

## Effect of improving flue gas cleaning on characteristics and immobilisation of APC residues from MSW incineration

D. Geysen<sup>a,\*</sup>, C. Vandecasteele<sup>b</sup>, M. Jaspers<sup>c</sup>, E. Brouwers<sup>c</sup>, G. Wauters<sup>c</sup>

<sup>a</sup> Public Waste Agency of Flanders, OVAM, Stationsstraat 110, B-2800 Mechelen, Belgium

<sup>b</sup> Department of Chemical Engineering, K.U. Leuven, de Croylaan 46, B-3001, Leuven, Belgium

<sup>c</sup> INDAVER, Dijle 17 a, B-2800 Mechelen, Belgium

### Abstract

The flue gas cleaning system of a MSW incinerator with a capacity of 350 kt/year was changed to improve the HCl elimination efficiency. Instead of the semi-wet operating spray reactor and subsequent baghouse, a two-step wet flue gas cleaning was added behind the baghouse.

Elemental composition, X-ray powder diffraction patterns and TGA measurements showed that the resulting APC residue was totally different from the former residue. As a consequence, leaching characteristics of both residues also differed and another treatment was required prior to disposal.

For the former residue, mainly leaching of Pb (>100 mg/l), necessitated treatment prior to landfilling. The lower alkalinity of the new residue resulted in a leachate pH of 9.7 and a Pb concentration of 0.8 mg/l. The leachate pH of the former residue was 12.4. The leaching of Pb and Zn increased above 100 mg/l when immobilising the new residue with cement. Better results were obtained when immobilising with micro silica.

The high  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  content of the new residue brought along clogging of the bag filter system. Adding 1.4% of CaO (or 1.9% of  $\text{Ca}(\text{OH})_2$ ) to the residue already improved these inconveniences but again significantly changed the leaching behaviour of the residue.

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### 1. Introduction

Air pollution control (APC) residues of municipal solid waste (MSW) incinerators are hazardous wastes due to the high content of heavy metals and organic pollutants so that they must be landfilled at specialised disposal sites. Safe disposal implies a treatment to prevent leaching of contaminants and soluble salts, to prevent dust formation and to preserve the stability and accessibility of the landfill. Immobilisation is the most commonly applied technique for treatment of APC residues. Other techniques are acid extraction and melting (Ecke et al. [1]). Main residue characteristics, such as alkalinity, soluble salt content, contents of major elements and mineralogical composition, determine the leaching behaviour of the hazardous compounds present in minor con-

centrations. Changes in residue characteristics and thus in leaching behaviour can require changes in the immobilisation recipe.

The aim of immobilising residues from waste incineration is to reduce leaching of heavy metals of which Pb and Zn are of most concern. The solubility of both metals is highly pH-dependent and is minimal at neutral pH. Various additives are promoted to be effective in reducing the solubility of these metals. Among these, often miscellaneous additives, cement is the cheapest additive that can reduce leaching of Pb and Zn in neutral to alkaline conditions. The immobilisation mechanism is supposed to be related to the incorporation of the metal in the calcium–silicate–hydrate structure, which is the main constituent of hydrated cement. Soluble phosphates are used because of the formation of low soluble pyromorphite. In a previous study, it was indicated that adding various silica-containing additives to APC residues can result in decreased leaching of Pb and Zn.

\* Corresponding author. Tel.: +32 15 284554; fax: +32 16 322991.

E-mail address: daneel.geysen@ovam.be (D. Geysen).

In this paper, we discuss the effect of changes to a flue gas cleaning (FGC) system to improve acid gas removal efficiency, on the chemical and mineralogical composition of the main phases of the APC residue. Also, the effect of these changes on leaching of the untreated and treated residues is compared and discussed. The studied residues were treated with cement, micro silica and  $\text{Na}_2\text{HPO}_4$  as soluble phosphate. The efficiency in reducing leaching of Pb, Zn, Cu and Cd by the different treatments for the different residues is compared.

The studied residues originate from the largest municipal waste incinerator of Flanders. In 2001, the capacity was increased from 200,000 t/year (two lines; 26 t/h in total) to more than 350,000 t/year (three lines; 48.5 t/h in total). This increase in capacity was attained by adding a third incinerator line consisting of a waste bunker, a grate furnace, a steam boiler and an electricity generator. The increase in total capacity made a decrease in emissions for the three lines necessary. Below 30 t/h total capacity, the emission limit values are  $30 \text{ mg/Nm}^3$  dust,  $20 \text{ mg/Nm}^3$  TOC,  $50 \text{ mg/Nm}^3$  HCl and  $300 \text{ mg/Nm}^3$   $\text{SO}_2$ ; above 30 t/h limit values are:  $10 \text{ mg/Nm}^3$  dust,  $10 \text{ mg/Nm}^3$  TOC,  $10 \text{ mg/Nm}^3$  HCl and  $50 \text{ mg/Nm}^3$   $\text{SO}_2$  (AMINAL [2]). Experience and studies have shown that the HCl removal efficiency of Ca-based sorbents increases with increasing humidity (Liu et al. [3]). Therefore, to guarantee these lower emissions, a wet FGC system was added and purged wash water was recycled in a spray dryer placed before the baghouse. The composition of the APC residue of the new plant differed significantly from the original plant as a result of this change. In addition, it was observed that with the new FGC system clogging or fouling of bag filters occurred at certain moments and that residue stuck to inlet valves of the baghouse. Adding 1.4% CaO (or 1.9%  $\text{Ca}(\text{OH})_2$ ) to the residue by injecting lime milk in the spray dryer or dry powder in the duct between spray dryer and baghouse could solve these problems to a large extent. Ideal results were obtained by adding 20% of  $\text{Ca}(\text{OH})_2$  to the residue. This optimisation is not part of this study. This supplementary  $\text{Ca}(\text{OH})_2$  again

changed residue characteristics. These changes and the effect on leaching and immobilisation were also studied.

The paper describes chemical characteristics, leaching and treatment of the former residue, the residue after installing the wet flue gas cleaning system (new residue) and the residue after supplementary CaO addition. The paper wants to illustrate that small changes in flue gas cleaning system can result in significant changes in residue characteristics. A correct cost estimate for the treatment of the residue from flue gas cleaning is most often not done. The knowledge described in this paper can be useful for a correct cost estimation of changes in flue gas cleaning system.

## 2. Materials and methods

### 2.1. Plant description

The former plant consisted of two identical lines each having a capacity of 13 t/h. Each line had a FGC system as shown in Fig. 1 consisting of a semi-wet spray reactor placed behind the steam boiler and before a baghouse. Activated carbon was injected in the cone of the spray reactor. Eighteen kilogram of lime per ton of waste was injected in the spray reactor as slurry to neutralise acid gasses, such as HCl and  $\text{SO}_2$ . A sample of the APC residue was taken from the baghouse and stored in airtight 10-l containers. The residue is called “former residue” throughout the text.

The new plant consisted of three lines (two of 13 t/h and one of 22.5 t/h). The adapted FGC system is shown in Fig. 2 and consists of a spray dryer placed behind the steam boiler and before a baghouse. Behind the baghouse, a wet FGC system is placed consisting of two stages. In the first stage, a slurry containing 25%  $\text{CaCO}_3$  is used to remove HCl. In the second stage, a 10%  $\text{Ca}(\text{OH})_2$  slurry is used to neutralise  $\text{SO}_2$  and residual HCl. Spent water from the wet FGC is passed through a hydro-cyclone to remove wet gypsum (300 g/l). Wet gypsum is passed over a belt sieve. Water from

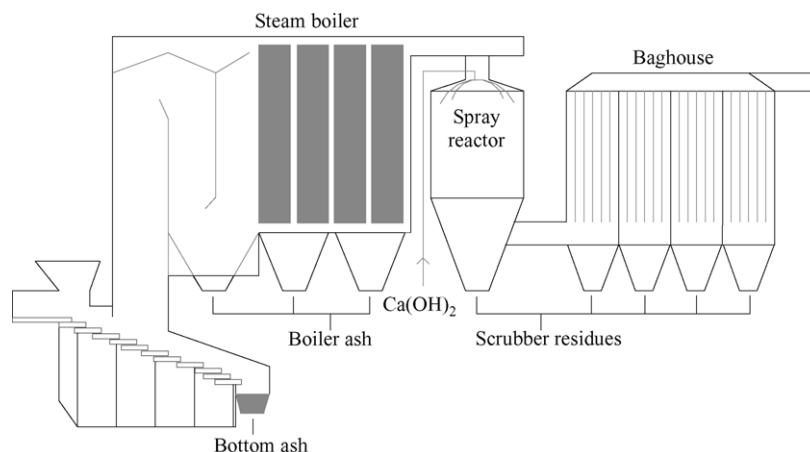


Fig. 1. Former flue gas cleaning system of the plant (two lines) with a total capacity of 26 t/h.

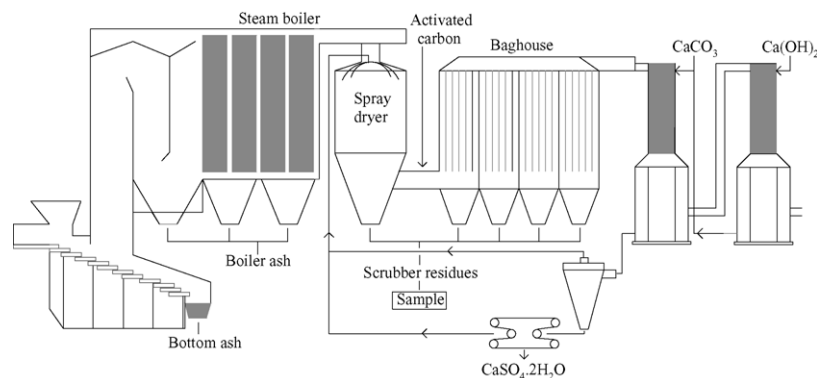


Fig. 2. New flue gas cleaning system of the plant (three lines) with a total capacity of 48.5 t/h.

the hydro cyclone and from the belt sieve still contains soluble salts and is recycled in the spray dryer to cool the gas stream from 250 to 150–175 °C (operating temperature of the baghouse). Water is evaporated and salts are retained on the bag filters. Activated carbon is injected in the duct between spray dryer and baghouse. In this way, the plant can operate with a wet flue gas cleaning system without discharging spent water, as in the former situation. The sample of the residue was taken from the baghouse and stored in airtight 10-l containers. The residue is called “new residue” throughout the text. The residue obtained from the FGC system with supplementary  $\text{Ca}(\text{OH})_2$  added in the spray dryer to overcome bag filter clogging and conveyer blocking is called “new residue +”.

## 2.2. Solid phase characteristics

The elemental composition of the residues was measured with ICP-MS (VG—PlasmaQuad 2 Plus) after digesting the residues in Teflon crucibles with separate addition of  $\text{HNO}_3$ ,  $\text{HClO}_4$  and HF. Total  $\text{Cl}^-$  content was measured by  $\text{AgNO}_3$  titration of a distilled water extract at a L/S = 1000. Total  $\text{SO}_4^{2-}$  content was determined based on gravimetric determination of  $\text{BaSO}_4$  formed by adding  $\text{BaCl}_2$  to the above-mentioned extract.

The acid neutralisation capacity (ANC) was determined by adding varying amounts of  $\text{HNO}_3$  to different suspensions of the residues which were stirred in closed bottles during 24 h at a total L/S = 10. Endpoint pH was measured with a Metrohm pH meter and glass electrode.

X-ray diffraction was used to determine the main crystalline phases of the different residues. X-ray diffractograms of powdered samples were taken with a Philips PW 1130/90 diffractometer working with a Co X-ray source at 30 kV and 20 mA.

Thermal analysis of residues was performed with a Setaram machine (type 92-18). The position of the endothermic or exothermic peaks was of main interest. For the residues, 40–60 mg of sample and for pure phases 20 mg of sample were weighted in a platinum crucible and heated in

He atmosphere. Temperature was varied from 20 to 900 °C at a speed of 5 °C/min. Loss of weight (mg) and heat consumption or heat production (mV) was recorded.

## 2.3. Immobilisation

The different residues were treated with cement, micro silica and  $\text{Na}_2\text{HPO}_4$ . The type of cement used was CEM I 52.5, because a previous study showed that with this type of cement the lowest Pb and Zn leaching could be attained (Geysen et al. [5]). In that study, the effect of cement and micro silica on immobilisation of various flue gas cleaning residues was studied and compared in more detail. The residue of the original plant also described in this paper and indicated as ‘former residue’ was one of the studied residues. 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: 0.1–0.5  $\mu\text{m}$ ). Technical grade water free  $\text{Na}_2\text{HPO}_4$  was used as soluble  $\text{PO}_4^{3-}$ .

To 20 g of residue (dry weight >99.9%) varying amounts ranging from 0, 2, 4, 6, 8 g of cement, micro silica or  $\text{Na}_2\text{HPO}_4$  were added as additive along with a minimal amount of water to prepare a paste (residue and additive were mixed before the addition of water). The ratios of additive to residue correspond to 0, 0.1, 0.2, 0.3, 0.4 and are indicated in this way on the abscissa of the graphs. For each residue–additive combination two series of samples (pastes) were prepared. The first series was leached after 1 week of curing; the second series was leached after 5 weeks of curing. Curing in open air-induced hardening of the samples. Cured pastes were ground to sizes smaller than 1 mm before leaching following the DIN 38414-S4 leaching protocol. For the treated former residue and the treated new residue only results after 5 weeks curing are given. For the new residue + also the results after 1 week curing are given to indicate the significant difference in leaching results obtained with this residue. Leaching after 5 weeks curing was always lower

than after 1 week curing. In case of micro silica, this was also due to the decrease in pH of 1 unit. In case of the former residue and the new residue, no such significant difference in metal leaching and pH was observed. The new residue + was only treated with cement and with micro silica. The treatment of new residue + with soluble  $\text{PO}_4^{3-}$  was not studied because with both other residues low Pb leaching was obtained indicating that with a high alkaline additive, as well as with a near neutral additive, low Pb leaching could be obtained. Leaching of Pb from  $\text{PO}_4$ -treated new residue + will give intermediate results.

Carbonation could take place during curing in open air. Carbonation could decrease pH and leaching of the metals. To compare the effect of adding an additive and to discriminate from possible carbonation or other reactions not assigned to the additive, also leachate concentrations are shown from residues only mixed with some water to make a paste without adding an additive (0 g cement/g residue or 0 g micro silica/g residue). To these samples will be referred with the notation “water-treated” samples.

#### 2.4. Leaching tests

The untreated residues and the immobilised samples were leached according to the German DIN 38414-S4 leaching test (DIN 38414-S4 [4]). This test is used in Flanders, Wallonia and Germany to evaluate the leachability of heavy metals by comparing 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 less 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 in the immobilisation mixture, the amount of water per gram of residue during leaching would also increase. By doing so, metals leached from 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 this “dilution” effect,  $L/S = 10$  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.

The effect of pH on heavy metal leaching was also studied with pH-dependent leaching. Samples were leached during 24 h at  $L/S = 10$  with DW water acidified to a varying extent with  $\text{HNO}_3$ . The pH was measured at the end of the leaching test. The acid neutralisation capacity was deduced based on the measured pH and the added amount of nitric acid (see above).

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% (volume), samples were measured by ICP-MS.

### 3. Results and discussion

#### 3.1. Plant emissions

The use of a wet FGC system at the MSW incinerator made it possible to reduce HCl emissions to below  $1 \text{ mg/Nm}^3$  and  $\text{SO}_2$  emissions to  $2 \text{ mg/Nm}^3$  (<sup>a</sup>Indaver [6]). With the former FGC system, the emitted concentrations of HCl and  $\text{SO}_2$  were  $29.5$  and  $40.0 \text{ mg/Nm}^3$ , respectively (<sup>b</sup>Indaver [7]). Table 1 shows the amounts of residues produced and the emitted amounts of dust, HCl and  $\text{SO}_2$  measured over 1 year of operation. The table shows that as expected, the amounts of bottom ash and boiler ash remained approximately the same. The amount of FGC residue per ton of incinerated waste was decreased to 59% of the amount produced with the former flue gas cleaning system. The HCl emission was reduced to 9% of the original emission and the  $\text{SO}_2$  emission was reduced to 3% of the original emission. The emission of dust remained approximately the same.

Table 2 shows the amounts of alkaline additives and activated carbon used in both FGC systems. The former FGC system, only used CaO as lime milk ( $\text{Ca}(\text{OH})_2$ ) in the semi-wet spray reactor. The new plant required almost 7.2 times less CaO. CaO is partly replaced by  $\text{CaCO}_3$ , which is much cheaper.  $\text{CaCO}_3$  is injected in the first reactor of the wet FGC. CaO is used to prepare  $\text{Ca}(\text{OH})_2$  which is injected in a second reactor of the wet FGC system.

#### 3.2. Total composition and mineralogical composition of major phases

The new residue differed significantly from the former residue as a consequence of the changed FGC system. Table 3 shows the elemental content of former and both new residues. The concentrations of Na, K, Fe, Ba, Cd, Cr, Cu, Sn, Pb, Zn

Table 1  
Amount of residues produced and amount of emissions of the MSW incinerator with the former and new FGC system

Plant emissions	Former flue gas cleaning	New flue gas cleaning
Bottom ash (kg/t)	250	270
Boiler ash (kg/t)	29	24
Flue gas cleaning residue (kg/t)	40	25
Dust (g/t)	13.1	14.2
HCl (g/t)	172.2	14.0
$\text{SO}_2$ (g/t)	245.4	16.1

Table 2  
Amounts of additive used in the former and in the new flue gas cleaning system

Incinerated waste (kg/t)	Former flue gas cleaning	New flue gas cleaning
CaO	18	2.5
$\text{CaCO}_3$	0	8.2
Activated carbon	0.5	0.5

Table 3

Total content (mg/g) of elements of the former residue, the new residue and the new residue +

Element	Former residue	New residue	New residue +
Al	4.5		13.4
As	<0.1	0.1	<0.1
Ba	0.4	0.8	0.8
Ca	349	227	193
Cd	0.1	0.2	0.2
Co	0.2	<0.1	<0.1
Cr	0.1	0.2	0.1
Cu	0.6	1.1	1.5
Fe	3.5	6.7	3.7
K	25.3	41.2	48.8
Mg	5.0	6.6	6.6
Mo	<0.1	<0.1	<0.1
Na	19.2	42.8	67.9
Ni	0.1	0.1	0.1
Pb	3.1	7.2	8.4
Sb	0.8	1.1	1.6
Se	<0.1	0.1	<0.1
Sn	0.4	0.7	1.0
Zn	6.5	13.5	10.3
Cl <sup>-</sup>	164.2	366	351
SO <sub>4</sub> <sup>2-</sup>	63.1	38.3	101
TDS (%)	18.8	55.6	55.0

are almost twice as high in the new residue than in the former residue. Pb and Zn were the heavy metals present in the highest concentration. In the new residue, 7.2 mg/g Pb and 13.5 mg/g Zn were present. The total amount of residue decreased from 40.5 kg/t of incinerated waste to 23.9 kg/t mainly because fewer reagents were injected (10.6 kg/t in case of the new system compared to 18.5 kg/t for the former system) and gypsum was removed (3.0 kg/t) in the new system. The lower amount of injected reagent (CaO) and the removal of gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O) are responsible for the lower Ca content in the new residue. The removal of gypsum was also responsible for the lower SO<sub>4</sub><sup>2-</sup> content of the new residue.

The spray dryer operated as an evaporator of water from the wet FGC containing high concentrations of salt. Consequently, the residue had a high total dissolvable solids content (%TDS) of 55.6% compared to 18.8% in case of the former residue. The Cl concentration of the residues of the new FGC system was more than twice as high as in case of the former FGC system.

Fig. 3 shows X-ray diffraction patterns of the three residues. Main diffractions of the former residue were similar to those of other European residues (Bodenan and Deniard [8]) and belong to Ca(OH)<sub>2</sub> and CaOHCl. Also, NaCl, CaSO<sub>4</sub>, CaCO<sub>3</sub>, SiO<sub>2</sub> and KCl could be identified clearly. No CaCl<sub>2</sub>·xH<sub>2</sub>O could be identified in the former residue. Also with SEM–EDX measurements (not shown here) no CaCl<sub>2</sub> was observed. The elemental composition of different spots showed that the atomic percentages of Ca were the same or only slightly higher than the atomic percentages of Cl. This is in accordance with the presence of CaOHCl. Bodenan and

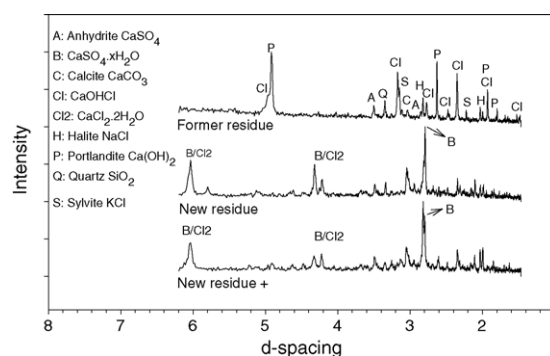
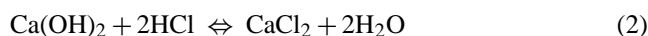
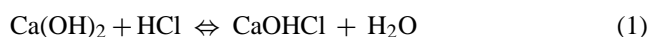


Fig. 3. X-ray diffraction patterns of former residue, new residue and new residue +.

Deniard [8] and Jozewics and Gullett [9] already discussed that the formation of CaOHCl (reaction (1)) would be more favourable than the formation of CaCl<sub>2</sub> (reaction (2)) in dry or semi-dry lime based acid gas neutralisation reaction:



The X-ray diffraction pattern of the new residue showed diffractions resulting from the presence of crystalline phases of CaCO<sub>3</sub>, CaSO<sub>4</sub>, NaCl, SiO<sub>2</sub> and of partly hydrated CaSO<sub>4</sub>·xH<sub>2</sub>O and/or CaCl<sub>2</sub>·2H<sub>2</sub>O. It was not possible to distinguish between the different possible hydrated phases (CaSO<sub>4</sub>·xH<sub>2</sub>O, x can be 0, 0.15, 0.5, 0.53, 0.62, 0.67, 1 or 2) (Badens et al. [10], Strydom et al. [11], Dweck and Lasota [12]). Also, CaCl<sub>2</sub>·2H<sub>2</sub>O diffractions overlap in that region (main diffractions at d-spacing 6.03 and 3.02). No Ca(OH)<sub>2</sub> or CaOHCl diffractions were present in the new residue and in the new residue +, indicating that the concentration of these minerals was below 3% which is roughly the detection limit of the X-ray diffractometer.

Fig. 4 shows thermograms (left) and TGA measurements (right) of pure Ca(OH)<sub>2</sub>, CaCO<sub>3</sub>, CaCl<sub>2</sub>·2H<sub>2</sub>O and CaSO<sub>4</sub>·2H<sub>2</sub>O. Pure CaCO<sub>3</sub> showed an endothermic peak at 720 °C and the corresponding decrease in weight due to the reaction CaCO<sub>3</sub> ⇌ CaO + CO<sub>2</sub>, started at 550 °C. Pure Ca(OH)<sub>2</sub> showed an endothermic peak at 430 °C assigned to the decomposition of Ca(OH)<sub>2</sub> following the reaction Ca(OH)<sub>2</sub> ⇌ CaO + H<sub>2</sub>O. The peak started from 330 °C and ended at 450 °C. A decrease in weight was observed in that same temperature interval. The weight loss above 500 °C is attributed to some CaCO<sub>3</sub> present in the Ca(OH)<sub>2</sub>. CaSO<sub>4</sub>·2H<sub>2</sub>O showed one endothermic peak at 140 °C having a shoulder at 130 °C. This can be attributed to two main dehydration reactions but the TGA curve could not distinguish between the two main species: CaSO<sub>4</sub>·2H<sub>2</sub>O ⇌ CaSO<sub>4</sub>·0.5H<sub>2</sub>O + 1.5H<sub>2</sub>O and CaSO<sub>4</sub>·0.5H<sub>2</sub>O ⇌ CaSO<sub>4</sub> + 0.5H<sub>2</sub>O. The corresponding decrease in weight started already at 100 °C. Pure CaCl<sub>2</sub>·2H<sub>2</sub>O showed two endothermic peaks, one at 150 °C having a shoulder at 120 °C and a second endothermic peak without corresponding weight loss at 780 °C. The loss of

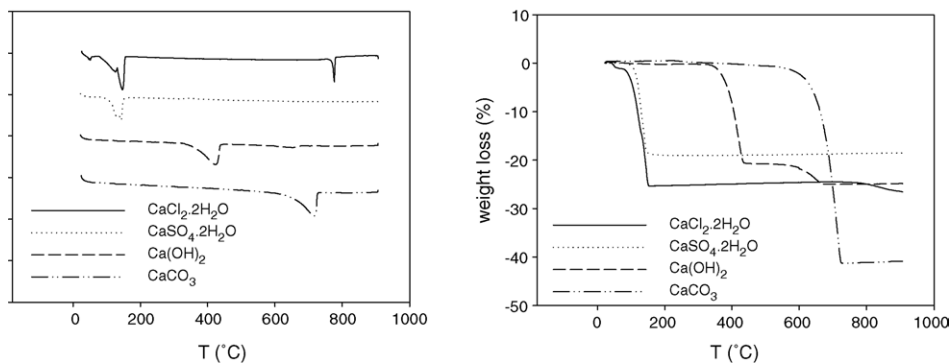


Fig. 4. Thermogram (left) and thermogravimetric analysis (right) of pure minerals.

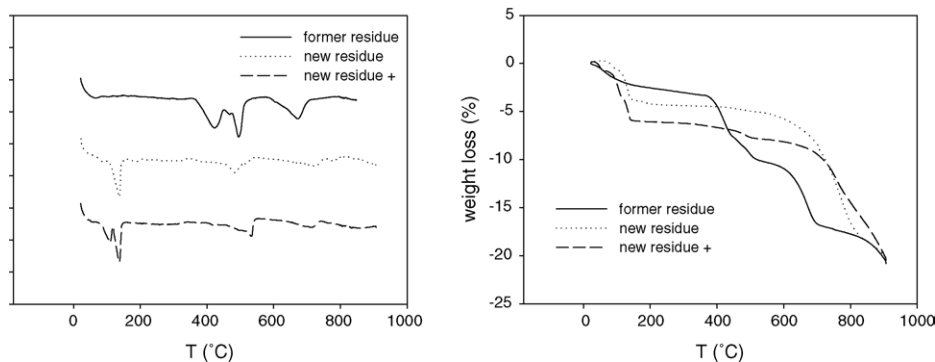


Fig. 5. Thermogram (left) and thermogravimetric analysis (right) of the different residues.

weight starting already at 80 °C is a result of the reaction  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O} \rightleftharpoons \text{CaCl}_2 + 2\text{H}_2\text{O}$  and corresponds with the first endothermic peak and the shoulder. The second endothermic peak was a result of a deformation in crystalline lattice structure. Pure  $\text{CaOHCl}$  and  $\text{CaOHCl}$  of APC residues have an endothermic peak in 465–600 °C interval (Bodenan and Deniard [8]). Peak position can vary slightly depending on the speed of heating and of the amount of the phase in the sample (Garea et al. [13]). The thermogram of the former residue (Fig. 5) showed endothermic peaks at 430 °C, 480 °C (small peak), 500 °C and 675 °C. The first peak was assigned to  $\text{Ca}(\text{OH})_2$ , the third to the destruction of  $\text{CaOHCl}$ . The peak at 675 °C was assigned to  $\text{CaCO}_3$ . Main endothermic peaks for the new residue were at 140 and 490 °C. Smaller peaks were found at 100, 200, 525, 730 and 790 °C. The peak at 140 °C was assigned to dehydration of  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  or dehydration of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ . The peak at 480 °C could correspond with  $\text{CaOHCl}$  but was much lower in intensity than the  $\text{CaOHCl}$  peak of the former residue. The peak at 730 °C or at 790 °C could correspond with  $\text{CaCO}_3$  or with the melting of the  $\text{CaCl}_2$  (772 °C; Otmer [14]). The melting temperature of  $\text{CaCl}_2$  can be decreased because of the presence of other salts. For example an equimolar mixture of  $\text{CaCl}_2$  and  $\text{NaCl}$  melts at 550 °C (Castrillejo et al. [15]). Similar peaks were observed for the new residue +. TGA scans of synthetic samples correlated well with the calculated loss of weight. TGA scans for the different residues did not. A

significant loss of weight, not associated with a loss or gain of energy, was observed for all residues.  $\text{CaCO}_3$  content was higher than expected from chemical analyses and the concentration of  $\text{CaCl}_2$ ,  $\text{Ca}(\text{OH})_2$  and  $\text{CaOHCl}$  were lower than expected from chemical analysis of Ca, Cl and the ANC.

Fig. 6 shows acid neutralisation capacities of the three residues. The former residue was clearly more alkaline than both new residues. The pH of the leachates without adding acid, of former residue, new residue and new residue + was, respectively, 12.3, 9.1 and 12.1. For the former residue, more than 8 mol  $\text{H}^+$ /kg residue had to be added to get the pH down

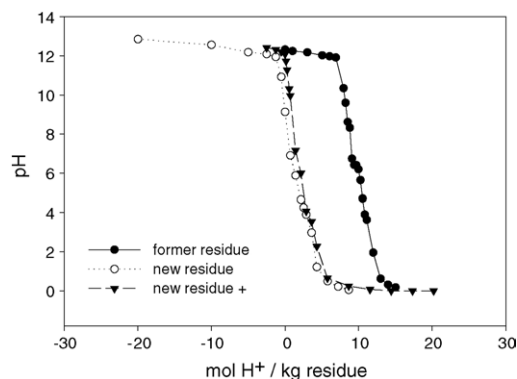


Fig. 6. Acid neutralisation capacity of former residue, new residue and new residue +.

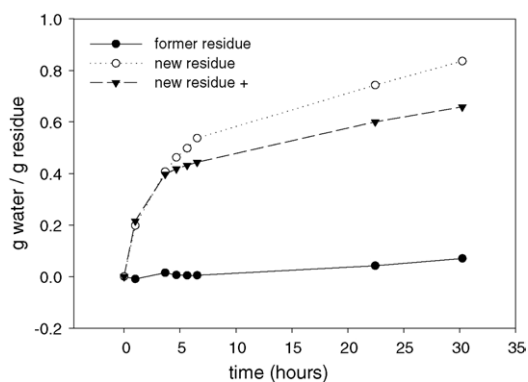


Fig. 7. Water uptake of the different residues in 100% air humidity.

to 7. To attain pH 7 with the new residue and the new residue +, 0.7 and 1.4 mol  $H^+$ /kg had to be added, respectively. For both the new residues, an immediate drop in pH is observed. Negative values in the abscissa indicate the amount of mol  $OH^-$  added per kilogram of waste instead of mol  $H^+$ . The slowly increasing pH upon addition of NaOH to the new residue is a result of the precipitation of  $Ca(OH)_2$  due to the reaction of NaOH with  $CaCl_2$ .

Fig. 7 shows the rate of water uptake of former and the new residue in 100% air humidity. In approximately 6 h, 0.5 g water was absorbed per gram new residue. After 1 week, 2 g water/g residue was absorbed. The former residue absorbed almost no water in that time. The water uptake of the new residue and the new residue + is similar during the first 3 h. After that, water uptake is slower for the new residue +. The high  $CaCl_2$  content of both new residues made them highly deliquescent. This was not the case for the former residue.

### 3.3. Implication of the high $CaCl_2$ content

The above-mentioned deliquescent characteristics of the new residue had some implications on bag filter performance and on handling of the residue. After 1 year of operation, an increase in pressure drop from around 20 to above 30 mbar over the bag filters was noticed as a result of a sticky filter cake. Back flushing of the bag filters with high-pressure compressed air (pulse jet cleaning) was not sufficient to remove this cake. Based on its deliquescent characteristics, total composition and X-ray diffraction pattern, it was concluded that the filter cake consisted mainly of  $CaCl_2 \cdot 2H_2O$  and  $CaSO_4 \cdot xH_2O$ . Seemingly, the residue trapped on the filter, absorbed moisture and subsequent heating to the normal operating temperature of 150 to 175 °C produced a cake sticking to the fibres of the filter material. Laboratory experiments showed that when drying moistened residue or pure  $CaCl_2 \cdot 2H_2O$  a hard cake was formed similar to the one observed on the bag filters. It was concluded that the filter cake could absorb water during periods of short shut down or when a module of the baghouse was put out of operation. Compressed air used for back flushing was sufficiently dry and also carry over of moisture from the spray dryer was

Table 4  
Leaching of former, new residue and new residue + following DIN 38414-S4 leaching protocol

Concentration (mg/l)	Former residue	New residue	New residue +	VLAREM
Ca	8400	14300	12900	
Cd	<0.1	0.9	0.1	0.5
Co	–	0.1	<0.1	
Cr (total)	0.1	0.7	0.1	0.5 (Cr VI)
Cu	0.3	0.1	2.4	10
K	2300	2900	3300	
Mg	1.2	33.3	1.6	
Na	2500	3600	3200	
Ni	0.1	0.6	0.3	2.0
Pb	103.1	0.8	330	2.0
Zn	5.6	1.0	3.8	10
pH	12.5	9.70	12.1	4–13

limited to the front of the duct between spray dryer and bag-house.

To prevent formation of this sticky cake, 0.4 kg  $CaO/t$  of incinerated waste was injected as lime milk in the spray dryer.<sup>1</sup>  $CaCl_2$  and  $Ca(OH)_2$  present in droplets leads to the formation of  $Ca(OH)_2 \cdot CaCl_2 \cdot 2H_2O$  with a weaker affinity for water (Stein et al. [16]). The  $Ca(OH)_2$  mixed with the  $CaCl_2$  containing residue was trapped on the bag filters. The cake that was still formed was easily removed by back flushing with compressed air. Also, problems with sticky residue on belt-conveyers and screw-conveyers were resolved by dosing supplementary  $Ca(OH)_2$ .

The total element concentration of the new residue with supplementary addition of  $Ca(OH)_2$  (new residue +) is given in Table 3. The only significant difference from the new residue without  $Ca(OH)_2$  injection was the higher content of  $SO_4^{2-}$ . This increase in  $SO_4^{2-}$ -content is probably due to the increased pH in the spray dryer. Also the combination of  $Ca(OH)_2$  and  $CaCl_2$  has shown to increase  $SO_2$  removal efficiency (Stein et al. [16], Liu et al. [3,17]). Other characteristics of the new residue + are discussed above.

### 3.4. Leaching

Table 4 shows DIN 38414-S4 leaching results of the three flue gas cleaning residues along with the acceptance criteria for landfilling of the Flemish regulation (VLAREM [2]). Between 1.5 and 1.7 times higher Ca concentrations and 1.3–1.5 times higher Na concentrations were measured in the leachate of the new residue and the new residue + compared to the leachate of the former residue. For the former residue, due to the high pH (12.3–12.5), the Pb concentration in the leachate of 103.1 mg/l was more than 50 times higher than the landfill limit value for Pb. The leaching of Zn (5.6 mg/l) was below the leaching limit value. For all other heavy metals,

<sup>1</sup> 0.4 kg  $CaO/t$  of incinerated waste corresponds with an increase of 1.4% of the total mass of residue.

leachate concentrations were at least five times lower than the corresponding leaching limit. The leachate pH of the new residue was significantly lower (9.7) than that of the former residue, so that leaching of Pb was strongly reduced (0.8 mg/l) and below the landfill limit. The Cd concentration of 0.9 mg/l exceeded the corresponding limit (0.5 mg/l). Only the total Cr concentration was measured (0.7 mg/l). The landfill limit of 0.5 mg/l is applicable only for Cr(VI). Based on these data, only Pb leaching constituted a problem for landfilling of the former residue. Based on the DIN 38414-S4 leaching test and due to the lower pH of the new residue, Pb leaching did not constitute a problem anymore, but Cd and possibly Cr leaching slightly exceeded the corresponding landfill limits.

pH-dependent leaching (Fig. 8) showed that the higher metal concentration of the new residue resulted in higher metal leaching in neutral to acid conditions compared to the former residue. Pb leaching in the pH range from 0 to 7 was 2–10 times higher for the new residue than for the former residue. Above pH 9, Pb leachate concentrations for both residues were similar. Zn leaching in the pH range from 0 to 7 was almost twice as high for the new residue, attaining a value of 1006 mg/l at pH < 1 compared to 556 mg/l for the former residue. Also, leaching of Cd and Cu was higher for the new residue than for the former residue. When leaching at a pH < 1, 90–100% of total Pb content, 75–85% of total Zn content, 85–90% of total Cu content and 100% of total Cd content was leached.

The supplementary addition of  $\text{Ca}(\text{OH})_2$  in the spray dryer of the new flue gas cleaning system changed the leach-

ing behaviour significantly. The pH of the DIN 38414-S4 leachate of the new residue + increased to 12.1 compared to 9.7 for the new residue. Due to this increased pH, Pb leaching increased from 0.8 to 330 mg/l, Zn leaching from 1.0 to 3.8 mg/l, which was still below the landfill limit of 10 mg/l.

### 3.5. Immobilisation

When leaching the cement-treated former residue, a decrease in Pb and Zn leaching was observed (Fig. 9, top) compared to the untreated residue and the residue only mixed with some water (0.0 g cement/g residue). At a dosage of 0.4 g cement/g former residue, a Pb leachate concentration of 2.3 mg/l and a Zn concentration of 0.8 mg/l was attained. The pH of the cement-treated former residue ranged from 12.2 to 12.3. Increasing the amount of cement in the immobilisation recipe of the new residue from 0 to 0.5 g/g increased the pH from 7.5 to 12.2. Due to this pH increase, an increase in Pb leaching was observed to a maximum of 110.9 mg/l at a dosage of 0.2 g cement/g new residue. At higher cement dosages, the Pb concentration decreased but at 0.5 g cement/g new residue still 30.7 mg/l Pb was measured in the leachate. The Pb concentration in the leachate of the cement-treated new residue was well above the Pb leaching limit for landfilling of 2 mg/l over the whole range of tested cement/residue ratios (0.1–0.5). Note that only adding water as treatment of the former residue decreased Pb leaching to 38.1 mg/l compared to 103.1 mg/l without treatment. Adding only water to the new residue (water-treated sample) resulted in a decrease of the pH down to 7.5 compared to 9.7 in the leachate of the

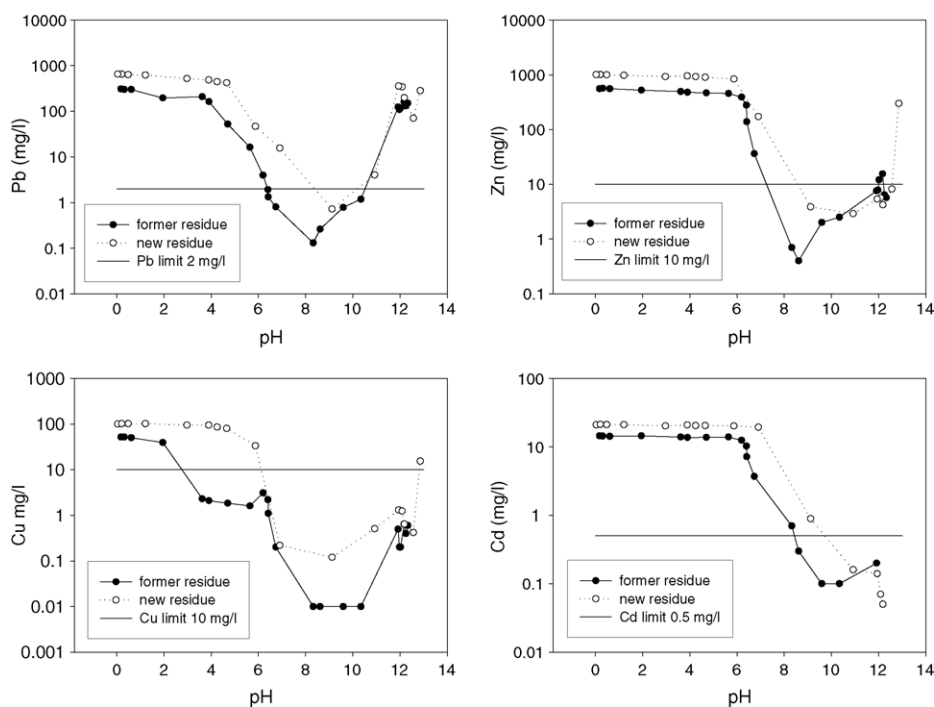


Fig. 8. Pb, Zn, Cu and Cd concentrations (mg/l) in pH-dependent leaching of the former and the new residue.



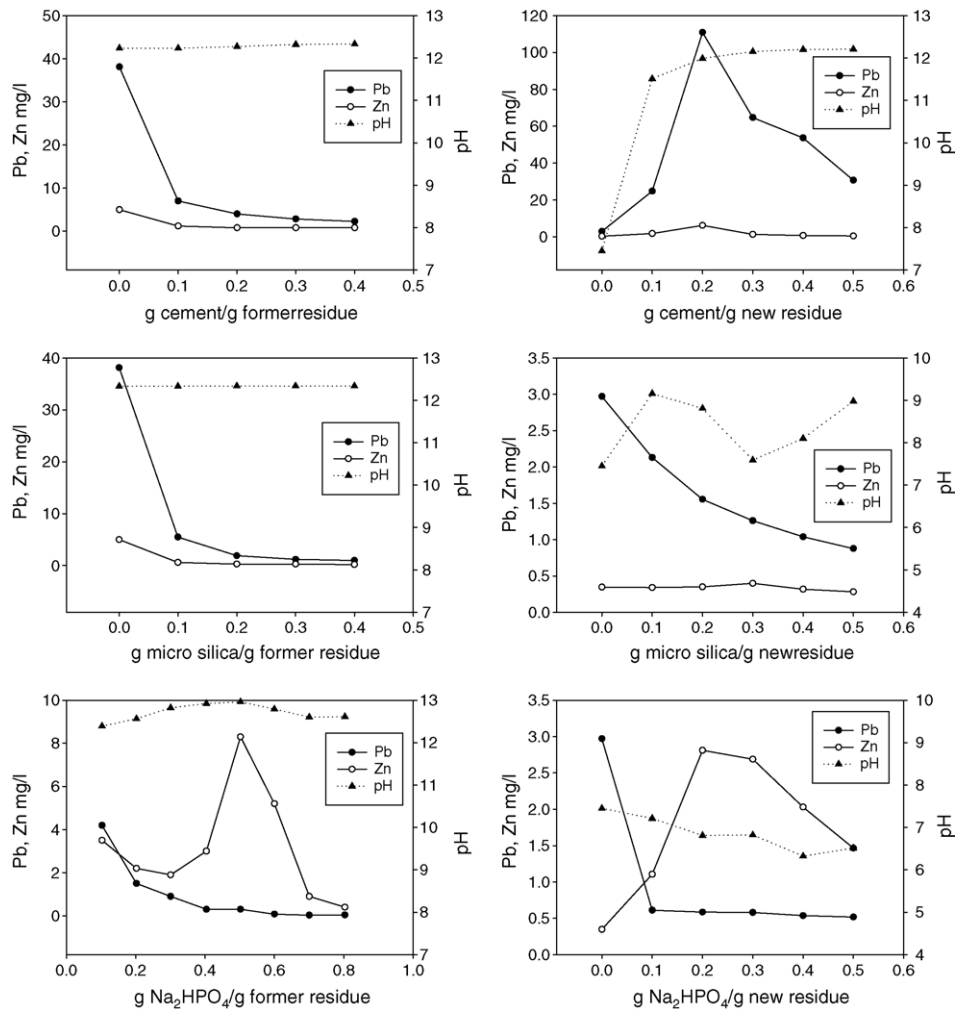
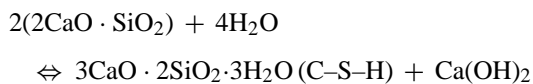
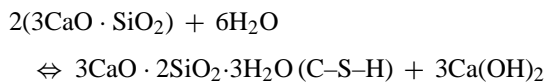


Fig. 9. Pb and Zn leachate concentrations and pH of DIN 38414-S4 leachates of former (left) and new residue (right) treated with cement, micro silica and  $\text{Na}_2\text{HPO}_4$  as soluble  $\text{PO}_4^{3-}$ .

untreated residue. At this pH, a higher Pb leaching (3.0 mg/l) was observed than for the untreated residue (0.8 mg/l). The increase in Zn leaching of the new residue was less extreme as for Pb but also here, a maximal value of 6.2 mg/l was noticed. The Zn leaching limit is however not exceeded (10 mg/l). The high leachate pH obtained when cement is used for immobilisation is an important disadvantage. The high pH is obtained in the leachate due to the formation of  $\text{Ca}(\text{OH})_2$  when  $\text{C}_3\text{S}$  ( $3\text{CaO}\cdot\text{SiO}_2$ ) or  $\text{C}_2\text{S}$  ( $2\text{CaO}\cdot\text{SiO}_2$ ) is hydrated to produce the strength developing C–S–H (Gougar et al. [18], Hewlett [19]):

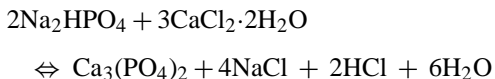


In a previous study was shown that with micro silica lower Pb and Zn leachate concentrations could be attained than with

cement (Geysen et al. [5]). A Pb concentration of 1.0 mg/l was attained at a dosage of 0.4 g micro silica/g former residue. Also for the new residue 1.0 mg/l was attained at a dosage of 0.4 g micro silica/g residue. The lower Pb leaching in case of the new residue compared to the Pb leaching of the micro silica-treated former residue is also due to the low pH ranging from 7.5 to 9.0 compared to 12.3 for the micro silica-treated former residue.

Also, the use of soluble  $\text{PO}_4^{3-}$  showed to be a good treatment for these APC residues. At an acceptable dosage of 0.4 g  $\text{Na}_2\text{HPO}_4$ /g former residue, a Pb concentration of 0.3 mg/l was attained and a Zn concentration of 1.9 mg/l. When the amount of  $\text{Na}_2\text{HPO}_4$  was increased, as discussed in a previous study, an increase in Zn concentration was observed together with an increase in pH (Geysen et al. [20]). In this study, the effect on leaching of Pb of various treated soluble phosphates was compared. The former residue was one of the studied residues. With the new residue, Pb leachate concentrations decreased to 0.6 mg/l upon addition of 0.1 g  $\text{Na}_2\text{HPO}_4$ /g

new residue but did not decreased much upon addition of more Na<sub>2</sub>HPO<sub>4</sub>. The high content of soluble CaCl<sub>2</sub>·2H<sub>2</sub>O of the new residue consumed the added soluble PO<sub>4</sub><sup>3-</sup> to form Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> and in this case pH decreased following the reaction:



In this case, the decrease in pH resulted in an increase in Zn leaching until enough PO<sub>4</sub><sup>3-</sup> was added so that also a Zn containing PO<sub>4</sub>-mineral precipitated.

Reducing the pH by adding Na<sub>2</sub>HPO<sub>4</sub> could decrease the leachate concentrations of Pb but the lower pH was however accompanied with an increased Cd leaching (Fig. 10). pH-dependent leaching of the new residue showed that at pH 6.9 more than 90% of the Cd was leached. Adding 0.1 g Na<sub>2</sub>HPO<sub>4</sub>/g new residue decreased the leachate pH to 7.2 and increased Cd leaching to a maximal value of 4.8 mg/l. Adding more Na<sub>2</sub>HPO<sub>4</sub> decreased Cd leaching, although

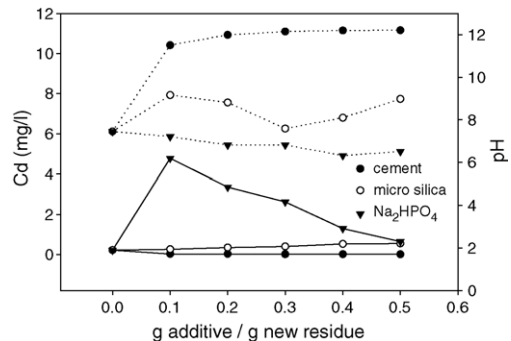


Fig. 10. Cd concentration in the leachate of cement-treated, micro silica-treated and PO<sub>4</sub><sup>3-</sup>-treated new residue. Solid lines are the Cd concentrations, dotted lines are the corresponding pH values.

pH decreased further. At a dosage of 0.5 g Na<sub>2</sub>HPO<sub>4</sub>/g new residue, the Cd concentration was decreased to 0.6 mg/l. Such an increase was not observed with cement and only slightly with micro silica.

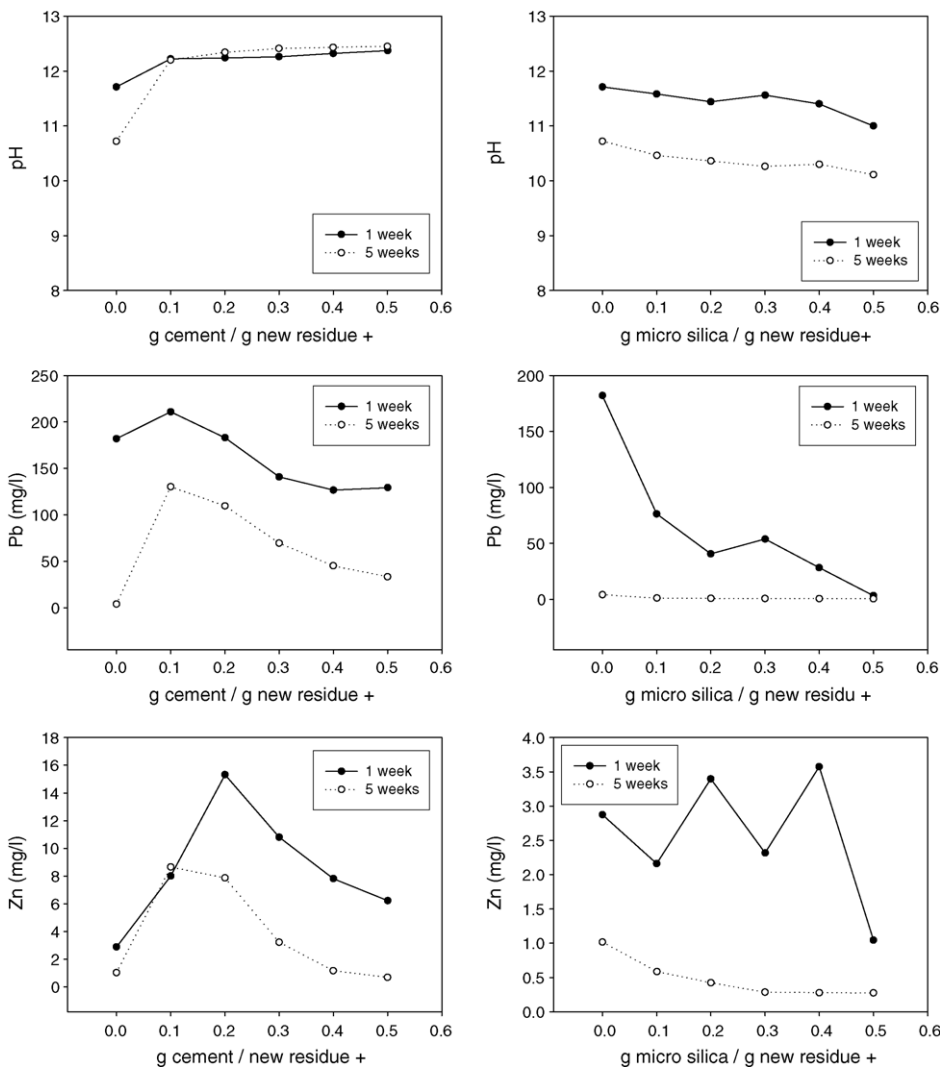


Fig. 11. pH, Pb and Zn leachate concentrations of the new residue + treated with cement (left) and treated with micro silica (right).

Adding supplementary  $\text{Ca}(\text{OH})_2$  in the spray dryer resulted in an increase of Pb (330 mg/l) leaching far above the landfill limit (2 mg/l).

Only treating the new residue + with water decreased pH down to 11.7 after 1 week curing and down to 10.7 after 5 weeks curing (Fig. 8, top). As a consequence also the Pb and Zn leachate concentrations were low. After 1-week curing, the Pb and Zn concentrations were 182.1 and 2.9 mg/l, respectively, and decreased to 4.2 and 1.0 mg/l after 5 weeks curing (Fig. 11, middle and bottom at 0.0 g cement or micro silica/g new residue +).

Adding 0.1 g cement/g residue in the immobilisation recipe increased pH to 12.2 and consequently also leaching of Pb and Zn. Adding more cement again decreased Pb and Zn leaching but the landfill limit of 2 mg/l for Pb was never attained; the lowest Pb leachate concentration was 33.6 mg/l.

Adding micro silica did not increase the pH of the leachate as was the case with cement. In contrast, pH decreased slightly upon addition of micro silica. At a dosage of 0.5 g micro silica/g residue, the pH decreased down to 11.0 after 1 week curing and down to 10.1 after 5 weeks curing. Pb and Zn leaching decreased upon addition of more micro silica in the immobilisation recipe. The Pb leachate concentration at a dosage of 0.5 g/g residue after 1 and 5 weeks curing was 3.4 and 0.6 mg/l, respectively. The Zn leachate concentration at that dosage and after 1 and 5 weeks curing was 1.0 and 0.3 mg/l, respectively.

Cd leaching was never higher than 0.2 mg/l and total Cr leaching never exceeded the landfill limit of 0.5 mg/l of Cr VI.

#### 4. Conclusions

The heavy metal concentration of a residue from a more efficient wet flue gas cleaning system almost doubled compared to the former semi-dry residue due to the lower amount of residue produced. The matrix composition of this new flue gas cleaning residue significantly differed from the matrix of the former residue. Although none of the analytical techniques could determine the presence of  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  unequivocally, we can conclude, based on the strong deliquescent characteristics, thermal analysis and the high soluble content of Ca and Cl that in the residue of this wet FGC system  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  is present instead of  $\text{Ca}(\text{OH})_2$  and  $\text{CaOHCl}$  which are the main minerals of the former residue of a semi-dry FGC system. The low  $\text{Ca}(\text{OH})_2$  content made that the DIN 38414-S4 leachate pH of the new residue decreased to 9.7 instead of 12.4 for the former residue. Leaching of Pb and Zn, the main metals of concern in the former residue, decreased to, respectively, 0.8 and 1.0 mg/l for the new residue, both below the leaching limit value for landfilling. Unfortunately, due to the lower pH and the higher Cd content, Cd leaching was slightly above the corresponding landfill limit. The pH of the leachate decreased from 9.7 to 7.5 after curing the water-treated residue in open air due

to the low buffering capacity (the residue does not contain  $\text{Ca}(\text{OH})_2$ ). Not enough (or no)  $\text{CaCO}_3$  was formed to control the leachate pH at 8.5. As a result of this pH decrease, Pb leaching increased slightly. Treatment prior to disposal is required.

When the residue was treated with cement in view of decreasing heavy metal solubility, leachate pH increased and thus also leaching of Pb and Zn. With micro silica no such pH increase occurred, Pb and Zn leaching remained below the landfill limit. The lowest Pb and Zn leaching values could be obtained with soluble  $\text{PO}_4$ . But, when using an acid containing  $\text{PO}_4$  source, pH decreased and Cd leaching increased.

Adding a small amount of supplementary  $\text{Ca}(\text{OH})_2$  to the residue of the new flue gas cleaning system at the level of the spray dryer to overcome bag filter clogging resulted in a small increase of the acid neutralising capacity (ANC) from 0.7 to 1.4 mol  $\text{H}^+$ /kg. The solubility of Pb increased from 0.8 to 330 mg/l due to an increase in leachate pH from 9.7 to 12.1. Immobilisation with cement could only reduce the solubility of Pb to 33.6 mg/l. The solubility of Pb in the leachate of the micro silica-treated residue decreased to 0.6 mg/l.

The residue of the wet flue gas cleaning system has the advantage that the leachate pH is lower compared to semi-dry  $\text{Ca}(\text{OH})_2$ -based residues so that leaching of amphoteric metals, such as Pb and Zn, at high pH is of no concern. The buffering capacity is however too low to assure an optimal pH with limit leaching of Pb, Zn and Cd. The treatment with micro silica as well as with phosphate can decrease leaching of Pb to below the leaching limit value. Attention is required for leaching of Cd. The residue obtained after supplementary addition of  $\text{Ca}(\text{OH})_2$  has a slightly higher buffering capacity. Micro silica can also result in decreased leaching of Pb especially after 5 weeks curing. Phosphates were not tested for this residue but out of the results obtained with the other residues it can be assumed that also the addition of phosphate can reduce leaching of Pb.

Adding cement for the treatment of both new residues cannot decrease leaching of Pb below the landfill limit of 2 mg/l.

The advantage of a lower production of residue in case of the new does not hold if supplementary  $\text{Ca}(\text{OH})_2$  is required to prevent fabric filter clogging and if cement is used for immobilisation.

The pH of the leachate is the main leaching controlling parameter. Forced carbonation is a possible solution to reduce alkalinity of the new residue + but Cd leaching has to be controlled.

Cl leaching from these residues could not be reduced after treatment. The percentage TDS of the new residue is more than 50% and was not changed after treatment. The question of how to manage these highly soluble residues is not solved yet. Washing necessitates a water treatment and discharging of a Cl-rich effluent, which is only acceptable in seawater and in case it is free of contaminants. If this effluent is discharged immediately it is possibly better not to implement this sup-

plementary step and control the discharge of Cl at the level of the landfill effluent.

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