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Abstract
Fly ash is generated in large quantities by waste incineration processes. Chloride is commonly present in the fly ash produced by the incineration of hazardous materials, such as PVC plastic. Major difficulties related to the disposal and handling of fly ash include the high concentration of easily leachable chlorides, heavy metals and toxic compounds. In order to avoid adverse environmental impacts from the disposal of fly ash, the content of soluble chlorides must be reduced. One of the most effective options for the chloride removal is leaching and displacement washing in a filter press. The primary aim of this study was to obtain efficient removal of chloride from fly ash by utilizing a leaching and displacement washing process, carried out in a filter press. The secondary objective was to obtain high filtration capacities and low filter cake moisture contents. The slurry was prepared by mixing fly ash with water at an ash/water ratio of 1:2 and filtered to separate the solids from the liquid. After solid-liquid separation, most of the dissolved residual chloride was removed from the filter cake by washing the cake with fresh water in the second stage of separation. It was possible to remove up to 98 % of the total chloride and to obtain sufficient filtration capacities. The residual moisture content of the filter cakes varied from 22 to 35 wt.%, which means that the cakes could be disposed of in landfill, or possibly utilized as a construction material.

Keywords
Fly ash, hazardous waste incineration, chloride removal, filter press, leaching, cake washing

Introduction

The increasing use of waste materials for energy production by incineration has reduced the unnecessary disposal of combustible waste in landfills. On the other hand, waste incineration always produces ash fractions, and these may contain a large variety of contaminants. Some fly ashes are characterized by their high chloride and heavy metal content (Aguiar del Toro et al., 2009; Pan et al., 2008), which sets challenges for their utilization and disposal from the technical and environmental points of view. Local groundwater pollution, for instance, can be caused by fly ash landfill leachates (Nzihou and Sharrock, 2002).

The chloride content in fly ash varies greatly, depending on the type of the material incinerated (Kumar et al., 2007). Other soluble and insoluble salts are present as well. Many of the chlorides produced, such as alkali metal chlorides and alkaline earth metal chlorides, have a high solubility in water. Therefore, chloride removal by leaching, also referred to as water-extraction, or dissolution, can be technically feasible. The washed solid fraction can be then separated from

the salt-containing liquid using filtration technology (Wilewska-Bien et al., 2007). As a result of successful fly ash washing and filtration, the leaching tendency of the solid cakes should be low. Squeezing of the cakes in a filter press at high pressures, after leaching at proper conditions, may help to achieve this requirement.

Residual chloride reduces the potentiality of ash utilization for applications such as cement and concrete production (Zhu et al., 2010; Poon et al., 2000) and road construction (Ahmaruzzaman, 2010) by its erosive effects. Treatment of the saline liquid after leaching is an important issue as well, although it is out of the scope of this study. For instance, chloride could be removed from the filtrate using ion-exchange resins (Jemaa et al., 1999; Brown et al., 1998). Concentration of the liquids using membrane technology, as well as stabilisation of the heavy metals in the filter cake, are among the most promising technologies for alleviating the environmental impacts of the process. Fly ash has been recognized as a potential adsorbent for acid wastewater neutralization and heavy metal removal (González et al., 2011; Wang and Wu, 2006). It has also been used as a soil ameliorant for improving crop production (Jala and Goyal, 2006). Irrespective of the end use of the solids, it is important to obtain an acceptable washing result, with minimal wash water consumption. The objective of this experimental study was to obtain a high degree of chloride removal using a filter press for the treatment of fly ash obtained from a hazardous waste incineration plant. A relatively similar process, comprising leaching of municipal solid waste incinerator (MSWI) fly ash followed by displacement washing, has been studied earlier by Wilewska-Bien et al. (2007). In their study, washing and dewatering of filter cakes was performed using both laboratory scale and pilot scale filters. Unlike the previous studies on this subject, the present study had the main focus on the pressure filtration stage. The effect of important operational variables of the vertical filter press on the washing result were investigated and modeled.

Materials and methods

Process description

The idea of the fly ash handling process (Figure 1) was to mix fly ash with water so as to dissolve soluble chlorides and to separate the washed solids from the saline waste liquid using a pressure filter. The fly ash sample was obtained from a Finnish hazardous waste incineration plant. Cake washing tests with different washing ratios were carried out for most filter cakes.
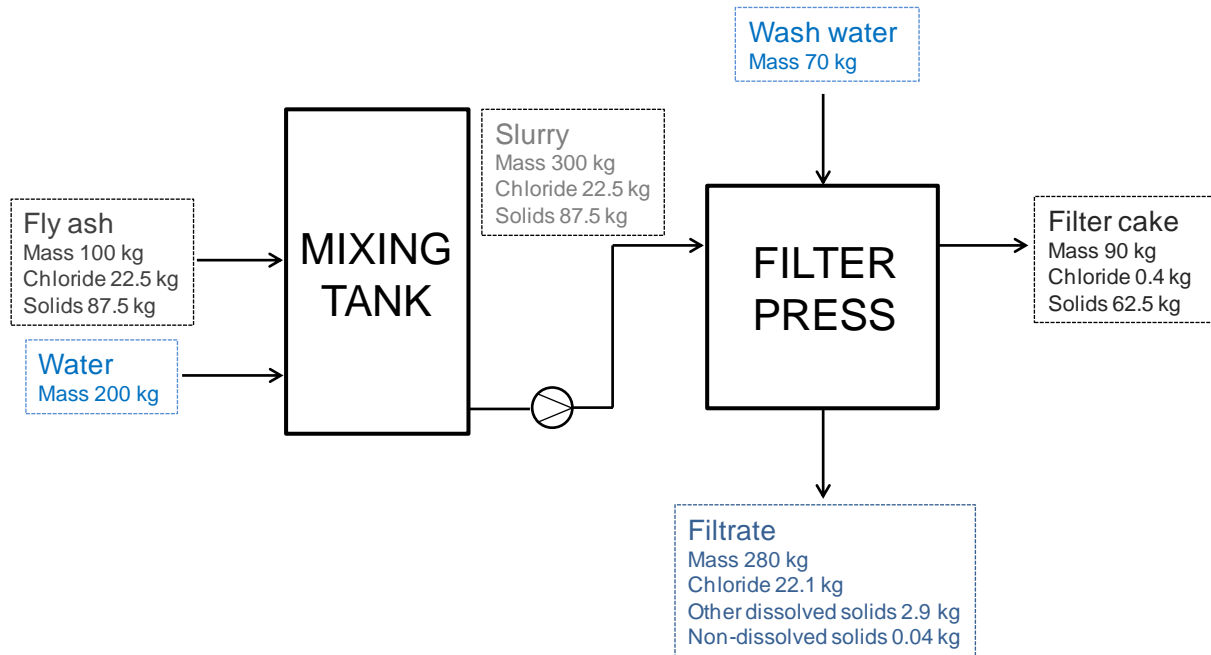
Figure 1.   The fly ash washing process, with an approximate mass balance for the treatment of 100 kg fly ash.

Slurry preparation

The fly ash sample for the washing experiments was received from Ekokem, a company, which operates a hazardous waste incineration plant in Finland. The main types of waste and hazardous waste incinerated at the plant include solid waste, solvents, paste-like waste, wastewater handling residues, and oils. Slurry batches of approx. 100 dm^3 were prepared by mixing dry ash with water in a constant mass ratio of 1:2. The average density of the slurry was 1230 kg m^{-3}. The chloride concentrations in the dry ash and in the slurry were 22.5 % and 7.5 %, respectively. The slurry was mixed in a 120 dm^3 tank overnight to ensure that there was equilibrium between the chloride content of the solid and the liquid. Additionally, dissolution of ash salts into water, together with mixing friction, generated heat, which raised the slurry temperature rapidly to about 40 °C. A constant slurry temperature of 30 °C was obtained during the mixing time of about 20 hours. Based on measurements carried out during the leaching period, chloride is dissolved almost completely within minutes. This means that the solid-liquid separation should be optimally performed very soon after the leaching, when the temperature of the slurry is still high and, consequently, the liquid viscosity is lower.

Test equipment

The filtration and washing experiments were conducted using a Larox PF 0.1 pressure filter unit (Figure 2). The filter system comprised a slurry tank, a diaphragm pump for feeding the slurry into the filter, a filter chamber ($A = 0.1$ m^2) with a height of 45 mm and a pressurized wash water tank. The wash water was distributed over the filter cake at a pressure of 1 bar, driven by compressed air. The mass of the filtrate, the pressure in the slurry feed pipe and the pressing pressure were continuously recorded.
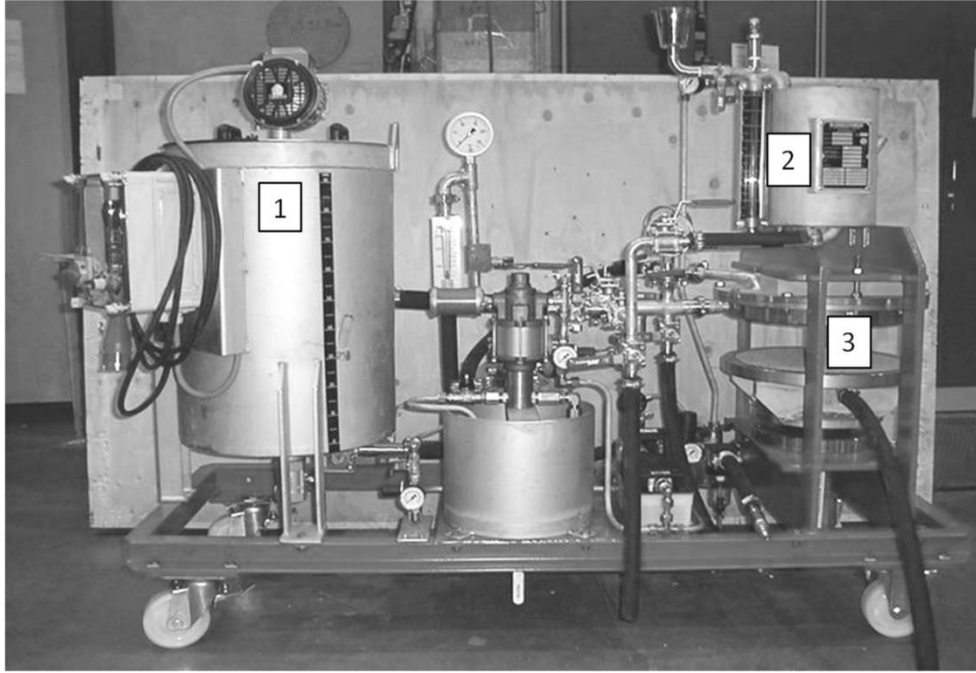
Figure 2.　　　Larox PF 0.1 pressure filter. The mixing tank (1), the wash water tank (2) and the filter chamber (3).

Filtration and cake washing experiments

All stages of the fly ash washing process including leaching, filtration and cake washing were performed using the filter shown in Figure 2. Five stages of operation were included in a typical filtration sequence in the pressure filter:

- Filtration
- 1st cake pressing
- displacement washing of the cake
- 2nd cake pressing
- air dewatering.

The test variables included 1) the filtration time, 2) pressing pressure after cake washing, and 3) air drying time. The ranges of these variables were 1) 100-300 s, 2) 10-13 bar, and 3) 0-240 s. The filtration pressure (6 bar), pressing pressure before cake washing (12 bar), washing pressure (2 bar), and air drying pressure (6 bar) were held constant. The duration of cake pressing varied from 50 to 100 s in the first pressing stage and from 140 to 250 s in the second pressing stage. The duration of the pressing was determined by the *X-point* that was reached at the point of time when a significant drop was observed in the feed line pressure, due to blocking of the slurry feed port by the compression diaphragm. Additionally, three experiments were conducted without cake washing, in order to obtain reference values for the chloride content in the unwashed cake. The L/S ratio (2:1) was kept constant during the experiments. Statistical design of experiments (DoE) was utilized to create the experimental plan shown in Figure 3. The value ranges of the variables were included into the experimental plan according to an augmented full factorial design. This kind of experimental design enabled good applicability of the results for regression modeling. Three reference tests in which the filter cakes were not washed were performed in addition to the plan.

The wash water consumption varied between 1.6 and 2.6 dm^3 per experiment, depending on the volume of the empty space above the filter cake after the first pressing. On the other hand, this volume was dependent on the duration of the filtration stage. Feeding of the wash water was stopped immediately when the pressure in the filter chamber was equal to the feed pressure (2 bar).
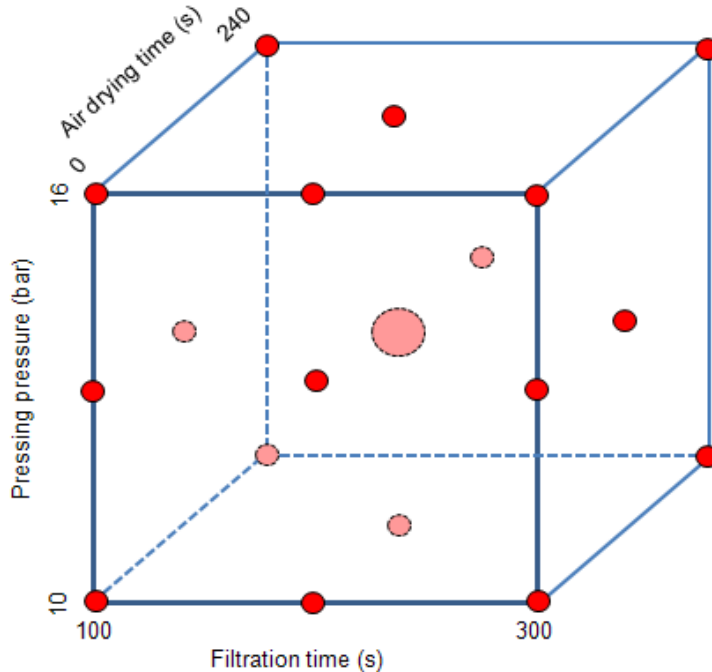

Figure 3.   An illustration of the experimental plan comprising 19 tests.

Analysis methods

Prior to the experiments, the slurry characteristics were determined. The analyses included particle size analysis, determination of the chloride content, electrical conductivity and determination of the density and solid content of the slurry. Concentrations of heavy metals were determined from the liquid phase after leaching (L/S = 10) at the incineration plant using ICP-OES, with the exception of Hg that was assayed with AAS. However, representativeness of the heavy metal concentrations for the ash sample used for the experiments in the laboratory can not be guaranteed, because the materials to be incinerated may vary considerably. Therefore, only approximate ranges for heavy metal concentrations are reported.

The particle size distribution of the fly ash, after the dissolution stage, was measured using a Beckman Coulter LS 13320 laser diffraction analyzer. The average values obtained from three parallel analyses were D_{mean} = 79.9 μm, D_{median} = 50.9 μm, D_{10} = 2.2 μm, and D_{90} = 205.5 μm. The size reduction of the solid particles during mixing, caused by mechanical forces and dissolution of soluble compounds, was also measured using the same particle size analyzer.

The settling velocity of ash particles in the slurry was determined in a graduated glass cylinder at 22 °C.

The cakes were analyzed for moisture content, chloride concentration and conductivity. When determining the chloride concentration and conductivity, the cakes were suspended in Millipore water by using a ratio of 1:9. The cake samples prepared this way were shaken occasionally, and kept at 22 °C for 48 h, to dissolve the soluble chlorides from the cake samples. A Sherwood

926 chloride analyzer was used to determine the chloride concentration. The operation of such robust but reliable chloride analyzer is based on coulometric titration and formation of an insoluble AgCl precipitate. According to the manufacturer of the analyzer, the accuracy of analysis is 1 mg L^{-1}. The conductivity of each sample was measured by using a Knick 702 conductivity meter.

Equations

In the equations shown below, *m* represents the mass and *V* represents the volume. The moisture contents *MC* in the filter cakes were determined by drying the cake samples (average dry weight of 270 g) to constant weight at 105 °C:

$$MC = 1 - \frac{m_{dry\,cake}}{m_{wet\,cake}} \qquad (1)$$

In cases when the cakes are fully saturated, the average porosity ε_{av} of the filter cakes can be determined by drying and calculating the pore volume from the loss of weight. Inversely, the average porosity can be calculated from the volumes of solids, after determining the density of solids. The cake volume is calculated based on cake dimensions.

$$\varepsilon = \frac{V_{pores}}{V_{cake}} = 1 - \frac{V_{solids}}{V_{cake}} \qquad (2)$$

There are two common ways to define the washing ratio, namely the mass of wash water per mass of dry solids (Eq. (3)) and the volume of wash water per pore volume of the cake (Eq. (4)). For cake washing by leaching, Eq. (3) is more commonly used, whereas Eq. (4) is more frequently used for displacement washing.

$$WR_1 = \frac{m_{wash\,water}}{m_{dry\,cake}} \qquad (3)$$

$$WR_2 = \frac{V_{wash\,water}}{V_{pores}} \qquad (4)$$

Results and discussion

General observations

The average particle size of solids in the slurry reduced while the slurry was mixed to dissolve the chloride. The median particle size, D_{median} decreased from 72 µm to 51 µm in 24 hours. Since the reduction of particle size is not favorable when considering filterability (because of increasing cake resistance and clogging of the filter medium) the leaching time should be kept as short as possible. Regarding the dissolution of soluble components, such as chloride, similar observations have been reported by Wilewska-Bien et al. (2007) and Wang et al. (2010).

The average cake resistance α_{av}, in the filtration tests at 6 bar, was about $4 \cdot 10^{10}$ m kg^{-1}. The suspended solid concentration in the filtrate ranged from 0.10 to 0.20 g L^{-1}, the majority of which was observed to accumulate during the first seconds of each filtration experiment, i.e. before any filter cake was formed.

Even though heavy metals were out of the scope of this study, their concentrations in the non-washed fly ash were determined. The analyses were performed for water-leached samples, which gave information about easily leachable heavy metal salts. The quality of the hazardous waste incinerated varies by time. Therefore, only approximate values for this type of fly ash are given: As, Cr, Mo, Sb, Hg < 1 ppm; Ba, Ni < 10 ppm; Cd, Pb < 150 ppm; Zn > 1000 ppm.

Settling properties of the slurry

Prior to the filtration tests, two settling experiments were carried out. Thickening of the slurry, for instance, by gravity settling would help to enhance the filtration capacities. A graduated glass (V = 1000 mL, h = 330 mm) was filled with the slurry at 25 °C and the height of the clarified layer was measured at certain time intervals. It was observed that a significant reduction (over 30 %) of the slurry volume can be obtained within 1-2 hours, even without flocculants or coagulants. The settling rate was slightly accelerated with the help of ferrous sulfate (Figure 4), which is typically used as an immobilization agent for trace elements. The mass of FeSO$_4$ added was 4.2 % of the mass of the fly ash. However, the action of FeSO$_4$ may have been impeded by the high salt concentration of the slurry.
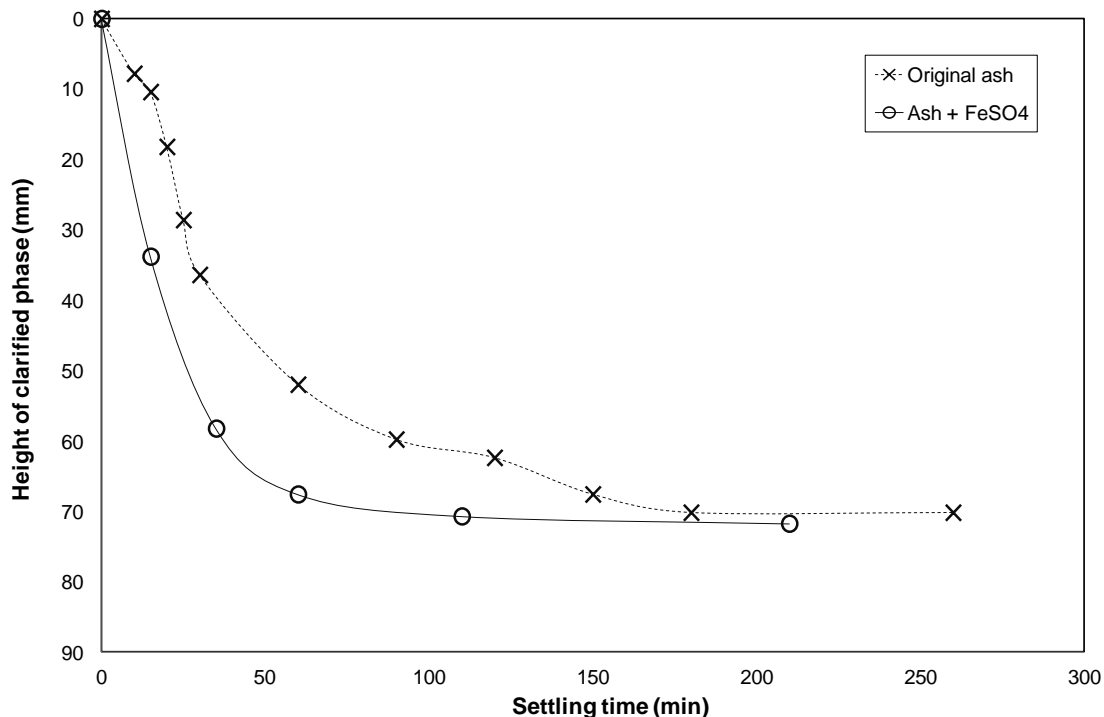

Figure 4.   Settling of fly ash particles in water at 25 °C.

Cake washing

The remaining chloride concentration after displacement washing was strongly dependent upon the washing ratio that ranged from zero to 1.85 (water: dry cake by mass). However, leaching followed by filtration accounted for most chloride removal, as illustrated in Figure 5. Leaching

using the L/S (water/ash) ratio of 2:1, followed by filtration without cake washing, resulted in 87-88 % chloride removal efficiency, while up to 98 % of the chloride was removed by the combination of leaching and cake washing. The most effective chloride removal was achieved when air drying of a filter cake was applied after the second pressing of the cake to remove the residual liquid from the pores in the cake.

The optimum S/L ratio in the leaching stage depends on the cost of fresh water, possibility to use countercurrent washing and the cost of treatment or regeneration of the wash water. From another point of view, the optimum S/L ratio is determined by the environmental regulations related to fly ash reuse and/or disposal.

There has been some research activity on fly ash handling issues in the recent years. Mulder (1996) obtained a 92 % decrease in the chloride concentration of municipal solid waste incineration (MSWI) fly ash by leaching at pH 4 (L/S = 10), vacuum filtration, two-stage cake washing (L/S = 2) prior to the 2nd and 3rd vacuum filtration steps. Zhu et al. (2010) investigated the presence of chlorides in MSWI fly ash. They found that $CaCl_2$, NaCl and KCl were the most important water-soluble chlorides, whereas insoluble chlorides were mainly in the form of Friedel's salt (calcium chloroaluminate). Chloride removal of about 90 % was achieved by Wilewska-Bien et al. (2007), who used leaching and subsequent cake washing in a filter press for the treatment of MSWI fly ash.

Since statistical design of experiments was utilized, the results were highly suitable for modeling purposes. The empirical model used for fly ash washing is linear in regards to filtration time x_1, pressing pressure x_2 and air drying time x_3. The exponential term x_4 represents the wash liquid volume. The model function is of the form

$$y = \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + e^{-\beta_4 x_4} \tag{5}$$

, where β_1, β_2, β_3 and β_4 are the coefficients of the variables (Table 1).

Table 1.   Coefficients of the variables in the cake washing model.

Variable x_i	Coefficient β_i
x_1 (filtration time)	$-2.056 \cdot 10^{-4}$
x_2 (pressing pressure)	$-5.874 \cdot 10^{-4}$
x_3 (air drying time)	$-3.048 \cdot 10^{-4}$
x_4 (volume of wash liquid)	$5.734 \cdot 10^{-1}$

The coefficient of determination (R^2) for this model is 97.5 %. The measured vs. modeled plot is shown in Figure 5.

Based on Table 1, it can be expected that the best washing result is obtained when the filtration and air drying times are long, pressing pressure is high and a high volume of wash liquid is used.
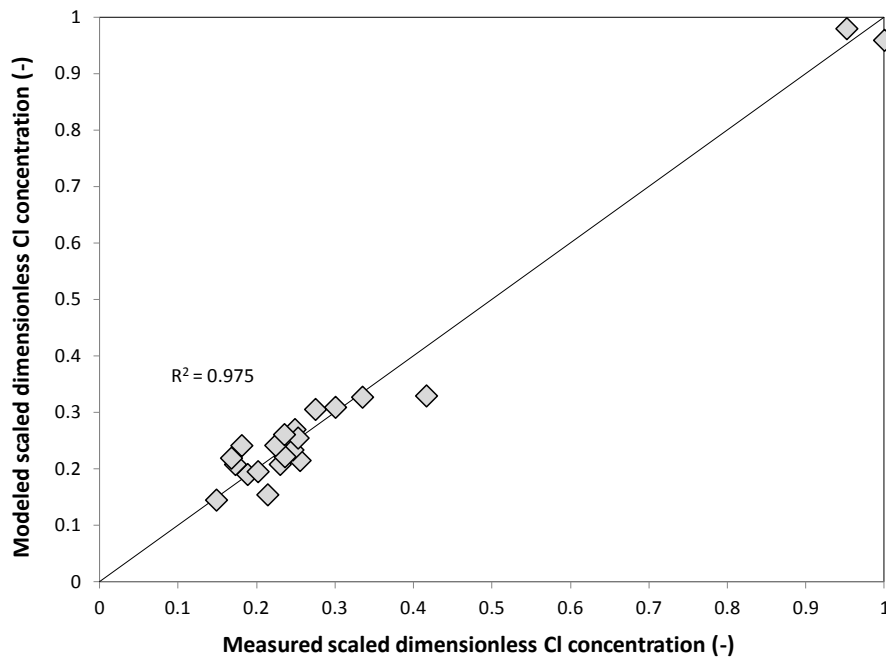
Figure 5.   Measured and modeled scaled values for the residual chloride concentration in the filter cakes.

The empirical model is a combination of the exponential decay model (Rhodes, 1934; Marecek and Novotny, 1980; Salmela and Oja, 1999; Salmela and Oja, 2006), and linear terms. Combining linear terms and exponential decay model in cake washing processes is more comprehensively discussed in the paper of Huhtanen et al. (2012).

The volume of water used in the cake washing step was measured after each experiment, based on the volume needed for complete re-filling of the wash water tank. Measured and modeled results as a function of the wash water volume are presented in Figure 6A. The dimensionless cl⁻ concentration is defined as the ratio of the cl⁻ content in a washed sample to the cl⁻ content in a non-washed sample. Most of the deviation of the values in the washing curve is caused by the variation in the experimental conditions. The wash water consumption was not actually a variable in this study, but it was a function of the filtration time (height of the cake).

Displacement washing proved to be an efficient method for chloride removal, even at low washing ratios. About 85 % of the chloride remaining after the leaching, filtration and cake pressing could be removed by displacement washing, using a washing ratio of 1.6 (water:dry cake by mass), which resulted in up to a 98 % reduction of soluble chloride concentration in the fly ash.
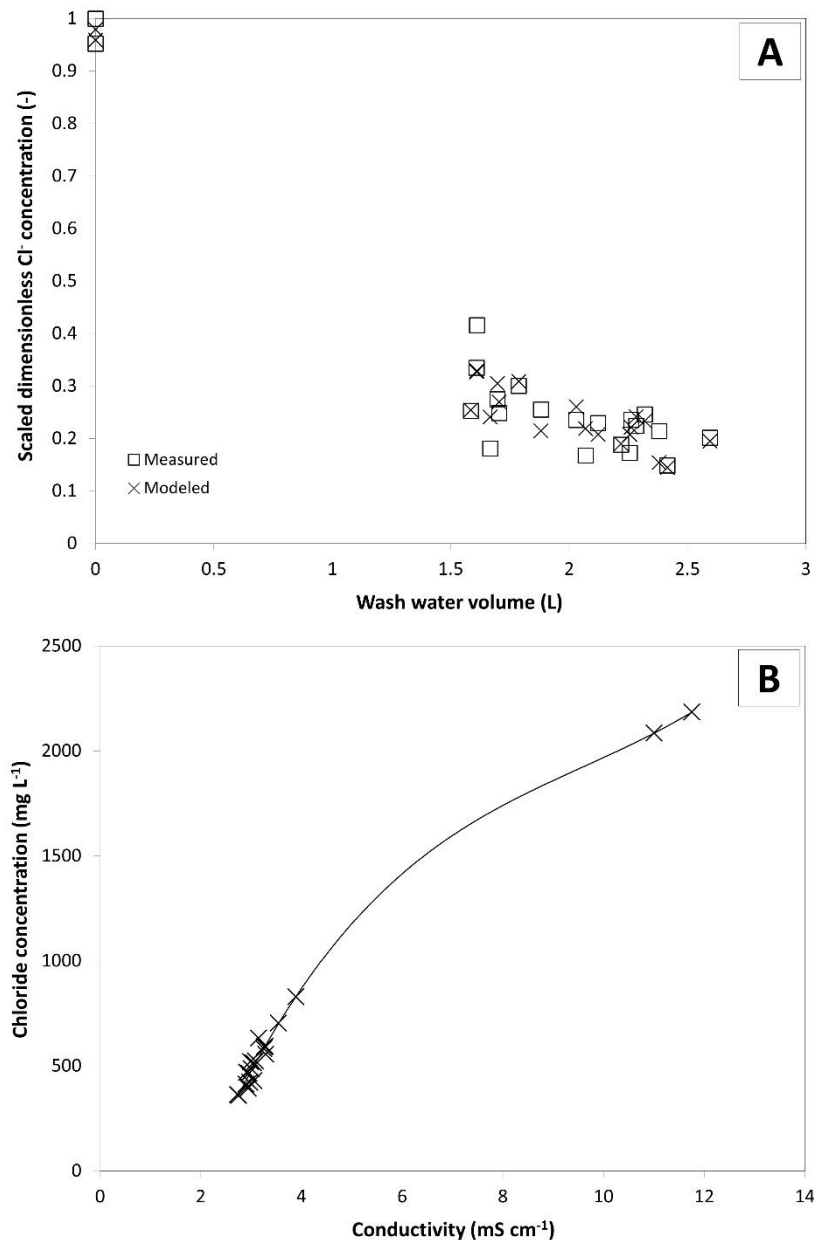
Figure 6.   A) Dimensionless scaled chloride concentration in dry fly ash in the filter cakes after leaching and pressure filtration (wash water volume = 0 L) and leaching followed by displacement washing and pressure filtration (wash water volume > 0.6 L). Both measured and modeled results are shown. B) Chloride content of the reslurried cake samples as a function of electrical conductivity.

Electrical conductivity and chloride concentration

A strong correlation was observed between the electrical conductivity and the chloride concentration in the samples (Figure 6B). However, the relationship was not linear. Conductivity of the filtrate is a commonly used measure of the performance of the cake washing stage.

Therefore, it is extremely important to be aware of the possible non-linear correlation between the conductivity and the chloride concentration. When the washing process is evaluated based on conductivity data, a plot similar to that shown in Figure 6B should always be created,

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because the electrical conductivity depends on the total quantity of dissolved compounds, not only on chlorides, and is also influenced by suspended solids.

Residual moisture and filtration capacity

The residual (dimensionless) chloride content had quite a clear correlation with the cake moisture content (Figure 7A). The significant difference between the chloride contents of washed and unwashed cakes is also seen in Figure 7A.
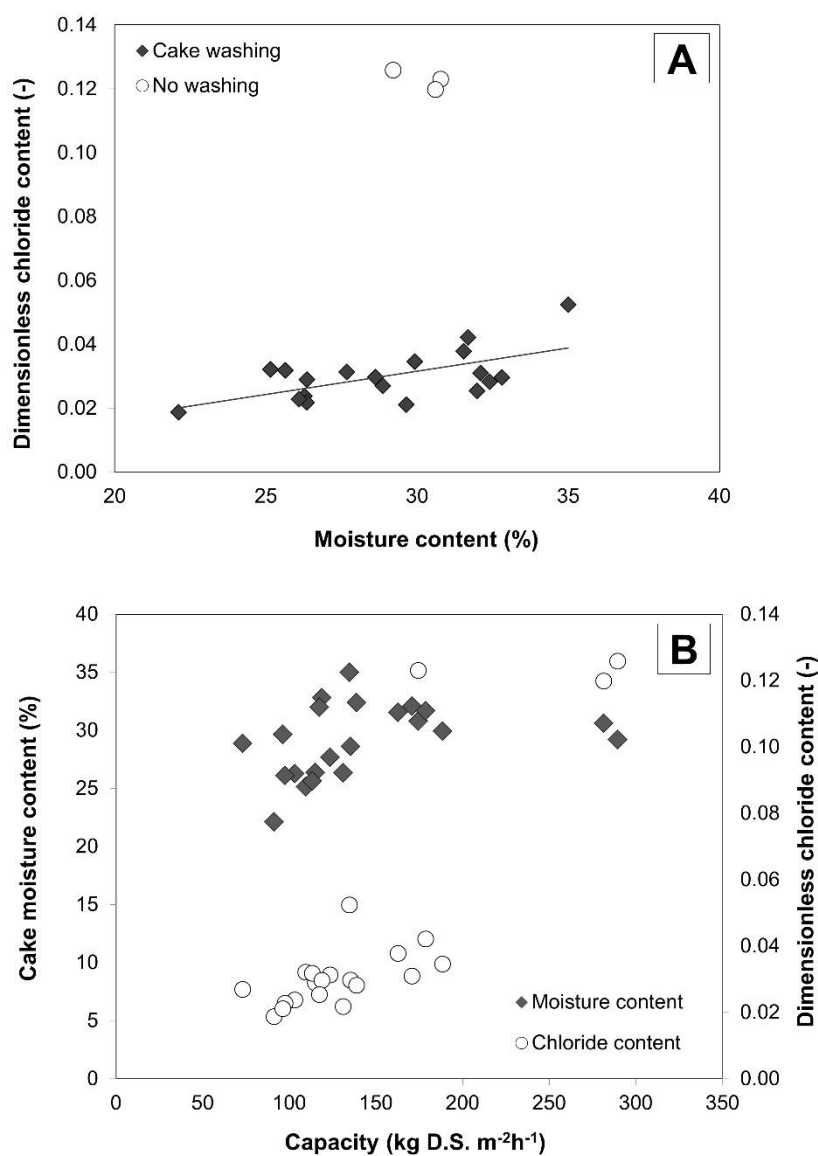

Figure 7.   A) Dependence of the residual chloride content on the moisture content in the filter cakes. B) Moisture content and the residual proportion of chloride in the filter cakes at different dry solids capacities.

An important aim of any filtration process is to obtain a sufficient production capacity. In this study, solid fly ash was washed in a vertical filter press and the main focus was on the final purity of the cakes. The importance of high enough filtration capacities in the fly ash washing process should not be underestimated, because the cost of such a waste treatment process depends largely on the required size of the filter. Both the moisture content and the chloride content of the filter cakes increased with the capacity (Figure 7B). This is simply explained by

the differences in the filtration cycle times and especially by the fact that higher cake moisture contents were obtained without air drying.

The moisture content of the filter cakes varied from 22 to 35 %. Both cake pressing at higher pressure and longer air drying were observed to reduce the moisture content and therefore also the chloride content.

Conclusions

Removal of chloride from fly ash obtained from a hazardous waste incineration process was investigated in this study. The results show that a filter press can be effectively used for the solid-liquid separation after the leaching step. Significant reduction in the chloride contents of the filter cakes can be obtained at moderate water consumption. Dissolution of chlorides from fly ash was observed to be a rapid process. Based on the results, a dissolution time of 15 minutes would suffice. The relationship between the chloride concentration and the electrical conductivity was non-linear, which should be kept in mind when evaluating the washing results based on the conductivity of the filtrate. Thickening or centrifugation prior to filtration should be considered, because the solid particles can be readily sedimented.

Washing of the filter cakes may be performed in order to further reduce the chloride content. Higher capacities could be obtained by thickening of the slurry after the leaching step before filtration. About 87-88 % of the chloride content from the slurry was removed by leaching (L/S = 2/1) followed by filtration. The maximum reduction of the chloride content in the fly ash was 98 % – obtained using a washing ratio of 1.85 (water:dry cake by mass). Filter cakes contained 22 to 35 % water and the filtration capacities ranged from 70 to 290 $kg_{dry\ solids}$ $m^{-2}h^{-1}$. Belt filter with countercurrent washing could be used to minimize the wash water consumption, but the main drawback would be the increase in the cake moisture contents.

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