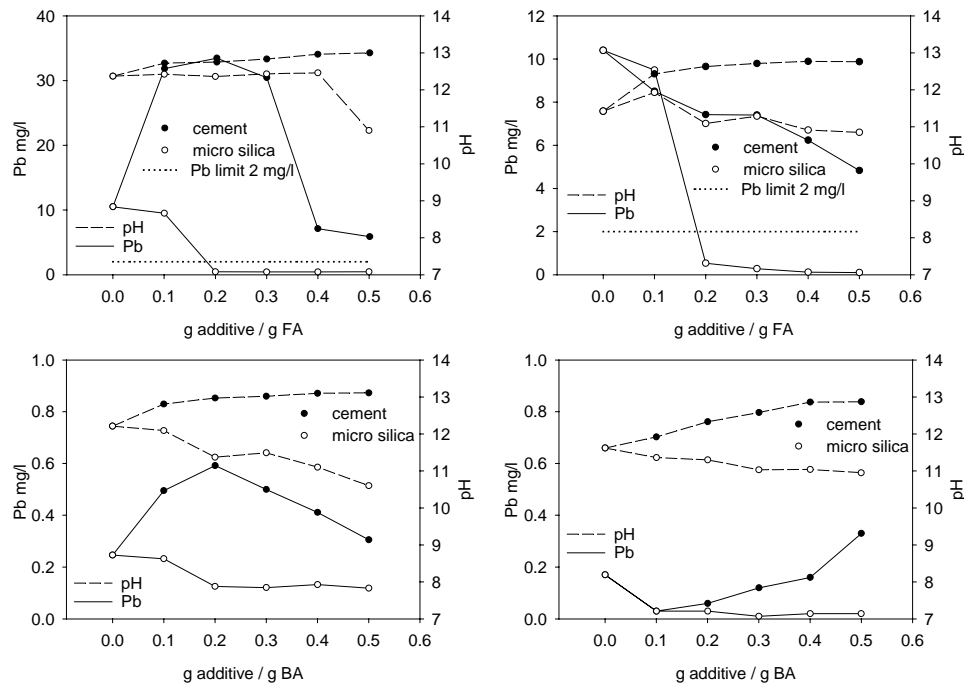


Fig. 8. Pb concentration in the leachate (solid lines) (mg/l) and pH of the leachate (dashed lines) for DIN 38414-S4 leaching of a fly ash and a boiler ash immobilised with cement and with micro-silica leached after 1 week of curing (left) and leached after 5 weeks of curing (right). The dotted lines correspond to the 2 mg/l Pb leaching limit.

leaching results for the different immobilised residues were compared with results of the cement-treated residues. CEM I 52.5 was used because it had the highest immobilisation efficiency as shown in Fig. 2.

Samples were prepared by adding micro-silica or cement to the residue followed by adding a minimal amount of water to get a homogeneous fluid paste. As a reference, samples were prepared by only adding water to the residues in the immobilisation mixture. Leaching of the reference samples after 1 and 5 weeks curing already showed a decreased leachability of Pb and Zn compared to leaching of the untreated residues. For SR1, the Pb leachate concentration decreased from 103.1 mg/l for the untreated residue to 48.5 mg/l after 1 week and to 38.1 mg/l after 5 weeks curing with water. For SR2 and SR3 almost no change was observed. The Pb leachate concentration decreased from 172.7 to 10.5 mg/l for the fly ash and from 5.5 to 0.2 mg/l for the boiler ash both after 5 weeks curing.

Figs. 7 and 8 show the effect on Pb leaching and on pH of adding increasing amounts of cement and micro-silica to the different residues. The graphs giving the Pb concentration in the leachate of the three treated lime-based scrubber residues have a similar profile (Fig. 7). After 1 week curing, at a micro-silica and cement dosage lower than 0.4 g/g, lower Pb leaching was attained with cement than with micro-silica. Above 0.4 g/g Pb leachate concentrations became lower for micro-silica. Also after 5 weeks curing, lower Pb leaching was obtained with micro-silica. With a dosage of 0.5 g cement/g residue, there was no difference in Pb leachate concentrations between leachates of samples

after 1 and 5 weeks curing. With cement it was not possible to reach the Pb limit of 2 mg/l for all the three scrubber residues. With micro-silica, the leachate concentrations after 5 weeks curing were 2–25 times lower than after 1 week. The Pb leachate limit of 2 mg/l was attained for all scrubber residues at a micro-silica dosage of 0.2 g/g residue. At that dosage, Pb leachate concentrations ranged from 1.2 to 1.9. The Pb concentration ranged from 0.2 to 1.2 at a dosage of 0.4 g micro-silica/g residue.

To better understand the effect of time on Pb leaching of micro-silica and cement-treated scrubber residues, the following experiment was carried out. Two series of immobilised samples of SR1 were prepared with micro-silica as additive at a dosage of, respectively, 0.1 and 0.2 g micro-silica/g residue. Two other series of immobilised samples of SR1 were prepared with, respectively, 0.2 and 0.3 g cement/g residue. The samples were stored in nitrogen atmosphere to avoid carbonation. Fig. 9 shows that with cement the Pb concentration in the leachate reached almost a constant value in less than 5 days. With micro-silica the Pb concentration decreased more slowly, but the final Pb concentrations were lower than with cement. The slower decrease in Pb concentration was attributed to a slower formation of C–S–H-like structures when combining micro-silica with Ca from the residue, compared to hydration of C<sub>3</sub>S or C<sub>2</sub>S grains of cement.

For SR2 and SR3 immobilised with micro-silica, after 5 weeks curing, the pH decreased from 12.3–12.5 to 10.0. The observed decrease of Pb concentrations in the leachates was partly attributed to this decrease in pH (Fig. 7), but

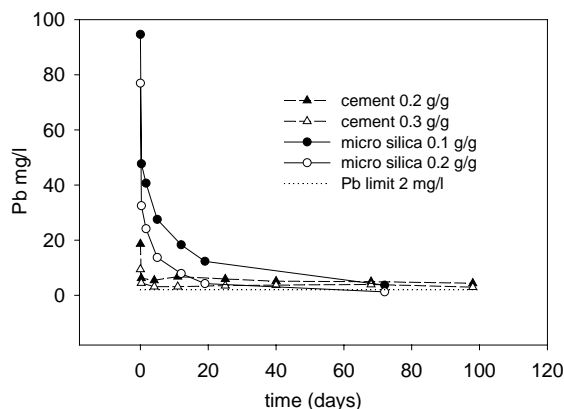


Fig. 9. Effect of curing time (days) on leachate concentration (DIN 38414-S4) of Pb (mg/l) from scrubber residue (SR1) immobilised with 0.1 and 0.2 g micro-silica per gram residue and immobilised with 0.2 and 0.3 g cement CEM I 52.5 per gram residue.

for residue 1 no such decrease in pH was observed and still Pb concentrations in the leachate were below the values obtained with cement. For SR1 the minimal obtained Pb concentration was 1 mg/l. Values as low as 0.2 mg/l were only obtained in case the pH dropped below 10 (SR2 and SR3). The decreased pH was attributed to the neutralisation reaction of acid  $\text{SiO}_2$  with  $\text{Ca}(\text{OH})_2$ . Measured acid neutralisation capacities were lower for SR2 and SR3 than for SR1.

To show that not only the pH controlled the Pb solubility, SR1 samples immobilised with cement and with micro-silica were leached at different pH values obtained by adding an amount of nitric acid to the leaching water. The pH was measured after 24 h leaching at a L/S = 10. Results are shown in Fig. 10(left) and compared with results obtained for untreated sample of SR1. All graphs clearly show the amphoteric nature of Pb and a minimal solubility of 0.1 mg/l at pH = 8. Pb leachate concentrations at pH > 12.0 are 100–150 times lower for micro-silica treated samples compared to the untreated residue leachates. With cement at pH > 12, the Pb leachate concentration was only 25 times lower than for the untreated residue. Also in the pH range from 2 to 6, up to 40 times lower Pb leachate

concentrations were obtained with micro-silica than for the untreated and cement-treated residue. Also Zn concentrations at variable pH are shown in Fig. 10(right). The Zn leaching limit (10 mg/l) is higher than for Pb and Zn is thus less a problem. With cement as well as with micro-silica, the Zn limit was easily attained. At low pH, however (lower than 9) no difference was observed between the Zn leachate concentrations of untreated, cement-treated and micro-silica-treated residues. A minimal Zn concentration of 0.2 mg/l was attained for the untreated residue around pH = 8.5. The Zn concentration increased less fast than the Pb concentration when increasing the pH up to 12.5. Above pH = 12.0, a maximal Zn concentration of 1.5 was observed for the cement-treated residue. 0.35 mg/l was measured for the micro-silica treated residue, as maximal value above pH = 12.0.

The graphs shown in Fig. 8 for fly ash and boiler ash are different from those for the three lime-based scrubber residues. For FA, Pb leaching from the residue mixed with a small amount of water to make a paste and cured prior to leaching is much lower (10.5 mg/l) than for the untreated residue (172.7 mg/l; without mixing with water an curing prior to leaching). For FA leached after 1 week of curing, the Pb concentration increased upon addition of more cement to a maximum in the curve of 33.5 mg/l at 0.2 g cement/g residue, probably due to the increased pH. With micro-silica, the pH did not increase and consequently no such an increase in Pb concentration was observed. After 5 weeks of curing, the pH increase when using cement was slightly lower and no increase in Pb concentration was observed. With cement, the Pb leachate limit of 2 mg/l was however not attained. With micro-silica the limit was attained at a dosage of 0.2 g micro-silica/g residue. For BA, the Pb concentration in the leachate was already low for the untreated residue (5.5 mg/l). The Pb concentration in the leachate is ~0.2 mg/l when the residue was mixed with a small amount of water to form a paste and leached after 1 week of curing. Again an increase in Pb concentration up to 0.6 mg/l was observed as a consequence of an increase in pH, for the residue treated with cement. The increase was not only observed after 1 week of curing but also after 5 weeks of curing. The

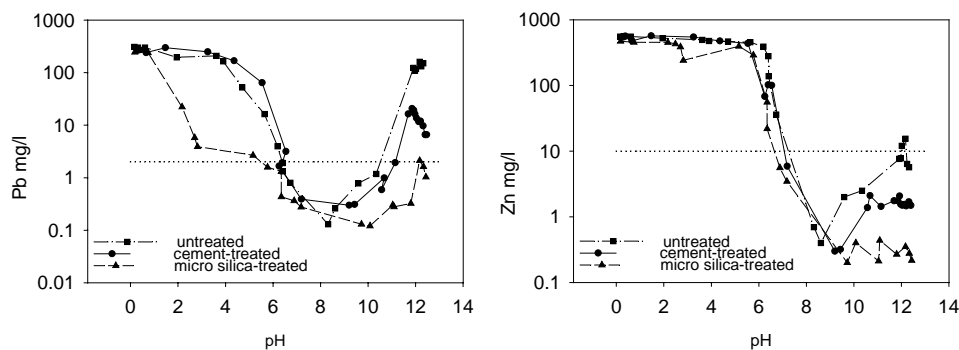


Fig. 10. Pb (left) and Zn (right) concentrations (mg/l) in pH-dependent leachates of untreated scrubber residue (SR1), cement-treated and micro-silica-treated scrubber residue SR1. The dotted lines are the Pb (2 mg/l) and Zn (10 mg/l) leaching limits.

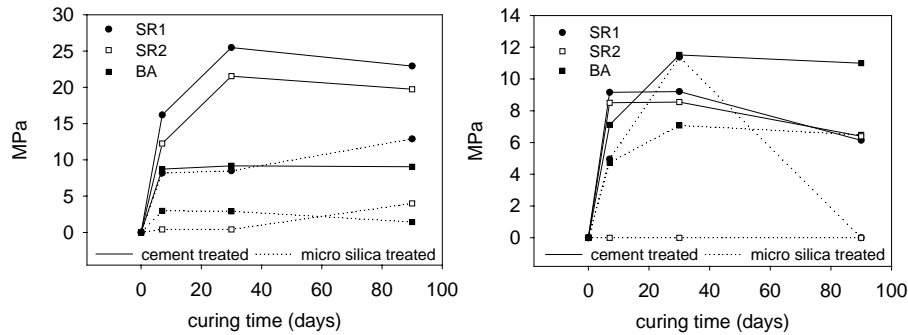


Fig. 11. Strength development in lab environment (left) and humid conditions (right) of SR1, SR2 and BA immobilised with cement (straight lines) and micro-silica (dotted lines).

Pb limit was however not exceeded. With micro-silica no such an increase was observed.

### 3.5. Strength development

Lower strengths were developed for micro-silica-treated samples than for cement-treated samples. The strength development was studied for three different residues (SR1, SR2 and BA). Samples were prepared by combining micro-silica and cement with residue at a dosage of 0.3 g additive/g residue. Samples were stored in lab environment and at an air humidity of 100%. Results of samples stored in lab environment are shown at the left side of Fig. 11, the right side of Fig. 11 are the results of samples stored in humid conditions. A maximal strength of 25 MPa was observed after 30 days of curing in lab environment for SR1-treated with cement. With micro-silica, a maximum strength of 13 MPa was observed for SR1 after 90 days of curing in laboratory environment. The strength developed for the micro-silica treated boiler ash after 90 days curing in laboratory environment was 1.4 MPa but was 6.4 MPa in humid conditions. With cement and boiler ash 9.0 MPa was measured after 90 days curing in laboratory environment and 11.0 MPa was measured in humid conditions.

Due to the high salt content in residues (see %TDS in Table 1), hydrations of salts (e.g.  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ ) in humid conditions induced swelling and crack formation. With micro-silica no strength development could be measured for scrubber residue SR2, after 7 days curing in humid conditions because water absorption took place from the beginning. For SR1, after attaining a maximum strength of 9 MPa after 30 days of curing with micro-silica, the strength dropped to zero after 90 days of curing, at that moment, the sample was very humid and full of cracks. The boiler ash did not contain  $\text{CaCl}_2$ , no water was absorbed and no cracks were observed.

Samples of SR1, SR2 and BA immobilised with cement absorbed less water than when the residue was immobilised with micro-silica. No cracks were observed although the strength decreases after 90 days of curing compared to the strength developed after 30 days of curing. For all mixes, a maximal strength of 25 MPa was measured for SR1-treated

with cement and cured for 30 days in laboratory conditions. With micro-silica in the same conditions, the developed strength was 2–3 times lower.

## 4. Conclusion

From this study it can be concluded that different Pb leachate concentrations were attained for air pollution control residue samples immobilised with different types of cement and leached after 1 week of curing. The more clinker the used cement contains and the finer the particle size of cement, the lower will be the leachability of Pb. Differences between types of cement are smaller when samples were cured for 5 weeks prior to leaching. The Pb leaching limit for landfilling (2 mg/l) could not be attained for samples immobilised with cement. The high pH of cement is an important disadvantage. With different silica-containing materials, the limit could be attained. With aerosil, very fine amorphous silica, the Pb leachate concentration could be decreased from 103.1 mg/l for the untreated residue to lower than 0.1 mg/l for the aerosil-treated residue. Micro-silica is a less expensive alternative for aerosil. Immobilisation and leaching experiments with different air pollution control residues showed that with micro-silica, for all residues, a lower pH and lower Pb leaching can be obtained than with cement.

Compressive strength measurements showed relatively high values for cement-treated samples stored in laboratory environment; a maximum of 25 MPa was measured. With micro-silica lower values were attained (maximum of 13 MPa) but they were still acceptable for landfilling. In conditions of 100% relative humidity, the developed strengths after 90 days curing are significantly lower. A maximal value of 11 MPa was obtained with cement. Samples of scrubber residues treated with micro-silica and stored in 100% relative humidity, absorb water due to the presence of  $\text{CaCl}_2$ . Cracks are formed and the compressive strength becomes too low for measurement.

Based on these compressive strength data, it can be concluded that the physical immobilisation of Pb is better in case of the cement-treated samples than of micro-silica treated samples. The formation of a monolith can prevent contact



with water and can thus prevent leaching. More information is needed to conclude whether chemical immobilisation is of more importance than physical immobilisation to minimise leaching of Pb from the studied residues. For example, the humidity in the landfill and changes in porosity of the cement-treated and micro-silica treated residues still have to be studied.

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