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Removal of hazardous trace elements from recovery boiler fly ash with an ash dissolution method

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Abstract

The presence of hazardous trace elements (HTE) in the chemical recovery cycle of Kraft pulp mills is the main obstacle for the utilization of the inorganic residues of the process. Electrostatically precipitated (ESP) recovery boiler fly ash (RBFA), consisting mainly of sodium sulfate Na_2SO_4 , is a solid side stream where HTE are concentrated. Unlike most other ashes, RBFA is to a great extent water-soluble. A novel reverse leaching method, based on the dissolution behavior of RBFA in water, is introduced in this paper. The method is founded on the use of an appropriate liquid/solid mass ratio and a favorable pH, which together contribute to the formation of a small and readily settling solid residue where almost all HTE are concentrated. This paper focuses on evaluating the influence of the treatment conditions on HTE removal, energy consumption and material losses. The results of this study show that the removal efficiency of the investigated HTE and other analyzed metals was excellent under alkaline conditions, the apparently suitable pH range for the removal of most of these metals being approximately 11.7-12.2. Lead was observed to be the most difficult HTE to remove: the highest obtained degree of removal of Pb was 89 %. The removal rate of Cd and Zn was approx. 100 % within the mentioned pH range.

Keywords: Hazardous trace elements; Heavy metals; Recovery boiler; Fly ash; Dissolution; Sodium sulfate; Energy consumption

1. Introduction

1.1. Background

Kraft pulp mills generate significant amounts of side streams which can be classified as waste or utilizable raw materials. In addition to the large discharge streams of the mills containing mainly organics, such as fiber and other polymeric substances, some inorganic streams are also produced in quantities large enough for extensive utilization. One of the large inorganic streams generated in the process is recovery boiler fly ash (RBFA), the amount of which corresponds to 3.5-10 % of the solids content of black liquor (Hart et al., 2010). RBFA is composed mainly of Na_2SO_4 (approx. 80-85 wt.%), Na_2CO_3 (8-15 wt.%), and other compounds, such as NaCl and potassium salts (Mikkanen, 2000; Leppänen et al., 2014). In some cases, the carbonate content may be much lower and the chloride content correspondingly higher, depending for instance on the wood species and the Cl content of the make-up chemicals (Jordan and Bryant, 1995; Chiarakorn et al., 2011; Rapp and Pfromm, 1998). RBFA is collected from the flue gas stream of the recovery boiler with electrostatic precipitators (ESP), after which it can be mixed again with black liquor at the evaporation plant to keep the valuable process chemicals Na and S in the recovery cycle. Part of

the precipitated RBFA is typically discharged from the recovery cycle one way or another, due to the need to adjust the sulfidity level of the pulping process to the desired level, to improve the operation of the evaporation plant, and to get rid of harmful non-process elements, especially Cl and K (Grace, 2007; Hart et al., 2010; Bajpai, 2017). When the purging of RBFA is increased, sulfidity is consequently reduced (Andersson, 2014; Hupa, 1993).

Hazardous trace elements (HTE) tend to concentrate in the recovery boiler when the organic content of black liquor is burned off. As a result, hazardous trace elements as well as other non-process elements are present at high concentrations in the material streams leaving the recovery boiler. In the mill scale, the most significant stream regarding the removal of non-process elements from the chemical recovery cycle is green liquor dregs. Dregs represent an abundantly available inorganic waste fraction that is typically disposed of in the landfill sites of mills. The reason for landfill disposal is that the high concentration of hazardous trace elements in the dregs complicates their use for any beneficial purpose, such as production of bulk materials for soil amendment or the use of dregs as a component in fertilizers (Kinnarinen et al., 2016).

RBFA differs from most other types of ashes and green liquor dregs by its behavior in aqueous environments: RBFA has high solubility in water, the maximum solubility of pure Na_2SO_4 being 497 g dm^{-3} or 33.2 wt.% at 32.4°C (Rodriguez-Navarro et al., 2000; Vener and Thompson, 1950). The most typically occurring crystalline phases of sodium sulfate are called mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) and thenardite (Na_2SO_4) (Genkinger and Putnis, 2007). The high solubility of RBFA in water and the favorable pH range of the aqueous suspensions of RBFA make it interesting from the point of view of the removal of hazardous trace elements from the chemical recovery cycle, because most hazardous trace elements are rather insoluble in alkaline RBFA solutions. Contrary to RBFA, most of the suspended solids present in green liquor dregs, consisting mainly of CaCO_3 , are practically insoluble unless the pH is adjusted to a highly acidic range. Therefore, the hazardous trace elements in dregs are very difficult to remove. Due to the difficulties associated with the treatment of dregs, it may be of great advantage to remove the unwanted trace elements from RBFA, and to reduce the concentrations of those elements in the dregs and in the recovery boiler as a desired consequence.

1.2. Focus of the study

This study was carried out in order to investigate a straightforward process for the removal of hazardous trace elements from electrostatically precipitated (ESP) recovery boiler fly ash (RBFA). The idea was to evaluate the effect of process conditions on the removal of HTE. A simplified flow diagram of the major material streams around the recovery boiler, including the HTE separation process, is presented in Fig. 1.

Previous studies with RBFA have focused on removing the problematic non-process elements Cl and K (Jordan and Bryant, 1995; Minday et al., 1997; Hiner et al., 2000), while the removal of HTE from RBFA has been practically omitted. The most typically applied techniques for a more or less selective removal of Cl and K include leaching, crystallization by cooling or evaporation, and ion exchange (GonCalves et al., 2008; Liedberg, 2015; Tran and Arakawa, 2001; Öhman and Delin, 2014). The commercialized methods have been described in the literature by Lundström (2007) and Johansson (2005). The present study focuses on the removal of HTE, omitting the

recovery of cooking chemicals from the solution. The target metals in the study are cadmium, lead and zinc, out of which zinc can be regarded as a nutrient rather than HTE. However, zinc is considered harmful when present in high concentrations in solids. The limit for fertilizer products in Finland is 1500 mg/kg, and thus it was clear that the removal of zinc should be included in the study.

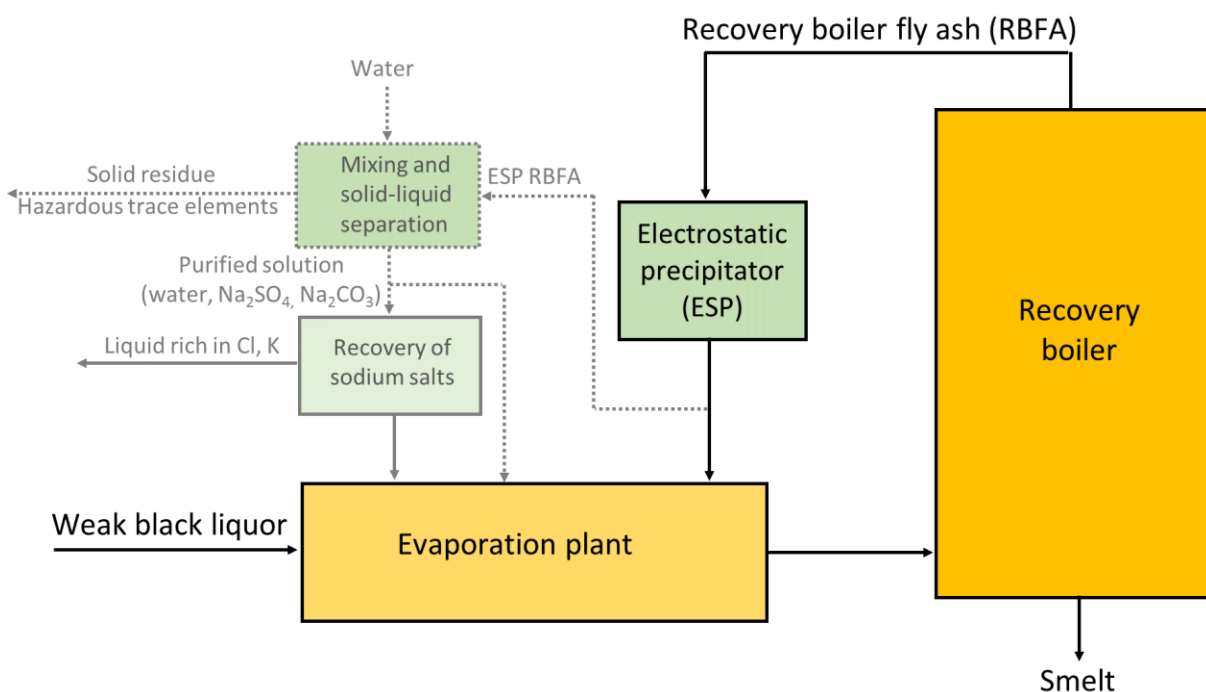


Fig. 1. A simplified sketch illustrating the ash dissolution method for the removal of hazardous trace elements from electrostatically precipitated recovery boiler fly ash (i.e. ESP RBFA) at Kraft pulp mills. The dashed part represents the scope of the present study.

The process for HTE removal, indicated by the dashed grey line on the left in Fig. 1, is based on the fact that a small fraction of RBFA containing most of HTE (e.g. Cd, Pb, Zn) stays in the solid state when RBFA is dissolved in water. To the best knowledge of the authors, the possibilities to concentrate (hazardous) trace elements in this small fraction have not been evaluated in the existing scientific literature.

A definite prerequisite for the purification process is that the mass ratio between RBFA and water is within a certain range, because forming a too dilute mixture results in increasing the dissolution of the target metals, ruining the whole idea of easy purification, while forming an excessively concentrated mixture beyond the maximum solubility limit results in unnecessary loss of process chemicals, as the cake fraction becomes unnecessarily large. In this light, this process differs significantly from existing ash leaching, such as Valmet AshLeach (Liedberg, 2015), but is more reminiscent of resin-based purification systems, e.g. Recoflo, introduced by Brown et al. (1998, 1999). The main objective of this experimental laboratory-scale study is to prove the validity of

the process concept for HTE removal by using real industrial samples, omitting the removal of Cl and K from the cycle. The influences of important process variables on the purification result and the economy of the treatment are evaluated.

2. Materials and methods

2.1. RBFA sample

The sample of recovery boiler fly ash (RBFA) was provided for the research by a Finnish Kraft pulp mill. Prior to the experiments, the sample was characterized for its elemental composition (Table 1) with scanning electron microscopy (SEM) and particle size distribution by laser diffraction (Fig. 2).

Table 1. Elemental composition of RBFA.

Trial #	<i>Element concentration</i>						<i>Total</i> (wt.%)
	<i>C</i> (wt.%)	<i>O</i> (wt.%)	<i>Na</i> (wt.%)	<i>S</i> (wt.%)	<i>Cl</i> (wt.%)	<i>K</i> (wt.%)	
1	4.2	39.7	30.3	20.9	0.7	4.3	100.0
2	3.8	40.0	30.8	20.5	0.7	4.2	100.0
3	3.9	39.9	30.6	20.7	0.7	4.2	100.0
Average	4.0	39.9	30.6	20.7	0.7	4.2	100.0

Scanning electron microscope (SEM) images were taken, and energy-dispersive X-ray spectroscopy (EDS) analyses on the elemental composition of RBFA were performed with a Hitachi SU 3500 scanning electron microscope. Knowing the typical composition of RBFA (Mikkanen, 2000), it is apparent in Table 1 that Na₂SO₄ was the main component in the sample, and other important components were most probably Na₂CO₃ and various potassium salts, most of which were in other forms than KCl. The chloride content of the sample was in the lower end of the typical range of 1-10 wt.% reported by Rapp and Pfromm (1998). An example of the distribution of the main elements in RBFA, as well as SEM images of the particle agglomerates are presented in Supplementary file 1. The presence of agglomerates in RBFA has been discussed e.g. by Samuelsson et al. (2014), Mikkanen (2000) and Lind et al. (2006).

The particle size distribution of the material was measured with Malvern Mastersizer 3000 by using ethanol as the dispersing liquid. As the differential volumetric particle size distribution presented in Fig. 2 shows, the particle size ranged from < 1 µm to tens of microns. The most important statistical particle sizes characterizing the volumetric undersize distribution were: $D_{10} = 4.2$ µm, $D_{50} = 11.3$ µm, and $D_{90} = 21.4$ µm.

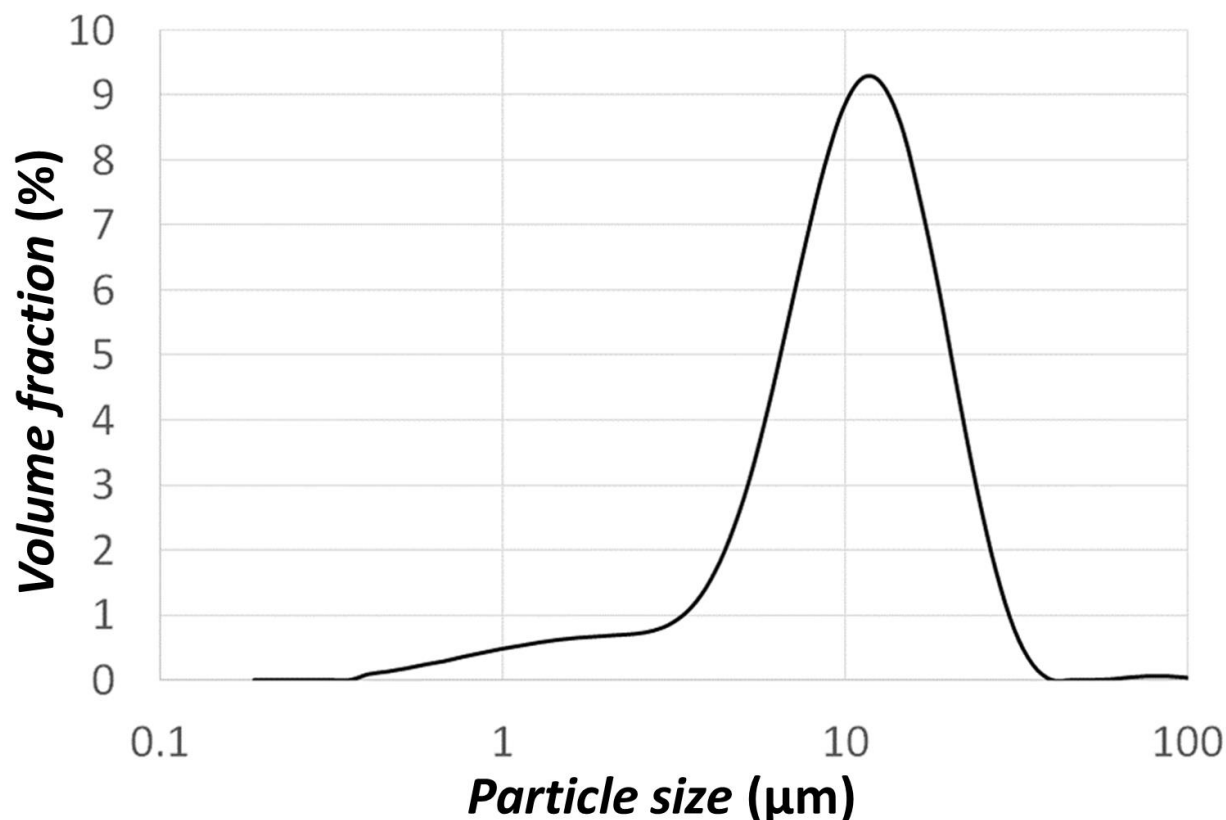


Fig. 2. Particle size distribution of electrostatically precipitated recovery boiler fly ash.

The elemental composition was measured also with an Agilent 7900 inductively coupled plasma mass spectrometer (ICP-MS) to obtain accurate values for the mass balances of the elements of interest. Acid digestion of the samples for ICP-MS analyses was performed for dry samples of 0.1-0.2 g and wet samples of 1-2 g with a Milestone Ultrawave microwave digestion system, using a mixture of HNO_3 and HCl (ICP-MS quality) with volumetric ratio 4:1. The digestion temperature and the duration of digestion were 250 °C and 20 min. The analyses for preliminary experiments (Section 2.2.2) were performed in an accredited laboratory by Ahma Group (Oulu, Finland) by using ICP-OES.

In this study, the mass balance of three hazardous trace elements, namely cadmium, lead and zinc was used as a measure of the separation efficiency. According to ICP-OES analysis, the concentrations of these elements in air-dry RBFA were 2.06 mg kg^{-1} (Cd), 1.25 mg kg^{-1} (Pb), and 49.2 mg kg^{-1} (Zn).

2.2. Separation experiments

The separation experiments discussed in this paper can be divided into two groups: 1) preliminary dissolution experiments, and 2) dissolution experiments aiming at more detailed investigation of the variables.

2.2.1. Preliminary dissolution experiments

The focus of the preliminary experiments was on finding favorable ranges for the RBFA concentration and the pH of the dissolution-based purification process. The experiments were performed in the following sequence:

- 1) Mixing of RBFA with pure water, dissolving part of RBFA solids;
- 2) Stabilization of the suspension at room temperature for 5 days, letting the non-dissolved suspended solids settle by gravity;
- 3) Centrifugation of the suspension to ensure a solids-free supernatant;
- 4) Measurement of the pH of the supernatant;
- 5) Decantation of the supernatant, leaving a wet cake at the bottom of the vessel;
- 6) Weighing of the wet solid cake;
- 7) Taking samples from both the cake and the liquid for analysis;
- 8) Performing ICP-MS analysis (with acid digestion for the cakes);
- 9) Calculation of removal R on the basis of elemental mass balance for the investigated metals ($R = m_{\text{metal in cake}}/m_{\text{metal in RBFA}}$).

The experimental conditions are presented in Table 2. Tests 1-7 listed in Table 2 were performed at room temperature (22 °C) by using different RBFA concentrations, ranging from 2.5 to 67 wt.%. The total mass of the mixture in these experiments was 200 g. Adjustment of pH with lime addition (1-10 wt.% of RBFA, 0.25-2.5 wt.% of slurry) was tested for mixtures similar to Test 4 (25 wt.% RBFA). The aim of increasing the pH was to keep the HTE in the solid phase, or to precipitate the already dissolved HTE as sparingly soluble (Scholz and Kahlert, 2015; EPA 625/8-80-003) metal hydroxides. The sample stabilization time was decided to be 5 days, in order to ensure relatively stable conditions at the moment of sampling. All pH measurements were carried out by using a WTW pH 340i pH meter and a SenTix® 41 electrode. The lime powder, manufactured by J.T. Baker Chemicals, was of analytical grade.

Table 2. Experimental plan for the preliminary study and the measured pH of the suspensions.

<i>Test</i>	<i>m, RBFA</i> (g)	<i>m, H₂O</i> (g)	<i>m, tot</i> (g)	<i>c, RBFA</i> (wt.%)	<i>m, lime</i> (g)	<i>c, lime</i> (wt.% of RBFA)	<i>c, lime</i> (wt.% of slurry)	<i>pH</i> (-)
1	133.33	66.67	200	66.7	0	0	0	12.17
2	100	100	200	50	0	0	0	11.96
3	75	125	200	37.5	0	0	0	11.77
4	50	150	200	25	0	0	0	11.45
5	25	175	200	12.5	0	0	0	11.33
6	10	190	200	5	0	0	0	11.14
7	5	195	200	2.5	0	0	0	10.96
8	50	150	200	25	0.5	1	0.25	12.44
9	50	150	200	25	1	2	0.5	12.79
10	50	150	200	25	2.5	5	1.25	13.06
11	50	150	200	25	5	10	2.5	13.20

As can be seen in Table 2, the pH of the formed RBFA/water suspension depended unsurprisingly on the concentration of RBFA and added lime. When lime was not added, the pH increased from approx. 11 to over 12 as the RBFA concentration was increased from 2.5 to 67 wt.%. The lime addition increased the pH sharply even at low dosages, and therefore the highest pH at the highest lime dosage was as high as 13.2.

2.2.2. Dissolution experiments at different combinations of variables

After the preliminary dissolution tests, a more detailed investigation of the effect of variables on HTE removal was carried out by using the results of the preliminary study for the experimental design and the same test procedure. The mass of each suspension was a constant 40 g. The experimental plan (Table 3), made in accordance with statistical factorial design, shows the used variations in the RBFA concentration, temperature and pH. The lime dosages were varied between 0.3 and 1.4 wt.% of the mass of RBFA. As stated above, the obtained pH depended on the combination of RBFA and lime concentrations. In other words, the same amount of lime added to suspensions of the same mass having different solid concentrations resulted in different pH during the 5 days of pH stabilization and settling of the samples. It is also important to note that although the liquid phase was 100 % saturated with Na₂SO₄, it was still possible to increase the pH by adding more RBFA to the suspension, which was seemingly due to the presence of other alkaline compounds in the used RBFA.

Table 3. Experimental plan for closer investigation of process variables.

<i>Test</i>	<i>m, RBFA</i> (g)	<i>m, H₂O</i> (g)	<i>m, tot</i> (g)	<i>c, RBFA</i> (wt.%)	<i>c, lime</i> (wt.% of RBFA)	<i>T</i> (°C)	<i>pH</i> (-)
1	10	30	40	25	0	22	11.63
2	12	28	40	30	0	22	11.65
3	14	26	40	35	0	22	11.69
4	10	30	40	25	0.03	22	11.67
5	10	30	40	25	0.27	22	11.75
6	10	30	40	25	0.73	22	12.16
7	10	30	40	25	1.42	22	12.88
8	12	28	40	30	0.04	22	11.73
9	12	28	40	30	0.27	22	12.28
10	12	28	40	30	0.74	22	12.56
11	12	28	40	30	1.43	22	12.77
12	14	26	40	35	0.02	22	11.7
13	14	26	40	35	0.26	22	12.32
14	14	26	40	35	0.73	22	12.57
15	14	26	40	35	1.42	22	12.64
16 ^{K,M}	14	26	40	35	0	32	11.55
17 ^M	16	24	40	40	0	32	11.65
18 ^M	18	22	40	45	0	32	11.69
19	14	26	40	35	0.26	32	11.65

20	14	26	40	35	0.73	32	12.37
21 ^M	14	26	40	35	1.42	32	12.99
22	16	24	40	40	0.26	32	12.23
23	16	24	40	40	0.73	32	12.74
24 ^M	16	24	40	40	1.42	32	13.1
25	18	22	40	45	0.26	32	12.58
26	18	22	40	45	0.73	32	12.92
27 ^{K,M}	18	22	40	45	1.42	32	13.12
1R1	10	30	40	25	0	22	11.67
1R2	10	30	40	25	0	22	11.67
2R1	12	28	40	30	0	22	11.64
2R2	12	28	40	30	0	22	11.63
5R1	10	30	40	25	0.27	22	11.74
16R1	14	26	40	35	0	32	11.57
16R2	14	26	40	35	0	32	11.56
17R1	16	24	40	40	0	32	11.65
20R1	14	26	40	35	0.73	32	12.74
20R2	14	26	40	35	0.73	32	12.79

^K Kinetics investigation
^M Mass balance investigation

The superscripts *K* and *M* in Table 3 indicate experiments used for rough investigation of reaction kinetics (*K*) and mass balance (*M*). The experiments for kinetics were performed by using sample stabilization time of 20 min, which was the duration of cake separation by the centrifuge, and longer stabilization times of one and five days. The difference between the mass balance experiments and corresponding experiments without mass balance was that the cake fraction was dried to determine its moisture content, which enabled reasonable mass balance estimations based on the assumption that the liquid phase was a saturated Na₂SO₄ solution.

It was difficult to obtain a pH level around 12 for most suspensions. This was due to the steep increase in pH at that range, resulting from only a small increase in the applied lime dosage.

3. Results and discussion

The results are discussed by considering the selection of process conditions for the removal of HTE, as well as the mass and energy balances of the treatment. The reported degrees of removal can be over 100 % in some cases, due to the overall uncertainty resulting from sampling, experimental work, and the ICP-MS analysis (see Table 6).

3.1. Preliminary dissolution study

The effectiveness of the removal of HTE was evaluated by calculating what percentage of the total Cd and Zn content in the used RBFA was removed in the form of cake fraction when most of the

RBFA sample was dissolved in water. When the pH was not adjusted with lime, the removal of HTE with the cake and the recovery of sodium in the liquid phase depended on the applied ash content. It can be seen in Fig. 3a and b that the optimal RBFA content was approximately 30 wt.%. Ash contents below 20 wt.% caused dissolution of Cd and Zn as well (Fig. 3a and b), which should be avoided, and ash contents above 40 wt.% caused significant losses of sodium due to exceeding the solubility of RBFA.

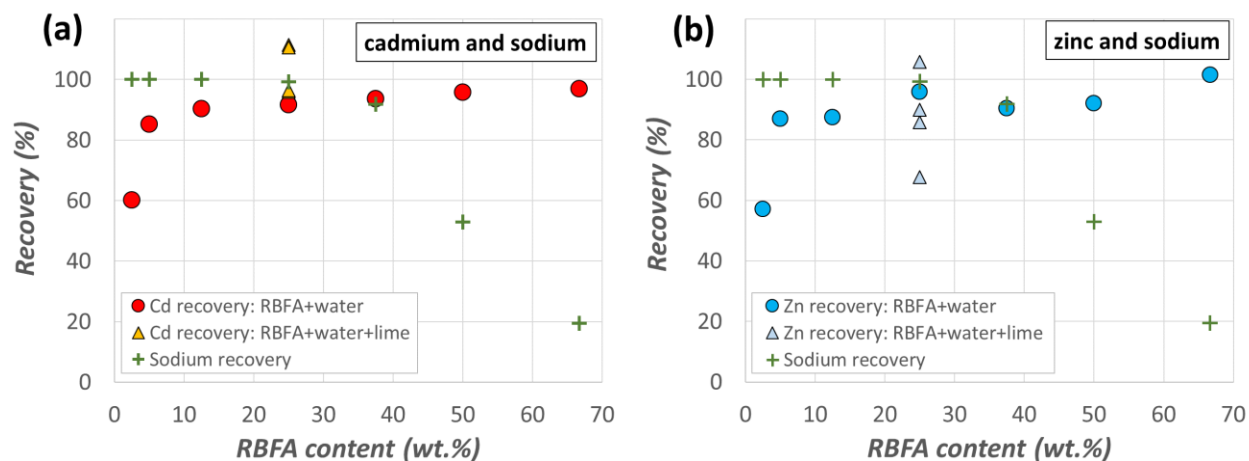


Fig. 3. Removal of Cd (a) and Zn (b) with the solid residue after dissolution of recovery boiler ESP ash in water by using different ash contents (wt.% of the formed suspension), and the corresponding recovery of sodium (a,b) with the supernatant separated from the solid residue by centrifugation.

There is an interesting point to be noted in Fig. 3b: the addition of lime to improve the precipitation of metals as hydroxides may either increase or decrease the removal of Zn. This is illustrated more clearly in Fig. 4a and b, where the removal of Cd and Zn are plotted as a function of the pH of the liquid phase. According to Fig. 4a, Cd stays in the solid form even at pH > 13, while Zn starts to dissolve again as the pH is increased to > 12.5, as visualized in Fig. 4b. The removal rate of Zn plunges from about 100 % to 68 % when the pH is increased from 12.4 to 13.2.

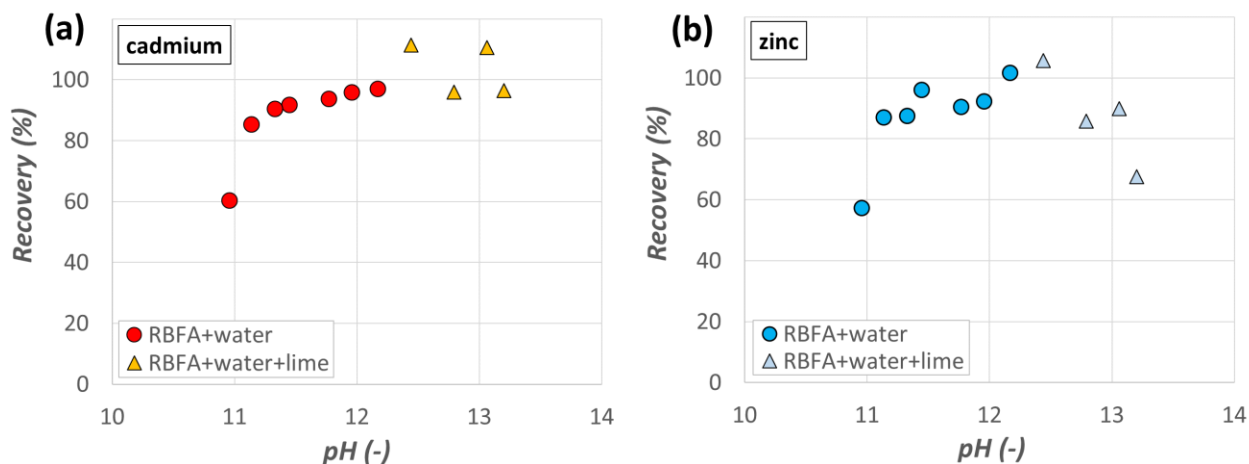


Fig. 4. Preliminary study: Dependence of removal of Cd (a) and Zn (b) on the pH of the ESP ash / water suspension.

The results presented in Figs. 3 and 4 are supported by Table 4, where the concentrations of different elements in the supernatant (liquid phase) after the separation of the cake fraction are shown. Excellent removal of Cd in most conditions is seen as its low concentration in the liquid, and the pH dependence of Zn is apparent as well. The concentrations of the readily soluble Na and K in the liquid phase indicate that the RBFA solution was saturated when the concentration of RBFA was higher than or equal to 37.5 wt.%. The results of Tests 8-11 performed with lime addition show that Mg was precipitated from the liquid to the cake fraction when pH was increased. The corresponding concentrations of Ca did not depend clearly on the amount of added Ca(OH)_2 within pH range 12.4-13.2.

Table 4. Concentration of different elements in the liquid phase after dissolution of ash in water at 22 °C.

<i>Test</i>	1	2	3	4	5	6	7	8*	9*	10*	11*
<i>c, RBFA</i> (wt.%)	66.6	50	37.5	25	12.5	5	2.5	25	25	25	25
<i>pH (-)</i>	12.17	11.96	11.77	11.45	11.33	11.14	10.96	12.44	12.79	13.06	13.2
Target metals											
<i>Element</i>	<i>Concentration in liquid (mg kg⁻¹)</i>										
Cd	0.067	0.026	0.023	0.023	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Pb	<0.15	<0.15	<0.15	<0.15	<0.15	<0.15	<0.15	<0.15	<0.15	<0.15	<0.15
Zn	2.3	0.48	0.54	0.61	0.48	0.48	0.2	0.43	1.5	2.4	3.5
Other elements											
Al	0.43	<0.30	<0.30	<0.30	0.47	<0.30	<0.30	0.68	0.54	0.47	0.51
B	17	4.2	2.6	1.9	1	0.6	0.38	1.9	2.2	2.2	2
Ba	<0.05	<0.05	0.39	0.3	0.2	0.12	0.066	0.086	0.14	<0.05	<0.05
Ca	2.4	2.1	1.9	3.1	7.8	12	4.2	2.4	2.7	2.5	2.7
K	17400	17600	17400	11800	5680	2300	1210	11500	12700	12900	11500
Mg	2.4	1.4	2.5	4.9	4.3	3.9	1.2	0.65	<0.25	<0.25	<0.25
Mn	1.8	0.15	0.18	0.23	0.2	0.23	0.05	0.15	0.037	<0.05	<0.05
Mo	0.43	0.23	0.14	0.11	0.077	<0.05	<0.05	0.12	0.14	0.13	0.12
Na	134000	125000	120000	79000	40400	15500	8140	80700	74700	76400	81700
P	22	12	7.8	5.7	3.9	1.9	0.98	5.9	6.5	5.8	4.6
S	48900	61400	68900	47400	23100	9260	4990	48300	43100	43900	48600
V	0.15	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.11
<i>Elements with concentration below the quantification limit: As (<0.15), Be (<0.05), Co (<0.03), Cr (<0.1), Cu (<0.05), Fe (<0.15), Ni (<0.05), Sb (<0.15), Se (<0.15), Sn (<0.15), Ti (<0.15) in all cases</i>											
<i>*Tests 8-11 with lime addition</i>											

3.2. Selection of favorable dissolution conditions

The influence of temperature and pH on the removal of Cd, Pb and Zn was studied on the basis of Table 3. Regarding pH, the results presented in Fig. 5 are in good agreement with those of the preliminary study, reflecting a complete removal of Cd at pH above 11.7, and a decline in the

removal of Zn at $\text{pH} > 12.2$. As illustrated in Fig. 5, complete removal of Pb could not be achieved, the maximum degree being 90 %.

The temperature where the samples were let to stabilize for the period of 5 days did not affect the removal of Cd and Zn significantly, and the influence on Pb removal was moderate. If only the removal of these three metals is considered, it does not seem to be necessary to operate at temperatures higher than 32 °C. On the other hand, the temperature determines the applicable RBFA concentration, being therefore a critical factor affecting the economy of the treatment process, as discussed in Section 3.4 below.

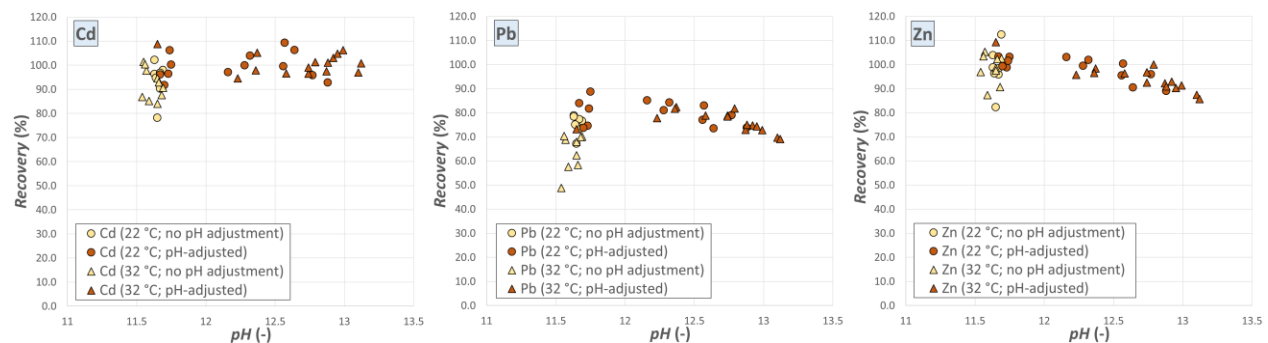


Fig. 5. Removal of Cd, Pb and Zn with the cake fraction at different pH values.

In addition to cadmium, lead and zinc, some other metals were separated together with them. The recoveries of iron and manganese, in particular, were observed to be proportional to the removal of Cd and Zn (Fig. 6). As can be seen in Fig. 6b and e, the removal of Pb did not have a clear correlation with the recovery of Fe and Mn. The recovery of Fe increased consistently with the pH, but Zn became less soluble at pH above 12.2, which was the main reason for the exceptional dependence between the removal rates of Zn and Fe seen in Fig. 6c. It is unclear to the authors whether the removal of all these trace metals might also help in preventing deposit formation on the surfaces of the recovery boiler. In the case of the most harmful non-process elements Cl and K, purging 100 % of ash has been simulated to result in about 70 % reduction of Cl levels and about 65 % reduction of K levels in RBFA (Saturnino, 2012).

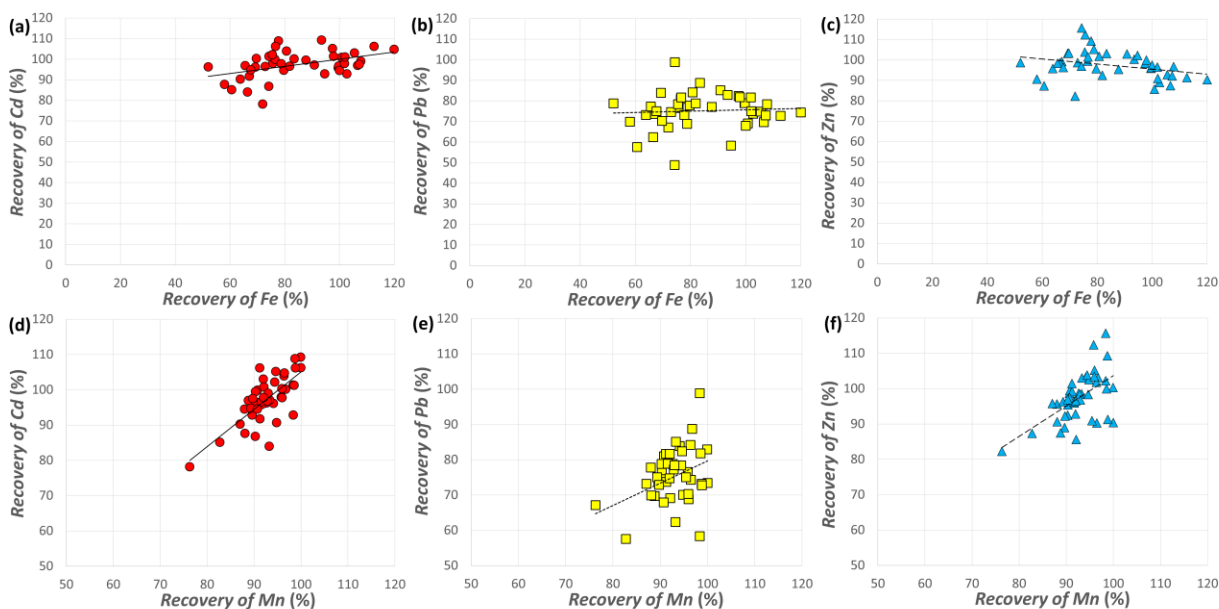


Fig. 6. Removal of Cd, Pb and Zn against the recovery of Fe (a-c) and Mn (d-f).

Evaluation of the repeatability of the HTE recovery experiments was performed by 2 or 3 parallel trials for five experiments. The obtained removal rates of each of the three trace metals, the means of the parallel trials, and the relative difference or relative average difference from the mean as percentages are shown in Table 5. The evaluation of repeatability implied that the variation in the results was a few per cents from the mean in most cases, and over 10 % in one case (Test 16) only.

Table 5. Repeatability of HTE removal experiments. *R* represents the removal of a trace element with the cake fraction.

<i>Test / Statistic</i>	<i>Trial</i>	<i>R, Cd (%)</i>	<i>R, Pb (%)</i>	<i>R, Zn (%)</i>
1	1	96.3	78.8	98.7
	2	90.3	73.2	95.8
	3	96.8	77.2	98.4
<i>Mean</i>	1-3	94.4	76.4	97.6
<i>Avg. diff. from mean (%)</i>	1-3	2.9	2.8	1.3
2	1	78.2	67.1	82.3
	2	94.7	75.0	96.3
	3	102.2	78.4	103.9
<i>Mean</i>	1-3	91.7	73.5	94.1
<i>Avg. diff. from mean (%)</i>	1-3	9.8	5.8	8.4
5	1	100.2	88.7	103.1
	2	106.2	81.7	101.5
<i>Mean</i>	1,2	103.2	85.2	102.3
<i>Diff. from mean (%)</i>	1,2	2.9	4.1	0.8
16	1	101.4	98.8	115.7
	2	97.7	68.8	105.2
	3	100.3	70.3	103.4
<i>Mean</i>	1-3	99.8	79.3	108.1

Avg. diff. from mean (%)	1-3	1.4	16.4	4.7
17	1	84.0	62.3	98.6
	2	94.5	67.9	97.4
Mean	1,2	89.3	65.1	98.0
Diff. from mean (%)	1,2	5.9	4.3	0.6

3.3. Required treatment time

The required treatment time was studied by performing six experiments at 32 °C with sample stabilization times of 20 min, 24 h, and 120 h between the sample preparation and solid-liquid separation steps. Two conditions differing from each other as much as possible were selected: Test 16 where the RBFA concentration was 35 wt.% and the pH 11.6, and Test 27 where the RBFA concentration was 45 wt.% and the pH was adjusted to 13.1 with lime. Fig. 7 illustrates the results of these experiments. It seems to be possible to obtain a high degree of removal for Cd and Zn in a short time, even without increasing the pH by lime addition. Generally, taking experimental error into account, it can be stated that a long sample stabilization time (a few days) might be beneficial for the removal of HTE when the pH is not adjusted with lime to promote precipitation of these metals as hydroxides. An opposite time-dependent behavior seems to be characteristic of the pH-adjusted suspensions at a high pH with respect to Pb and Zn, but not with respect to Cd. However, the differences are relatively small and apparently do not justify making detailed conclusions about the state of the suspension.

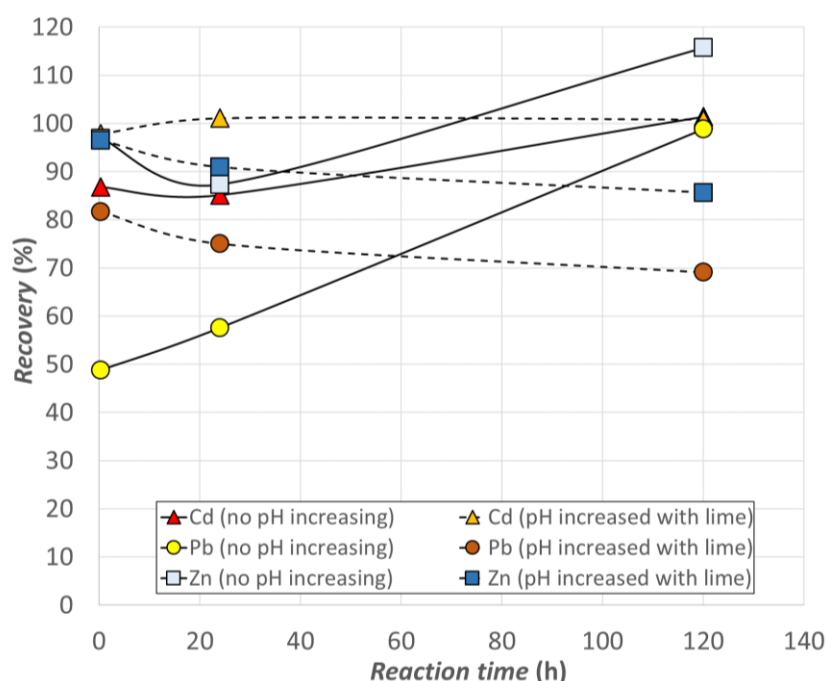


Fig. 7. Removal of Cd, Pb and Zn at 32 °C when the reaction times prior to solid-liquid separation were 20 min, 24 h, and 120 h. RBFA without pH increasing (pH 11.6) or with pH increasing with lime (pH 13.1).

3.4. Mass balance and energy consumption

The total mass balance for the solid-liquid separation stage was determined by performing six tests at three RBFA concentrations at 32 °C, with and without pH adjustment. In these experiments, the supernatant was completely removed from the top of a centrifuged sample, leaving only a compact cake for analysis. This wet cake was dried in an oven at 60 °C until the weight reached a constant value for measuring the solid content. The dry cake was then crushed, digested in acid with the same procedure as used for the wet samples, and analyzed for elemental composition with ICP-MS. The results regarding the removal of the target metals are included in Figs. 5 and 6 above. The experimental conditions and the resulting cake properties are presented in Table 6.

Table 6. Conditions and results of the mass balance experiments. Symbols S_{cake} and ϵ_{av} represent the total solid content and the average porosity of the centrifuged cake, respectively.

Test	m_{ash} (g)	m_{H_2O} (g)	C_{ash} (wt.%)	m_{lime} (g)	C_{lime} (wt.% of ash)	pH (-)	$m_{supernatant}$ (g)	$m_{dry\ cake}$ (g)	S_{cake} (wt.%)	ϵ_{av} (-)
16 ^M	14	26	35	0	0	11.59	38.7	0.78	58.2	0.39
17 ^M	16	24	40	0	0	11.66	35.3	3.32	71.1	0.37
18 ^M	18	22	45	0	0	11.68	30.7	6.71	72.1	0.52
21 ^M	14	26	35	0.2	1.42	12.87	38.6	0.79	57.7	0.40
24 ^M	16	24	40	0.2	1.42	12.95	35.2	3.54	73.0	0.38
27 ^M	18	22	45	0.2	1.42	12.88	30.4	7.09	73.7	0.50

As can be seen in Table 6, the mass of dry cake depended on the used RBFA concentration, but was influenced by the pH increasing only in the case of the highest RBFA concentrations (40 and 45 wt.%). The solid content of the cake became higher when the cake mass increased, i.e. when the RBFA concentration was further above the point of saturation. The average porosity of the cake was calculated from the cake dimensions and the void volume, assuming that the liquid in the cake was a saturated Na₂SO₄ solution with the maximum solubility in water of 0.497 kg dm⁻³ at the reaction temperature. The porosity increased with the mass of the cake, which in this case could be associated with the increase of the non-dissolved suspended solids content of the cake.

The elemental composition of the waste cake was determined with SEM-EDS for the samples used for mass balance estimation. The results are summarized in Table 7. When comparing Tables 1 and 7, the following conclusions can be drawn regarding the chemical composition of the cake fraction:

- 1) Only the main elements were detected by the EDS technique – the resolution of EDS was not high enough for trace elements with concentrations of a few or tens of mg kg⁻¹. However, EDS enabled the measurement of concentrations of other interesting elements, such as C, Cl, O and Si.
- 2) Most Na and S were in the form of Na₂SO₄, while the carbonate content was much lower.
- 3) Calcium was present in significant quantities only when CaO was added.
- 4) The potassium concentration increased with the weight of the cake, but chlorine was not detected in the samples where the K contents were the highest.

Table 7. Elemental composition of the dried cake fractions in the mass balance experiments (Tests 16^M, 17^M, 18^M, 21^M, 24^M, and 27^M) measured by using SEM-EDS.

<i>Test #</i>	<i>c, ash (wt.%)</i>	<i>pH (-)</i>	<i>Element concentration (wt.%)</i>									
			<i>C</i>	<i>O</i>	<i>Na</i>	<i>Al</i>	<i>Si</i>	<i>Mg</i>	<i>Ca</i>	<i>S</i>	<i>Cl</i>	<i>K</i>
16 ^M	14	11.55	3.7	41.4	30.9	0.2	0.3	-	0.4	21.5	0.7	1.8
17 ^M	16	11.65	2.9	40.5	30.2	-	-	-	-	21.3	-	2.2
18 ^M	18	11.69	3.2	40.5	30.2	-	-	-	-	21.3	-	4.8
21 ^M	14	12.99	10.9	42.6	14.6	0.1	0.2	0.2	20.1	9.7	0.5	1.2
24 ^M	16	13.10	6.4	41.4	25.5	-	-	-	6.7	17.9	0.5	1.7
27 ^M	18	13.12	5.3	40.5	25.9	-	-	-	3.0	19.3	-	6.0

EDS mapping illustrating the distribution of the main elements in particles of the dried cake fraction (Tests 16^M and 27^M) spread on a carbon tape background is presented in Supplementary file 2.

The loss of process chemicals, using the mass fraction of total solids of RBFA in the cake as the measure, increased from 5 to almost 40 % when the RBFA content of the suspension was increased from 35 to 45 wt.%, as illustrated in Fig. 8. This was due to exceeding the solubility of RBFA, which resulted in incomplete dissolution and a larger cake fraction. An interesting observation regarding mass balance was that lime addition caused a slight increase in the loss of RBFA. A similar trend was seen also in the cake masses presented in Table 7. The diamond markers in Fig. 8 describe the situation after the centrifugal separation performed in this study, and the lines reaching close to the solid content of 100 % describe the calculated loss for higher solid contents of the cakes. The most potential methods that can be used to reach a higher solid content include 1) effective dewatering e.g. with a vacuum or a hyperbaric filter, 2) squeezing moisture from the cake in a belt press or a filter press, and 3) a combination of cake squeezing and dewatering by air blowing in a filter press. On the other hand, the loss of process chemicals can be minimized by using a lower RBFA concentration in the slurry preparation stage.

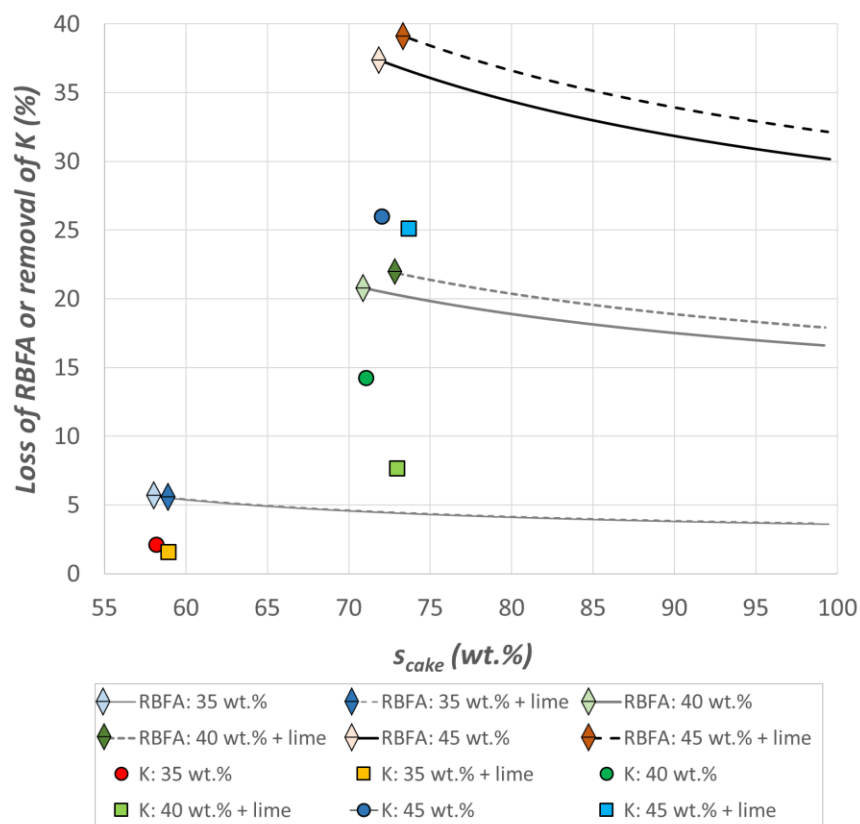


Fig. 8. Loss of RBFA (mass of total solids in cake / mass of RBFA used) with the HTE-rich cake fraction against the total solids content of the cake for different slurries (32 °C, 35-45 wt.% RBFA). The diamond marker indicates the loss and the corresponding total solids content of the cake obtained by centrifugation in this study, and the lines describe the calculated dependence of loss on the total solids contents of the cakes.

Another point of view to the loss of chemicals is the removal of an unwanted non-process element, potassium, with the cake fraction (Fig. 8). Considering the relative degree of K removal to the loss of RBFA, it can be concluded that a small cake fraction produced at low RBFA concentration contains relatively less K than a large cake fraction. Increasing the pH with lime seems to change the potassium balance between the cake and the supernatant, increasing the share of K in the supernatant.

The proposed method for HTE removal requires the addition of extra water to the process, which causes a need for extra evaporation capacity, either before or during the black liquor concentration stage, where the purified solution is typically pumped in Kraft pulp mills. This means that the energy consumption of RBFA purification has to be paid attention to if the proposed method is implemented in plant scale. The required amount of water that should be evaporated (unless recrystallization is used) from the supernatant obtained by using RBFA concentrations of 35-45 wt.% is visualized for cakes with different dryness in Fig. 9. The amount of water that has to be evaporated from the purified liquid containing the valuable process chemicals depends on the dryness of the cake, so that the effect of cake dryness on the evaporation requirement is more pronounced for large cakes. The situation presented in Fig. 9 represents a worst case scenario,

where the added water must be completely removed by evaporation. In practice, however, it is more reasonable to remove only part of the extra water by evaporative crystallization of sodium sulfate, and to dissolve the formed crystals in black liquor. This process is currently in use at some mills which are forced to purge chloride and potassium from the chemical recovery cycle.

Similarly to the amount of water, the specific energy consumption of evaporating the added water is shown in Fig. 9. The energy requirement varies from less than 0.8 to about 1.3 MWh per ton of treated RBFA. Comparison of Figs. 8 and 9 explains how the used RBFA concentration affects the loss of process chemicals and energy consumption. The smaller the loss of Na and S in the form of Na_2SO_4 is, the higher the specific energy consumption becomes, so aiming at negligible chemical loss would probably require approximately 1.5 MWh ton^{-1} for evaporation (unless Na_2SO_4 is crystallized). A good point regarding the operational cost is that there is plenty of low-pressure steam available at Kraft pulp mills, so the cost of heat energy is not likely to be especially high.

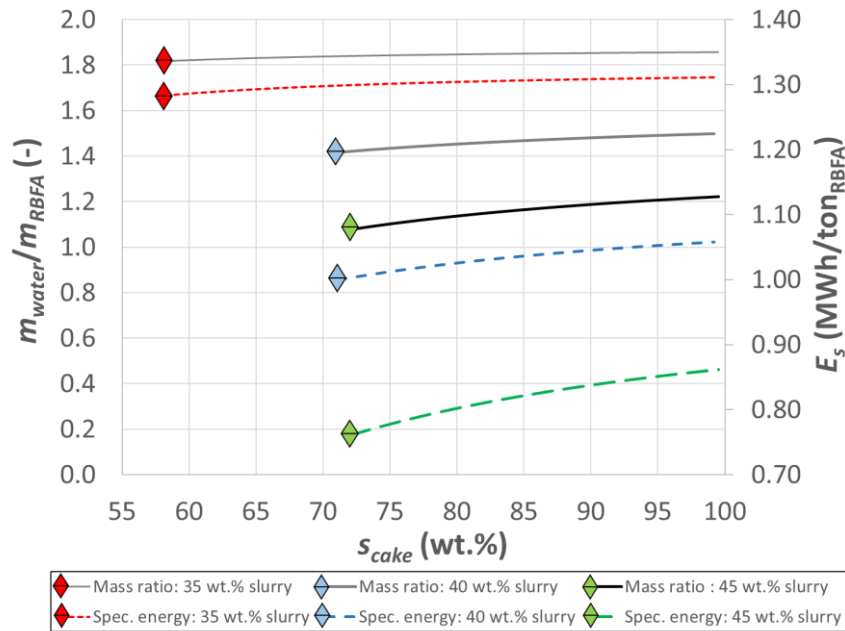


Fig. 9. Water/RBFA mass ratio and specific energy requirement of evaporating the added water (MWh per ton of ash treated) against the total solids content of the cake fraction for different slurries (32 °C). The diamond marker indicates the total cake solids content obtained by centrifugation in this study.

It is important to note that the material losses and energy requirement reported in this paper are far above the levels obtainable by optimizing the process conditions and implementing modern ash crystallization systems, such as the HPD Chloride Removal Process (CRP), Ash Re-Crystallization (ARC) by Andritz, and Precipitator Dust Recovery (PDR) by Eka Chemicals (Tran and Earl, 2004; Minday et al., 1997). Therefore, conclusions regarding the economy of the process should not be made on the basis of the material and energy evaluations presented in this paper.

4. Conclusions

Removal of hazardous trace elements Cd, Pb and Zn from recovery boiler fly ash (RBFA) was studied by using a wet separation method based on different solubilities between the process chemicals and hazardous trace elements. The removal of Cd, Pb and Zn was most effective within the pH range 11.7-12.3, for which a complete removal of Cd and Zn was a typical result, and Pb removal rate of 80-90 % could be reached even in a short time. The removal of cadmium was the least sensitive to even a higher pH, whereas Pb and Zn became more soluble again at pH > 12.3. The concentration of ash in the wet separation process was seen to have a significant influence on the removal of Cd, Pb and Zn, as well as on the process economy. The used ash concentration also determines the economy of the process, due to the fact that the extra water added to the existing chemical recovery cycle of a pulp mill has to be removed from the ash recirculation loop to enable optimal operation of the recovery boiler. Further studies on the topic could focus on disposal possibilities of the cake fraction and long-term impacts of metal removal in mill scale.

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