

The effect of isosaccharinic acid (ISA) on the mobilization of metals in municipal solid waste incineration (MSWI) dry scrubber residue

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Abstract

Co-landfilling of incineration ash and cellulose might facilitate the alkaline degradation of cellulose. A major degradation product is isosaccharinic acid (ISA), a complexing agent for metals. The impact of ISA on the mobility of Pb, Zn, Cr, Cu and Cd from a municipal solid waste incineration dry scrubber residue was studied at laboratory using a reduced 2^{5-1} factorial design. Factors investigated were the amount of calcium isosaccharinate ($\text{Ca}(\text{ISA})_2$), L/S ratio, temperature, contact time and type of atmosphere (N_2 , air, O_2). The effects of pH and $\text{Ca}(\text{ISA})_2$ as well as other factors on the leaching of metals were quantified and modelled using multiple linear regression ($\alpha=0.05$). Cd was excluded from the study since the concentrations were below the detection limit. The presence of $\text{Ca}(\text{ISA})_2$ resulted in a higher leaching of Cu indicating complex formation. $\text{Ca}(\text{ISA})_2$ alone had no effect on the leaching of Pb, Zn and Cr. A secondary effect on the mobilization was predicted to occur since $\text{Ca}(\text{ISA})_2$ had a positive effect on the pH and the leaching of Pb, Zn and Cr increased with increasing pH. The leaching of Pb varied from 24 up to 66 wt.% of the total Pb amount ($1.74 \pm 0.02 \text{ g}(\text{kg TS})^{-1}$) in the dry scrubber residue. The corresponding interval for Zn ($7.29 \pm 0.07 \text{ g}(\text{kg TS})^{-1}$) and Cu ($0.50 \pm 0.02 \text{ g}(\text{kg TS})^{-1}$) were 0.5–14 wt.% of Zn and 0.8–70 wt.% of Cu. Maximum leaching of Cr ($0.23 \pm 0.03 \text{ g}(\text{kg TS})^{-1}$) was 4.0 wt.%. At conditions similar to a compacted and covered landfill (4 °C, 7 days, 0 vol.% O_2) the presence of ISA can increase the leaching of Cu from 2 to 46 wt.% if the amount of cellulose-based waste increases 20 times, from the ratio 1:100 to 1:5. As well, the leaching of Pb, Zn, and Cr can increase from 32 to 54 wt.% (Pb), 0.8–8.0 wt.% (Zn), and 0.5 to 4.0 wt.% (Cr) depending on the amount of cellulose and L/S ratio and pH value. Therefore, a risk ($\alpha=0.05$) exists that higher amounts of metals are leached from landfills where cellulose-containing waste and ash are co-disposed. This corresponds to an additional 29 t of Pb and 17 t of Cu leached annually from a compacted and covered landfill in the north of Sweden.

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1. Introduction

Approximately 1×10^6 t of ashes are generated annually in Sweden, of which 0.45×10^6 t come from municipal solid waste incineration (MSWI) and $0.2\text{--}0.3 \times 10^6$ t from energy generation [1]. Furthermore, residues in the hundreds of thousands of tons containing cellulose are generated in the paper industry each year [2]. A combination of dry scrubber residue and cellulose-rich waste is common at many landfills accepting ashes. The

dry scrubber residue itself contains unburned material, though admixtures of cellulose can also exist in the landfill if, for example, unburned material is landfilled due to insufficient capacity at the incineration plant. An interaction can occur if leachate from the dry scrubber residue comes into contact with cellulose material below or downstream from the dry scrubber residue.

The initial pH value in MSWI dry scrubber residue is usually ≥ 12 [3–5]. MSWI dry scrubber residue contains also metals, usually in high amounts [6].

Under alkaline conditions, peeling reaction or alkaline hydrolysis may degrade cellulose. During peeling reaction, glucose units are gradually eliminated from the reducing end of the cellulose chain. Products from peeling reaction are water-soluble

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compounds with low molecule weight [7]. Alkaline hydrolysis is the cleavage of glycosidic bonds in a cellulose chain [7] and is important for the further degradation of cellulose since it results in new reducing end-groups where the peeling reaction can take place [8,9].

Products from the peeling reaction are polyhydroxycarboxylic acids [10], mainly erythro and threo isomers of isosaccharinic acid (ISA) [9,11]. ISA comprises 70–85 wt.% of the total mass of compounds produced [7]. Results from modelling the long-term alkaline degradation of cellulose reveal rapid degradation during the first years. Of the total cellulose, 15–25 wt.% had degraded after 3 years [7], possibly due to the high amount of reducing end-groups. After approximately 5 years, alkaline hydrolysis is the rate-limiting step, and a much slower reaction than the peeling reaction. The degradation might be completed after 150–550 years [7].

At moderate pH values (pH < 9), cellulose might undergo a mainly biological degradation, *i.e.* it is converted to carbon dioxide and methane, while the peeling reaction might be negligible. If high pH values persist, the microbiological activity may be very slow and the degradation of the cellulose matter may be dominated by non-biological reactions such as the peeling reaction.

Polyhydroxycarboxylic acids are complexing agents [7,10–12]. The complexation of metal ions by polyhydroxycarboxylic acids can involve the carboxyl group, the hydroxyl group or a combination between them [10,12]. Groups of hydroxyl are more important than carboxyl at high pH values due to their greater abundance and the complex formed depends on the number of hydroxyl groups as well as their position in the chain [10]. Information regarding complexation between ISA and metal ions is limited, with most being found in the literature about radioactive waste disposal [11–13]. Information on speciation mainly concerns the formation of complexes between ISA and certain radionuclides of the elements thorium, europium and plutonium.

1.1. MSWI dry scrubber residue and cellulose-based waste

The alkaline dry scrubber residue can initiate an alkaline degradation of the cellulose-based waste when both come into contact with each other, and eventually lead to the formation of ISA. ISA might form complexes with metal ions in the leachate from the dry scrubber residue and enhance the mobilization of metals.

1.2. Objective

The MSWI dry scrubber residue was from Ålidshemverket in Umeå, Sweden. Focus was placed on the mobility of Pb, Zn, Cd and Cr since Ecke [3] identified them as critical in this matrix. Also the change in mobility of Cu was investigated since it easily forms complexes with organic substances [e.g. 14–16]. The objective was to identify if there is a risk of increased leaching of Pb, Zn, Cd, Cr and Cu from MSWI dry scrubber residue co-disposed with cellulose-laden waste. The change in mobility was to be assessed.

2. Materials and methods

2.1. Dry scrubber residue

The dry scrubber residue was sampled at the MSWI plant Ålidshemverket located in Umeå, Sweden. Air pollution control occurs in several steps. Ammonia is added into the combustion chamber to reduce nitrous gases and sodium sulphide is added to remove mercury while calcium hydroxide neutralizes acidic compounds. Bag fabric filters separate particulate matter, *i.e.* the dry scrubber residue studied in this research.

MSWI dry scrubber residue totalling 501 was sampled once at Ålidshemverket.

2.2. Isosaccharinic acid

A combination of two methods was used to synthesise calcium isosaccharinate, Ca(ISA)₂ [13,17].

Lactose monohydrate weighing 100 g and 27.2 g of calcium hydroxide were dissolved in 1 l of nitrogen-flushed water, while being gently heated in a water bath for a few minutes. After being stored at room temperature for 3 days in a sealed vessel, the mixture was boiled for 6 h. During boiling, small amounts of water were added to keep the volume constant. The warm solution was filtered (0.45 µm) and the filtrate was boiled again until the volume was reduced to ~180 ml. The solution was then allowed to cool slowly to room temperature. White crystals were precipitated. The solution was stored at 4 °C for 8 h and then filtered (0.45 µm) to separate the precipitates. The solid phase was rinsed with cold water, ethanol and acetone before it was dried overnight in an oven (75 °C). This procedure generated ~12 g of Ca(ISA)₂.

2.3. Experimental design

The experiments were performed according to a 2⁵⁻¹ reduced factorial experiment with center points [18]. The factorial design resulted in a total of 38 runs. The five controlled factors were the amount of Ca(ISA)₂, liquid-to-solid ratio (*L/S*), temperature (temp.), contact time (time) and atmosphere (atm.) (Table 1). The levels of the factors were chosen to include a wide but still reasonable span of values.

Ca(ISA)₂, 100 ml of distilled water and dry scrubber residue were added to glass flasks of 200 and 250 ml in volume.

Table 1
Factor levels of the two-level factorial design including centre points used to investigate the amount of leached critical metals and DOC as well as the pH as a function of Ca(ISA)₂, *L/S*, temperature, time and atmosphere

Factor	Unit	Levels		
		Low	Center	High
Ca(ISA) ₂	g(kg TS) ⁻¹	2	20	40
<i>L/S</i>	–	5	20	50
Temp.	°C	4	20	80
Time	Days	0.2	3	7
Atm.	Vol.% O ₂	0	21	100

Ca(ISA)₂ was dissolved in the water before the dry scrubber residue was added. Aerobic conditions (atmosphere of 100 vol.% O₂) were obtained by continually adding O₂ throughout the experiment; flushing the flasks with N₂ before any additions yielded anaerobic conditions (atmosphere of N₂, *i.e.* 0 vol.% O₂). The flasks were sealed and placed in either a water bath (80 °C) or in a cold-storage room (4 °C). Flasks representing the centre points were kept open (atmosphere of air, *i.e.* 21 vol.% O₂) at room temperature (20 °C). The flasks were continuously shaken during the experiments. The suspensions were filtered (0.45 μm) and the pH, metal concentrations and dissolved organic carbon (DOC) were determined in the leachate.

All plastics and glassware were acid washed before use.

2.4. Analyses

The total solids (TS) content of the fresh dry scrubber residue was determined according to Swedish standard [19] ($n=7$).

The total concentrations of Cd, Pb, Zn, Cr and Cu in the fresh dry scrubber residue were analyzed at Analytica, Luleå (Sweden) using ICP-AES ($n=3$). Before analysis, the samples were decomposed through a mixture of nitric acid, hydrochloric acid and hydrofluoric acid in a microwave oven.

Total organic carbon (TOC) in the dry scrubber residue ($n=3$) and in the Ca(ISA)₂ ($n=5$) were analyzed using a TOC-SSM-500A (Shimadzu Corporation, Kyoto, Japan).

The pH ($n=38$) in the leachate was measured using a pHC2011-8 electrode (Radiometer analytical S.A., Villeurbanne, Cedex, France). The metal concentrations in the leachate were analyzed using ICP-SMS and ICP-AES technique by Analytica, Luleå (Sweden). DOC was analyzed at CENOX (Sweden) according to Swedish standard [20].

2.5. Statistics

Mean values with standard deviations were calculated for the water content, the total concentrations of metals and TOC in the fresh dry scrubber residue, TOC in Ca(ISA)₂, and the pH in the leachate.

The composition of the leachate (pH, Pb, Zn, Cr, Cu and DOC) was modelled using multiple linear regression ($\alpha=0.05$) [21]. The pH value in the leachate was modelled against the controlled factors (Table 1), while the metal concentrations as well as DOC in the liquid phase were modelled against both the pH and the controlled factors. First, the impact of pH on the metal mobility was determined. Second, the residuals from the pH modelling were used to quantify the influence of the controlled factors on the mobilization of metals and DOC.

The empirical models were used to predict the leaching at different factor settings. At each factor setting of interest, the leaching of the investigated metals and DOC as well as the pH caused by the studied factors were predicted. The predicted pH values were then used in the models describing the leachability of the metals and DOC caused by the pH. The predicted values from the two modelling steps were added and resulted in the totally leached Pb, Zn, Cr, Cu and DOC, respectively.

3. Results

3.1. Fresh dry scrubber residue and Ca(ISA)₂

The water content in the fresh dry scrubber residue was determined to $13.7 \pm 0.5 \text{ g kg}^{-1}$ ($n=7$). The total content of Pb was determined to $1.74 \pm 0.02 \text{ g (kg TS)}^{-1}$, Zn $7.29 \pm 0.07 \text{ g (kg TS)}^{-1}$, Cr $0.23 \pm 0.03 \text{ g (kg TS)}^{-1}$ and Cu $0.50 \pm 0.02 \text{ g (kg TS)}^{-1}$ ($n=3$).

TOC in the dry scrubber residue was $8.7 \pm 1.0 \text{ g (kg TS)}^{-1}$ ($n=3$) while it was $333 \pm 4 \text{ g (kg TS)}^{-1}$ ($n=3$) in the synthesised Ca(ISA)₂.

3.2. Leachate

Cd was eliminated from the evaluation, since all the concentration values were reported under the detection limit ($<4.2 \mu\text{g l}^{-1}$). Two values for the Cr concentration were reported under the detection limit as well ($<9 \mu\text{g l}^{-1}$). For the subsequent calculations, the values of the detection limit were used to represent the two unknown concentration values of Cr.

The pH in the leachates from the experimental runs was determined to 12.3 ± 0.2 ($n=38$).

The leaching of Pb and Zn in the experimental runs were significantly ($\alpha=0.01$) higher at pH values above 12.5 than pH values below 12.5. At pH values above 12.5, the leaching of Pb was $846 \pm 129 \text{ mg (kg TS)}^{-1}$ and the leaching of Zn was $332 \pm 189 \text{ mg (kg TS)}^{-1}$ ($n=10$), compared to $430 \pm 261 \text{ mg (kg TS)}^{-1}$ leached Pb and $93.6 \pm 106 \text{ mg (kg TS)}^{-1}$ ($n=27$) leached Zn at pH values below 12.5. For Cr, the leaching was significantly ($\alpha=0.01$) higher at pH values above 12.2 ($2.9 \pm 2.0 \text{ mg (kg TS)}^{-1}$) ($n=28$) than at pH values below 12.2 ($0.61 \pm 0.46 \text{ mg (kg TS)}^{-1}$) ($n=9$).

3.3. Empirical models

The following empirical models were developed: (1) the effect of pH on the mobility of Pb, Zn, Cr, Cu and DOC in the leachate (Table 2), (2) the effect of the controlled factors on the variation of pH in the leachate (Table 3), and (3) the effect of the controlled factors on the mobility of Pb, Zn, Cr, Cu and DOC in the leachate (based on the residuals from the modelling against the pH) (Table 3). The regression coefficient is representing the effect of each significant ($\alpha=0.05$) factor. The empirical models are valid within the investigated factor intervals (Table 1) and pH varying between 11.9 ± 0.1 up to 12.7 ± 0.1 .

Table 2
Empirical models for the concentration of critical metals (mg (kg TS)^{-1}) and DOC (g (kg TS)^{-1}) in the leachate from the treated dry scrubber residue ($\alpha=0.05$) against the uncontrolled factor pH

Term	Response				
	[Pb]	[Zn] ^a	[Cr] ^a	[Cu] ^a	[DOC] ^a
Constant	-1.1×10^4	-2.2×10^1	-2.2×10^1	-3.2×10^1	-1.8×10^1
pH	$+9.0 \times 10^2$	$+1.9 \times 10^0$	$+1.8 \times 10^0$	$+2.7 \times 10^0$	$+1.5 \times 10^0$
R ²	0.36	0.47	0.51	0.38	0.24

^a log₁₀-transformed.

Table 3
Empirical models for the concentration of critical metals ($\text{mg}(\text{kg TS})^{-1}$) and DOC ($\text{g}(\text{kg TS})^{-1}$) as well as pH in the leachate from the treated dry scrubber residue ($\alpha = 0.05$) against the controlled factors

Term	Response					
	[Pb]	[Zn] ^a	[Cr] ^a	[Cu] ^a	[DOC] ^a	pH
Constant	$+2.0 \times 10^2$	$+1.5 \times 10^0$	-1.3×10^0	$+8.1 \times 10^{-1}$	$+1.5 \times 10^{-1}$	+12.09
Ca(ISA) ₂	$+1.5 \times 10^{0b}$	0	0	$+3.8 \times 10^{-2}$	$+1.7 \times 10^{-2}$	$+4.4 \times 10^{-3}$
L/S	0	$+1.9 \times 10^{-2}$	$+1.8 \times 10^{-2}$	$+9.2 \times 10^{-3}$	$+8.7 \times 10^{-3}$	$+8.4 \times 10^{-3}$
Temp.	$+1.6 \times 10^{0b}$	-1.5×10^{-4}	$+3.9 \times 10^{-3b}$	-5.2×10^{-3}	-9.9×10^{-3}	-4.5×10^{-4}
Time	-3.0×10^{0b}	-7.7×10^{-2}	$+8.0 \times 10^{-2}$	-6.2×10^{-2}	-1.4×10^{-2b}	-3.0×10^{-3}
Atm.	-7.4×10^{-1}	$+7.0 \times 10^{-3b}$	$+8.2 \times 10^{-3b}$	0	-1.6×10^{-3}	$+7.0 \times 10^{-4b}$
Ca(ISA) ₂ × L/S	0	0	0	-4.2×10^{-4}	-1.8×10^{-4}	0
Ca(ISA) ₂ × temp.	-5.1×10^{-2}	0	0	-3.0×10^{-4}	0	-5.8×10^{-5}
Ca(ISA) ₂ × time	-5.7×10^{-1}	0	0	0	$+1.8 \times 10^{-3}$	0
Ca(ISA) ₂ × atm.	$+3.2 \times 10^{-2}$	0	0	0	-7.8×10^{-5}	0
L/S × temp.	0	0	0	$+2.0 \times 10^{-4}$	$+1.7 \times 10^{-4}$	0
L/S × time	0	0	0	0	-1.8×10^{-3}	0
L/S × atm.	0	-2.2×10^{-4}	0	0	$+6.8 \times 10^{-5}$	-2.7×10^{-5}
Temp. × time	$+2.4 \times 10^{-1}$	0	0	0	$+6.1 \times 10^{-4}$	-2.9×10^{-4}
Temp. × atm.	-1.9×10^{-2}	-9.1×10^{-5}	-1.6×10^{-4}	0	0	0
R ²	0.67	0.53	0.51	0.83	0.95	0.89

The models of Pb, Zn, Cr, Cu and DOC are based on the residuals from the modelling against the pH.

^a \log_{10} -transformed.

^b No significant ($\alpha = 0.05$) effect.

The degree of explanation (R^2) for the modelling of the leaching of Pb, Zn, Cr, Cu and DOC against the pH varied from 0.24 (DOC) up to 0.51 (Cr) (Table 2).

The controlled factors explained the residuals of Pb, Zn and Cr fairly well, R^2 values varied from 0.51 (Cr) up to 0.67 (Pb). The models of the residuals of Cu and DOC had both high R^2 value (0.83 for Cu and 0.95 for DOC) (Table 3).

The modelling against the controlled factors accounted for 43% (Pb), 28% (Zn), 25% (Cr), 51% (Cu) and 72% (DOC) of the explanation of the total variation in leaching of the investigated metals and DOC. Combining the two modelling steps 79% of Pb, 75% of Zn, 76% of Cr, 89% of Cu and 96% of DOC variations could be explained.

In both modelling steps, the data of Zn, Cr, Cu and DOC were \log_{10} -transformed, achieving a normal distribution of the data set.

If a factor occurs in an interaction, its main effect has to remain in the model regardless if the factor is significant or not. This is the reason to include the main effect of the factor atmosphere in the model of the residual Zn. The factor alone had no effect ($\alpha = 0.05$) on the residual Zn, but the factor atmosphere occurred in an interaction ($L/S \times \text{atm.}$) and thus, its main effect needs to remain in the model. Likewise, the factors Ca(ISA)₂, temperature and contact time (in the model of residual Pb), temperature and atmosphere (in the model of residual Cr), contact time (in the model of residual DOC) as well as atmosphere (in the model of pH) were included in each respective model even though they had no effect ($\alpha = 0.05$).

3.4. Factor effects

The mobilization of the metals and DOC were positively affected by the pH (*i.e.* higher pH resulted in a higher mobi-

lization of metals and DOC), according to each empirical model.

Atmosphere was the only factor that alone significantly affected the mobility of Pb, all other controlled factors affecting the mobilization occurred in interactions. The interactions of Ca(ISA)₂ × temperature and Ca(ISA)₂ × time as well as temperature × atmosphere had a negative effect on the leaching of Pb, while the interactions temperature × time and Ca(ISA)₂ × atmosphere affected the leaching of Pb positively. The leaching of Zn was affected by the negative impact of contact time, temperature and the interactions $L/S \times \text{atmosphere}$ and temperature × atmosphere. The factor L/S ratio was the only controlled factor with a positive effect on the mobilization of Zn. The factors L/S ratio and contact time showed a positive effect on the mobility of Cr. The interaction temperature × atmosphere affected the mobility of Cr negatively. In the case of Cu it were the factors Ca(ISA)₂, L/S ratio and the interaction $L/S \times \text{temperature}$ that had a positive effect on the leaching, while temperature, contact time, Ca(ISA)₂ × temperature and Ca(ISA)₂ × L/S affected the mobility negatively.

No factor or interaction was superior in the models describing the residual Pb and Zn. The L/S ratio had the largest effect on mobilization of Cr according to the model of residual Cr. Still, the effects of the controlled factors on the leaching of Pb, Zn and Cr were inferior to the effect of pH. The factor Ca(ISA)₂ had the largest effect on the leaching of Cu, and the effect of the studied factors was superior to the effect of the pH.

Ca(ISA)₂ had the largest effect on the DOC in the leachate, the pH had only a minor impact, but still significant ($\alpha = 0.05$), on the mobilization of DOC.

The factors L/S ratio and temperature had the largest effect on the pH in the leachate. The factor atmosphere did not have a significant effect on the pH.

3.5. Predicted leaching

The empirical models were used to predict the leaching of Pb, Zn, Cr, Cu and DOC at different factor settings.

The maximum predicted leaching were 1140 ± 190 mg (kg TS)⁻¹ (66 wt.%) of Pb, 990 ± 470 mg (kg TS)⁻¹ (14 wt.%) of Zn, 9.6 ± 4.8 mg (kg TS)⁻¹ (4 wt.%) of Cr, 350 ± 210 mg (kg TS)⁻¹ (70 wt.%) of Cu and 20 ± 9.0 g (kg TS)⁻¹ of DOC. All the maximum predicted values of the investigated metals and DOC occurred at 40 g Ca(ISA)₂, *L/S* ratio 50, 4 °C, 0.2 days of contact time and an atmosphere of 0 vol.% of O₂. This factor setting also predicted the highest pH value, 12.7 ± 0.1 . The lowest predicted leaching of Pb, Zn and Cr occurred at the factor settings of 40 g Ca(ISA)₂, *L/S* ratio 5, 80 °C, 0.2 days and an atmosphere of 100 vol.% of O₂. At this factor setting, the predicted pH was 12.0 ± 0.1 and 410 ± 240 mg (kg TS)⁻¹ (24 wt.%) of Pb, 36 ± 17 mg (kg TS)⁻¹ (0.5 wt.%) of Zn as well as 0.72 ± 0.33 g (kg TS)⁻¹ (0.3 wt.%) of Cr were predicted to be leached from the dry scrubber residue. The lowest predicted values of the leaching of Cu and DOC were 3.9 ± 2.1 mg (kg TS)⁻¹ (0.8 wt.%) of Cu and 1.4 ± 0.60 g (kg TS)⁻¹ of DOC, these occurred at 2 g Ca(ISA)₂, *L/S* ratio 5, 80 °C, 0.2 days and an atmosphere of 100 vol.% of O₂. At this factor setting, the pH was predicted to its lowest value, 11.9 ± 0.1 .

Predicted concentrations of the leaching of the investigated metals at conditions that can be related to a compacted and covered landfill in northern Sweden (4 °C, 7 days, 0 vol.% O₂) varied from 560 ± 140 mg (kg TS)⁻¹ up to 940 ± 190 mg (kg TS)⁻¹ (Pb), 60 ± 20 mg (kg TS)⁻¹ to 620 ± 290 mg (kg TS)⁻¹ (Zn), 1.1 ± 0.41 mg (kg TS)⁻¹ to 10 ± 4.5 mg (kg TS)⁻¹ (Cr) and 9.2 ± 4.1 mg (kg TS)⁻¹ to 230 ± 160 mg (kg TS)⁻¹ (Cu), depending on the amount Ca(ISA)₂ and *L/S* ratio. The pH was predicted to vary between 12.1 ± 0.1 and 12.7 ± 0.1 , while the predicted DOC varied from 2.6 ± 0.81 g (kg TS)⁻¹ to 18 ± 6.0 g (kg TS)⁻¹.

4. Discussion

The leaching of Pb, Zn and Cr was significantly higher at higher pH values in the leachates from the experimental runs. This led to the procedure to first develop empirical models of the leaching of the metals and DOC against the uncontrolled factor pH and to second use the residuals in another modelling step against the controlled factors. The residuals from an empirical model are the un-modelled part, the mismatch between the observed and modelled values. Using the residuals from the models of metal mobility and DOC against pH, *i.e.* the variations that could not be explained by the pH alone, in a second modelling step gave the opportunity to distinguish the effect on metal and DOC mobilization caused by the pH and the effect caused by the factors.

About 50% of the mobility of Zn and Cr could be explained by the pH alone. For Pb and Cu, the degree of explanation was lower, but still almost 40% of the variations in mobility were explained by the pH alone. For the leaching of DOC, the pH explained about 25%. All the investigated metals as well as the DOC were positively affected by the pH, meaning that a higher pH value

would lead to a higher mobilization of the metals and DOC. The controlled factors explained only about 25% of the leaching of Zn and Cr which is less than the explanation of the pH. The pH and the controlled factors explained the leaching of Pb almost to the same extent, while the major part of the leaching of Cu and DOC were explained by the significant ($\alpha = 0.05$) controlled factors. The pH is thus more important for the leaching of Zn and Cr than it is for the leaching of Cu. Although the leaching of Zn and Cr was mostly affected by the pH, the controlled factors contact time, *L/S* ratio, temperature and atmosphere had a significant ($\alpha = 0.05$) effect on the mobility of them.

The factor atmosphere is included in the model of Pb as a main effect and in the models of Zn and Cr as an interaction with temperature. The impact of atmosphere was negative, meaning that reducing conditions may favour the leaching of these metals. Sulfur compound can form sulfides under anaerobic conditions. Metals may be bound as metal sulfides and thus be demobilized [22,23]. The results presented in this study seem to contradict that statement since anaerobic conditions favoured the leaching of Pb, Zn and Cr. However, mechanisms controlling element mobility are not investigated. It is, *e.g.* unknown if the sulfur content of the ash was sufficient to enable a sufficient sulfide formation or if maybe other remineralization processes mobilizing critical elements were dominating. In addition, the kinetics of the chemically and/or microbiologically catalyzed reactions are unknown for the investigated environment. Nevertheless, in a long-term perspective, the formation and degradation of metal sulfides can have an important role in the mobilization and demobilization of metals from landfills [23–25]. Leached Cr from air pollution control (APC) residues at reducing and alkaline conditions is mainly trivalent [26,27]. These conditions also favoured the leaching of Cr in this presented study, which might also reduce the toxicity of the leachate since Cr(III) is less toxic than Cr(VI).

The leaching of Cu and DOC followed the same pattern with respect to significant factors and their effect in the models of Cu and DOC. Ca(ISA)₂ was the factor with the highest effect on the mobilization of both Cu and DOC. This is explained by the ability of Cu to form complexes with organic substances [*e.g.* 14–16]. In accordance with van der Sloot et al. [16], the importance of DOC-Cu complexes on the leaching of Cu was higher at *L/S* ratio 5 than at *L/S* ratio 50. The interaction between Ca(ISA)₂ and *L/S* ratio had a negative effect on the leaching of Cu. The DOC-Cu fraction is about two orders of magnitude higher than the free Cu concentration at pH values above 12 [16], which imply that all of the Cu in the leachate existed as complexes with ISA.

The leaching of both Pb and Zn were higher ($\alpha = 0.01$) at pH values above 12.5 compared to pH values between 11.9 and 12.5. Pb and Zn are known to form soluble hydroxides in alkaline solutions and thus have a high mobility at high pH values [16]. In a study of Christensen & Christensen [28], the pH dependence of complexation between DOC and Cd, Ni and Zn up to a pH value of 8 was investigated. The complexation between DOC and the metals was found to increase with increasing pH. The addition of Ca(ISA)₂ had a positive effect on the pH in the leachate and a higher pH value led to a higher mobilization of Pb, Zn and Cr.

The need of investigations on the impact of complex formation, caused by organic compounds, on metals with high leachability at alkaline conditions, *i.e.* above 12, is pointed out as future research areas in order to achieve more knowledge about their leaching properties. For such an investigation, pH_{stat} leaching [29] may be useful.

A longer contact time and higher leaching temperature resulted in a lower mobilization of Zn and Cu. These negative impacts can be explained as a formation of stable secondary phases trapping metals. Water causes the hydration of the dry scrubber residue as well as the possible formation of calcium aluminosilicate hydrates [3]. This phase has the potential to retain metals both by bonding and adsorption [3,30].

The concentration of DOC in the leachate depended mostly on the addition of $\text{Ca}(\text{ISA})_2$, considered reasonable since the addition of an organic salt should increase the concentration of DOC in the leachate. The solubility of the salt $\text{Ca}(\text{ISA})_2$ is 1.19 g in 100 g hot water [17]. Between 4 and 800 mg of the salt and 2 and 20 g of the dry scrubber residue were added to 100 ml of water (room temperature) and all of the salt should have entered into solution. According to Ferrari et al. [31], the dominant carbon species in fly ash is elementary carbon, while the majority of organic carbon is not extractable with water. Also, the TOC in the dry scrubber residue was ~ 40 times lower compared to that in $\text{Ca}(\text{ISA})_2$ (8.7 ± 1.0 compared to $334 \pm 4 \text{ g}(\text{kg TS})^{-1}$). The leaching of DOC from the dry scrubber residue itself is therefore negligible compared to the addition from $\text{Ca}(\text{ISA})_2$.

The maximum and minimum values of the predicted leaching of Pb, Zn and Cr occurred at the same factor settings. The maximum predicted leached Pb, Zn and Cr coincided with the maximum predicted pH value, which stressed out the importance of pH on the leachability of these metals. When the predicted pH was at its lower values, ~ 12.0 , the leaching of Pb, Zn and Cr caused by the factors become more important for the total leached amount of the metals. The predicted leaching of Cr and Zn was overall minor, up to a maximum of 4 wt.% of Cr and 14 wt.% of Zn in the dry scrubber residue was predicted to be leached. The leaching of Pb was predicted to be fairly high, varying between 24 wt.% to 66 wt.% of the total amount of Pb in the dry scrubber residue. The predicted leaching of Cu was mainly determined by the addition of $\text{Ca}(\text{ISA})_2$ and pH affected the leaching of Cu only to a minor extent. For Cu, the predicted leaching varied from 0.8 wt.% up to almost 70 wt.% of the total amount of Cu in the dry scrubber residue.

Evidence of the ability of ISA to form complexes is given elsewhere [11–13] as well as the potential of complex formation between DOC and metals [e.g. 14,15,32–34]. According to the empirical models in this study, the higher the concentration of $\text{Ca}(\text{ISA})_2$ the more pronounced the leaching of Cu. Maximum leaching of Pb, Zn and Cr also occurred with the largest addition of $\text{Ca}(\text{ISA})_2$, this as a secondary effect caused by the increase in pH.

The complexation between metals and ISA as well as metals and DOC could also be affected by competition between the different metals and other elements present in the leachate. Ca^{2+} is one possible competitor for the critical metals at alkaline con-

ditions [11,12,35]. Ca is an abundant [36] and soluble element [3] in the dry scrubber residue from Ålidshemverket.

4.1. Risks and opportunities in co-disposal of cellulose based wastes and MSWI dry scrubber residue

Pavasars [7] found that 15–25 wt.% of the cellulose is degraded under alkaline conditions (pH 13.4) during the first 3 years of treatment at room temperature and an *L/S* ratio of 200. ISA constitutes 85 wt.% of the products. Alkaline degradation of 1 kg of cellulose results in ~ 200 g ISA. An addition of 40 g of $\text{Ca}(\text{ISA})_2$ ($\text{kg TS})^{-1}$ (high level) is represented by a co-disposal of cellulose-based waste and MSWI dry scrubber residue in a relationship of 1:5, whereas 2 g $\text{Ca}(\text{ISA})_2$ ($\text{kg TS})^{-1}$ (low level) is represented by a relationship of 1:100.

A biological degradation of the cellulose and ISA is also possible. The dry scrubber residue can then undergo carbonation when CO_2 is formed. Carbonation affects the metal mobility, where metals are initially demobilized by the formation of metal carbonates [3]. If CO_2 is excessively added, a degradation of the metal carbonates is possible, thereby leading to an increase in metal mobility [3]. However, at high pH, microbiological activity can be inhibited and the effect due to carbonation is negligible.

As landfills evolve, different biological and chemical environments are established [23–25]. During the anaerobic phase, sulfur compounds can form sulfides and bind metals as metal sulfides, causing metal demobilization. When oxygen intrudes in the deposits, the metal sulfides may oxidize. Metal sulfide oxidation bears the risk of metal mobilization and metal leaching [22,23].

At conditions similar to a compacted and covered landfill in northern Sweden with waste containing cellulose and MSWI dry scrubber residue (4°C , 7 days, 0 vol.% O_2), 32–54 wt.% of the total amount of Pb and 2–46 wt.% of the total amount of Cu as well as $2.6\text{--}18 \text{ g}(\text{kg TS})^{-1}$ of DOC are mobilized depending on the pH as well as the availability of ISA and the *L/S* ratio. Zn and Cr risk to be leached to a minor extent (0.8–8.0 wt.% of Zn and 0.5–4.0 wt.% of Cr) but since the amount of Zn in the MSWI dry scrubber residue is high ($7.29 \pm 0.07 \text{ mg}(\text{kg TS})^{-1}$) the total amount of leached Zn may be high. About 75×10^3 t of air pollution control residue is generated annually in Sweden [1]. If this amount is co-disposed with cellulose-based waste, an additionally of 17 t Cu, 29 t Pb, 39 t Zn and 0.6 t Cr can be leached annually. This assumes that the relationship between the cellulose-based waste and the dry scrubber residue increases 20 times from 1:100 to 1:5, an increasing *L/S* ratio from 5 to 50 as well as an increase in pH from 12.1 to 12.7. The change in pH is depending on the changes in the relationship between the cellulose-based waste and the MSWI dry scrubber residue as well as changes in the *L/S* ratio.

The models above, however, do not cover long-term landfill processes such as e.g. biologically induced carbonation. To improve the assessment of metal mobility with respect to the co-disposal of cellulose-based waste and MSWI dry scrubber residue, the consideration of metal demobilizing and metal mobilizing processes is suggested:

4.1.1. Metal demobilization

Biological degradation of the cellulose and ISA causes the formation of CO₂, leading to the demobilization of the metals [3]. The metal mobility can also decrease due to potential bonding and adsorption on calcium aluminosilicate hydrates [3,30] as well as the formation of metal sulfides [23–25].

4.1.2. Metal mobilization

The alkaline leachate from the MSWI dry scrubber residue can cause an alkaline degradation of the cellulose and thus the formation of ISA, which may in turn form complexes with metals from the dry scrubber residue and increase the metal mobility. Further, biological degradation of cellulose and ISA could lead to such a large addition of CO₂ that metal carbonates degrade and metals are therefore mobilized [3]. In a long-term perspective, metal sulfides may be oxidized and result in a release of metals [22,23].

The second scenario can be regarded as a risk in an existing co-disposal site. However, the knowledge can also be exploited to develop a pre-treatment technique for dry scrubber residue, e.g. with a combination of alkaline degradation of cellulose followed by a biological degradation. Prior to disposal, metals are separated from the ash matrix due to the complexation to ISA. In a subsequent step, carbon dioxide from biological degradation is used to stabilize the remaining content of metals in the ash matrix through carbonation.

5. Conclusions

Co-disposal of municipal solid waste incineration (MSWI) dry scrubber residue with cellulose-laden waste should be prevented due to the risk of an increased leaching of critical metals, in particular Cu, Pb and Zn. The leaching of contaminants in MSWI dry scrubber residue can be promoted by isosaccharinic acid (ISA), *i.e.* a product from the alkaline degradation of cellulose.

In laboratory experiments, calcium isosaccharinate (Ca(ISA)₂) had a positive effect on the leaching of Cu from MSWI dry scrubber residue ($\alpha=0.05$). Ca(ISA)₂ only had a minor effect on the leaching of Pb and it did not affect the leaching of Zn and Cr at all ($\alpha=0.05$). However, Ca(ISA)₂ affected the pH value in the leachate positively and the leaching of Pb, Zn and Cr were increased with increasing pH.

Cd was eliminated from the evaluation since all the values of the concentration were reported under the detection limit.

Complexation with ISA caused the increased leaching of Cu, while the alkaline pH caused the increased leaching of Pb and Zn due to the formation of soluble hydroxides at high pH values.

In a landfill where cellulose-based waste and MSWI dry scrubber residue are co-disposed, the alkaline degradation of cellulose may mobilize metals from the dry scrubber residue. For a compacted and covered landfill in northern Sweden, the leaching of Pb was estimated to increase from 32 to 54 wt.%, 0.8 to 8.0 wt.% for Zn, 0.5 to 4.0 wt.% for Cr and 2.0 to 46 wt.% for Cu when the relationship between cellulose-based waste and dry scrubber residue increased from 1:100 to 1:5 as well as an increased *L/S* ratio from 5 to 50. These changes also initiated

an increased pH in the leachate from 12.1 to 12.7. This corresponds to an additional 29 t of Pb, 39 t of Zn and 17 t Cu leached annually in Sweden.

The ability of ISA to form complexes can be used to develop techniques to separate metals from MSWI dry scrubber residue, either as a pre-treatment or *in situ*.

Further detailed studies on the mechanisms of complexation between DOC and metals from MSWI APC residues, at controlled and alkaline pH values are recommended. The laboratory results call for field investigations of the presence and impact of ISA in landfill leachates. This requires first developing reliable methods to analyze ISA in complex matrixes such as landfill leachates.

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