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Effective removal of hazardous trace metals from recovery boiler fly ashes

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Abstract

The objective of this study is to introduce a treatment sequence enabling straightforward and effective recovery of hazardous trace elements from recovery boiler fly ash (RBFA) by a novel method, and to demonstrate the subsequent removal of Cl and K with the existing crystallization technology. The treatment sequence comprises two stages: dissolution of most other RBFA components than the hazardous trace elements in water in Step 1 of the treatment, and crystallization of the process chemicals in Step 2. Solid-liquid separation has an important role in the treatment, due to the need to separate first the small solid residue containing the trace elements, and to separate the valuable crystals, containing Na and S, from the liquid rich in Cl and K. According to the results, nearly complete recovery of cadmium, lead and zinc can be reached even without pH adjustment. Some other metals, such as Mg and Mn, are removed together with the hazardous metals. Regarding the removal of Cl and K from the process, in this non-optimized case the removal efficiency was satisfactory: 60-70 % for K when 80 % of sodium was recovered, and close to 70 % for Cl when 80 % of sulfate was recovered.

Keywords: Kraft pulp mill; hazardous trace element; heavy metal; removal; chemical recovery

1. Introduction

The recovery boilers of Kraft pulp mills are responsible for the recovery of process chemicals and conversion of the energy content of black liquor to heat and power [1-3]. The material streams leaving the recovery boiler include the smelt, which contains the process chemicals sodium and sulfur, mainly as Na_2CO_3 and Na_2S , and recovery boiler fly ash (RBFA), also referred to as recovery boiler salt or dust, having Na_2SO_4 and Na_2CO_3 as its major components. The amount of fly ash generated is approximately 80 kg per metric ton of black liquor fired [4]. Fly ash is removed from the flue gas of the boiler with electrostatic precipitators, and mixed again with black liquor in the evaporation stage, usually after removing part of its Cl and K content, with a certain loss of process chemicals. The recirculation of the salt contributes to the chemical balance of the mill primarily by reducing the need for make-up chemicals, improves the operation of evaporators, and enables adjusting the sulfidity of the pulping process [5]. An extensive review on the inorganic pulp mill residues, including the separation and treatment of recovery boiler fly ash, has been published by the authors [6], and formation of fly ash particles in the recovery boiler has been discussed comprehensively by Mikkanen [7].

Along with the necessary elements Na and S present in the pulping chemicals, the streams in the Kraft recovery cycle contain elements which do not contribute to the pulping process, and are therefore called non-process elements [8]. The most abundant of the highly soluble, and consequently the most harmful, non-process elements are Cl and K. Other important non-process elements include Ca, Mn, Al, Si, P, and Fe [9]. High concentration of non-process elements in the recovery cycle may cause various problems, such as corrosion, plugging of the recovery boiler, and ring formation in the lime kiln [4,10-12]. Removal of the highly soluble non-process elements from the recovery cycle can be implemented by ash treatment with a number of different strategies.

Leaching is a straightforward treatment method widely applied in the industry, using small liquid/solid ratios, dissolving only part of the RBFA. Ash leaching systems, such as Valmet AshLeach and Valmet AshLeach Duo [13], and ALE (Ash LEaching) [14] by Andritz, are currently used in several mills. Another approach is to dissolve the salt completely and to recover the process chemicals in the next process stage, e.g. by evaporation crystallization or freeze crystallization [15]. Commercial processes utilizing evaporation crystallization include HPD CRPTM, i.e. Chloride Removal Process, ARC (Ash Re-Crystallization) supplied by Andritz, and PDR (Precipitate Dust Recovery) of Eka Chemicals [16,17]. Cooling crystallization, which is usually called freeze crystallization in the related literature, has been commercialized by Mitsubishi [16], and is in use in some Japanese pulp mills. The removal of Cl and K from the salt solution can also be carried out by ion exchange techniques, for instance according to the PDP (Precipitator Dust Purification) process of Eco-Tec. However, this process is effective only for Cl, and its selectivity for K is poor [18].

The weakness of the existing ash treatment methods is that they are practically unable to remove hazardous trace metals and other trace elements from the chemical recovery cycle, which increases the occurrence of those elements in the process, and most importantly, in the green liquor dregs. The current situation at most mills is that green liquor dregs cannot be utilized outside the mill area for any value-added purpose, such as for production of fertilizers and soil amendments. This is mainly due to the high concentrations of hazardous trace metals, especially cadmium, in the dregs. The removal of hazardous trace metals from RBFA may help in reducing the concentrations of those metals in the green liquor dregs, and together with removal of Cl and K by a subsequent crystallization process, it is possible to mitigate also the problems caused by non-process elements in the recovery boiler.

The purpose of this study is to introduce a treatment sequence where hazardous trace elements are separated from RBFAs obtained from the electrostatic precipitators of two Finnish Kraft pulp mills. The valuable solutes contained in the remaining liquors are then crystallized by cooling crystallization to recover the process chemicals in the solid form and to remove the unwanted non-process elements with the liquid residue. The metals separation step is the novel part of the study, whereas the chemical recovery part is included to double-check that the target metals are adequately recovered in the metals separation step, and that metal recovery will not cause any unexpected difficulties in the crystallization process.

2. Description of the treatment sequence

The novel treatment stage (Step 1) integrated in a commonly applied ash treatment procedure (Step 2) is illustrated in Fig. 1. The RBFA collected from the electrostatic precipitator (ESP) is dissolved in water at 32 °C, where the solubility of Na_2SO_4 is 33 wt.%, and the small residue of suspended solids is separated from the liquid e.g. with a centrifuge or a filter. A bucket centrifuge was used to separate the residue from the salt liquid in this study. After this primary solid-liquid separation, the liquid is cooled down to the desired terminal temperature in order to crystallize Na_2SO_4 and Na_2CO_3 . The block of crystals, or pieces of it if agitation is used, is then readily separated from the liquid e.g. by decantation or by filtration and air drying. In this study, the crystal separation was demonstrated with a vacuum filter. The separated crystals may then be returned back to the recovery cycle, and the liquid containing most of the non-process element content may be discharged to the sewer or pumped to a further treatment stage, e.g. ion exchange.

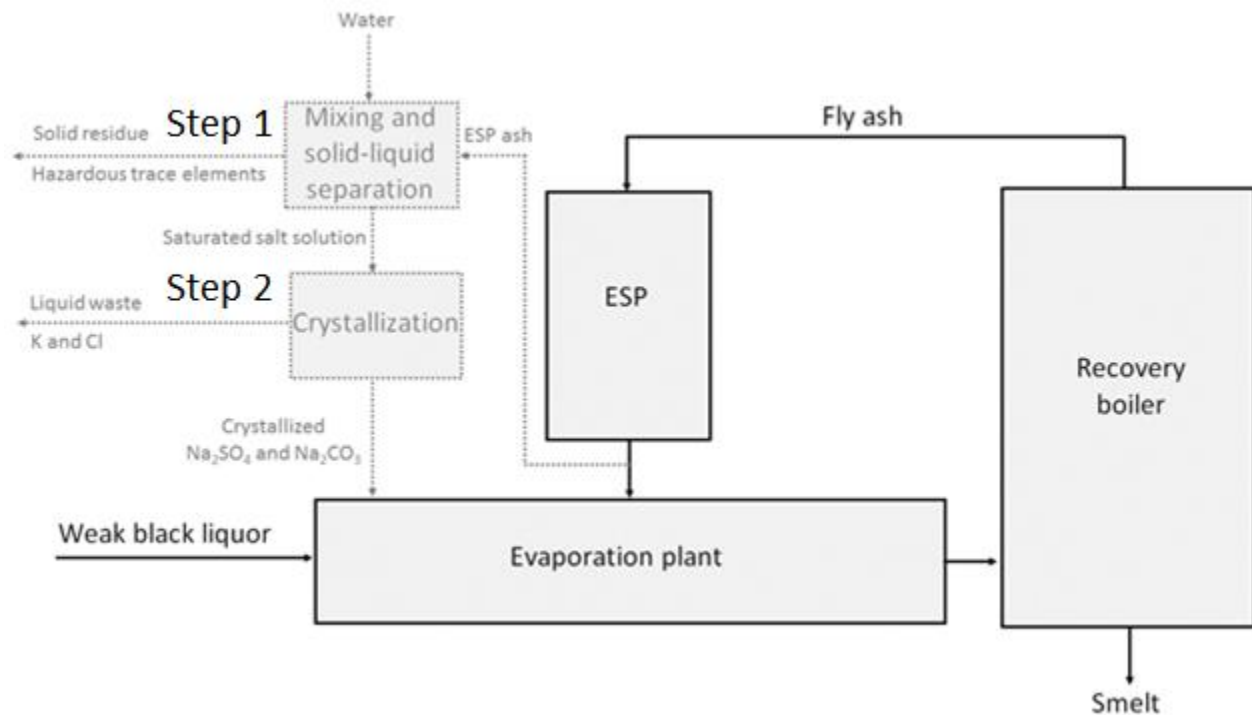


Fig. 1. Treatment process comprising the removal of hazardous trace metals, chloride and potassium from electrostatically precipitated recovery boiler fly ash.

3. Materials and methods

3.1. Samples and analyses

Two samples of recovery boiler fly ash collected from electrostatic precipitators at two Finnish pulp mills (capacity > 600,000 tons/year) were used in the experimental study. Preliminary analyses were performed for both samples, including the following methods: 1) scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDS) for general characterization of the materials and their elemental compositions, 2) inductively coupled plasma mass spectrometry (ICP) for metal concentrations, and 3) laser diffraction for particle size distributions.

The analyses were carried out by experienced professionals in the analysis center of Lappeenranta University of Technology (LUT), unless otherwise mentioned.

A Hitachi SU 3500 scanning electron microscope was used to take SEM images of both ash samples and to characterize them for their main elemental compositions. The SEM-EDS equipment was operated by using an acceleration voltage of 10 kV and a carbon tape background. The results of elemental analysis are summarized in Table 1.

Table 1. Elemental compositions of the RBFA samples measured with SEM-EDS.

Mill #	Measurement #	<i>Element concentration</i>					
		<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	1	4.2	39.6	32.2	19.8	0.8	3.4
1	2	4.6	39.4	31.6	20.1	0.9	3.5
1	3	4.3	39.6	32.0	20.0	0.8	3.4
1	Average	4.4	39.5	31.9	20.0	0.8	3.4
2	1	1.4	39.6	28.0	24.2	-	6.9
2	2	1.6	39.8	27.4	24.4	-	6.9
2	3	1.5	39.6	27.5	24.3	-	7.0
2	Average	1.5	39.7	27.6	24.3	-	6.9

Table 2 shows the concentrations of metals in the ash samples, measured by using ICP-MS. The sulfur concentrations could not be measured with the method used in the analysis.

Table 2. Metal contents of the ash samples measured with ICP-MS. Note that the unit g/kg indicated by * applies exceptionally for Na and K.

Sample	<i>Element concentration (mg/kg) or (g/kg)*</i>															
	Na	K	Mg	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Mo	Ag	Cd	Pb
Mill 1	364*	35*	< 110	2.3	< 40	54	< 200	< 10	< 70	< 7	62.2	< 10	< 3	< 50	1.7	1.8
Mill 2	301*	67*	< 110	0.9	< 40	39	< 200	< 10	< 70	< 7	31.0	< 10	< 3	< 50	2.3	1.0

SEM images of the ash materials on a carbon tape background with 50, 500 and 2000 x magnifications are presented illustratively in Fig. 2. Two essential differences were detected between the ashes: the Mill 2 ash contained randomly distributed, spherical aggregates, which were relatively large. On the other hand, the sample of Mill 1, containing a large number of smaller and more irregular-shaped aggregates, was more homogeneous. These differences can be observed in the images with 50 x magnification only, because the locations of the 500 x and 2000 x images were selected so that the largest aggregates were not included in the images.

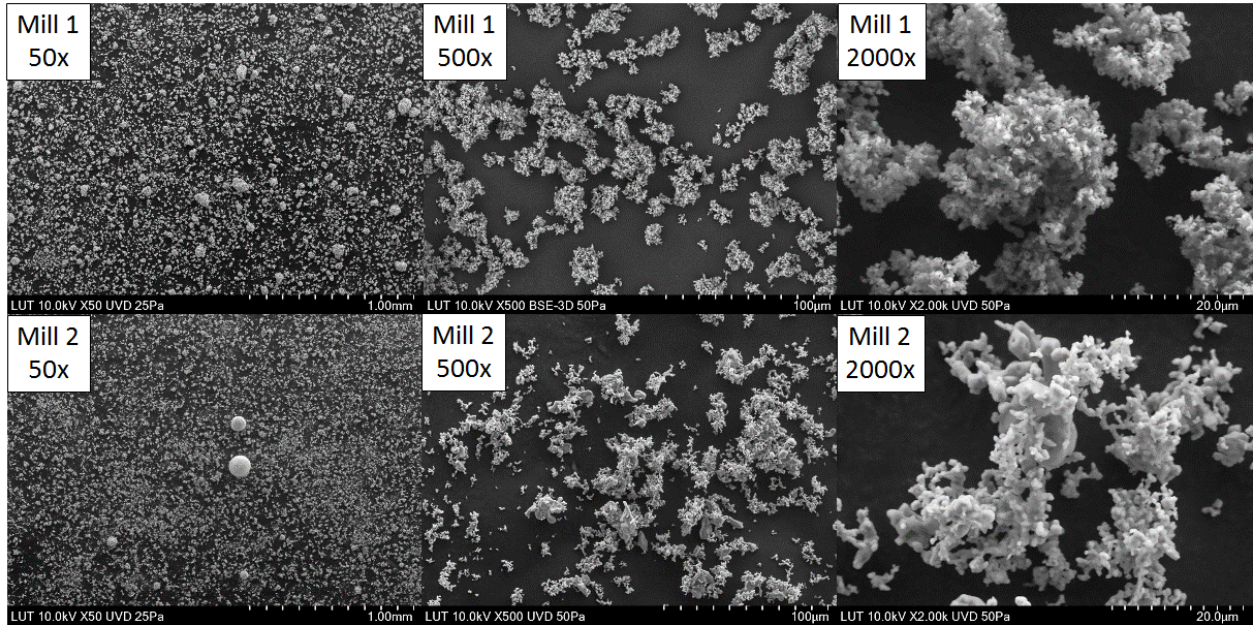


Fig. 2. SEM images of the RBFA samples with 50, 500 and 2000 x magnifications.

The coarser particle size of the Mill 1 sample was very clearly visible in the volumetric particle size distributions as well, as can be observed in Fig. 3. The particle and/or aggregate sizes varied from 0.2 μm to over 10 μm in the sample of Mill 1, and from 0.5 μm to 40 μm in the sample obtained from Mill 2.

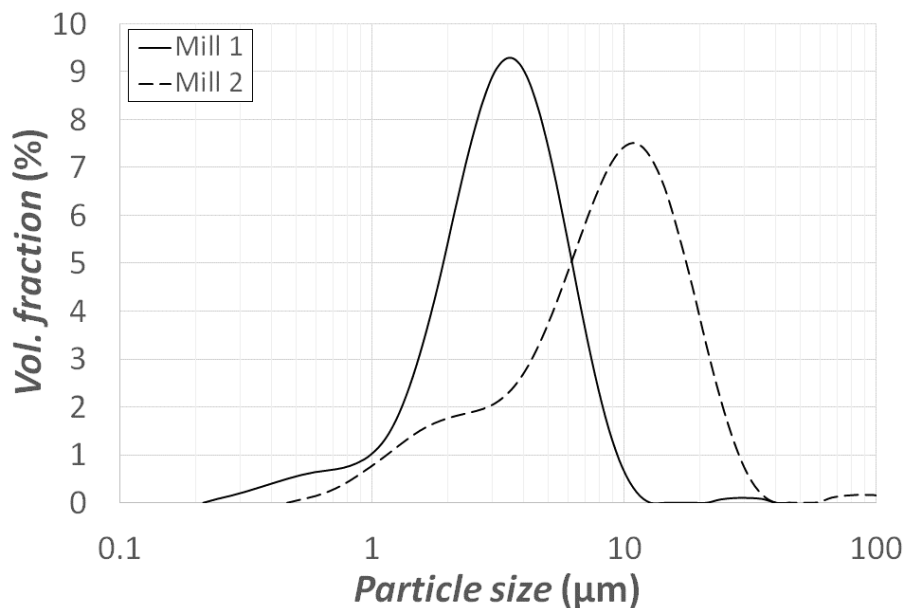


Fig. 3. Volumetric particle size distributions of the materials.

The metals were analyzed with an Agilent 7900 inductively coupled plasma mass spectrometer (ICP-MS). The dry ash samples of 0.1-0.2 g were first digested in a strong acid solution by using a Milestone Ultrawave microwave digestion system and a mixture of nitric and hydrochloric acids

(vol. ratio $\text{HNO}_3:\text{HCl} = 4:1$) of ICP-MS quality. The digestion temperature and the duration of the digestion were 250 °C and 20 min, respectively.

A Malvern Mastersizer 3000 laser diffraction particle size analyzer was used to measure the volumetric particle size distributions of the ash samples. The Fraunhofer approximation was applied as the optical model. The samples were dispersed in ethanol and mixed in a 1 dm³ beaker at 3000 rpm in the manual wet dispersion unit (Hydro EV) of the device. The ultrasonic vibrator integrated in the unit was also kept on to promote the dispersion of the particles. The measurements were performed a few times for both materials and the average distributions were then formed by automatic calculation by the data analysis program of the device.

Services provided by external laboratories were used for the determination of a large number of elements in the cakes, including rare earths. The analyses were performed with ICP-OES and ICP-MS after digestion with four acids (HCl, HNO_3 , HF, HClO_4) at Labtium Oy (Kuopio, Finland). The chloride contents of the residual salt liquids remaining after crystallization of the process chemicals for Mill 1 were analyzed with IC at Ahma Ympäristö Oy / Suomen Ympäristöpalvelu (Oulu, Finland).

3.2. *Equipment and experiments*

The treatment sequence comprised two main stages, namely removal of hazardous trace metals (Step 1) and removal of non-process elements (Step 2).

3.2.1. Removal of hazardous trace metals

The experiments summarized in Table 3 were performed in two series by using plastic bottles ($V = 50 \text{ cm}^3$) as reaction vessels for the suspensions. The aim of the first part of the study was to study the recovery of hazardous trace metals and to have an impression of the mass balance of the metal removal. The main variable in these experiments was the ash content of the suspension, which ranged from 25 to 33.3 wt.% (Mill 1) and from 28.6 to 35.7 wt.% (Mill 2). These ash contents were selected on the basis of the maximum solubility of Na_2SO_4 , 497 g/dm³ at 32 °C (see e.g. [19-21]) and observations made in preliminary testing, because the ash samples did not have exactly the same solubility properties as pure Na_2SO_4 .

The pH of the suspensions with 33.3 wt.% ash content was adjusted with lime to 12.3 in Tests 4 and 8 to compare the recovery of hazardous trace metals with those obtained in Tests 3 and 6 without pH adjustment. To summarize the experimental procedures, removal of hazardous trace elements was performed in the natural pH of the ash solutions and in elevated pH to simulate the conditions used in conventional hydroxide precipitation of metals.

Table 3. Experimental plan for the *first* part of the study (Step 1).

<i>Mill #</i>	<i>Test #</i>	m_{water} (g)	m_{RBFA} (g)	C_{ash} (-)	C_{lime} (% of RBFA)	pH (-)
1	1	30	10	0.25	0	12.05
1	2	25	10	0.286	0	12.07
1	3	20	10	0.333	0	12.11
1	4	20	10	0.333	0.4	12.34*
2	5	25	10	0.286	0	9.76
2	6	20	10	0.333	0	9.69
2	7	18	10	0.357	0	9.64
2	8	20	10	0.333	0.8	12.35*

* pH adjusted to a favorable level for hydroxide precipitation

The ash dissolution procedure was performed as follows: 10.0 g of ash per test was weighed in plastic vessels, after which deionized water was added in the samples to form suspensions with different ash contents, according to Table 3. Each ash/water suspension was then shaken strongly and left in an incubator to stabilize at 32 °C for 24 h. After the stabilization time, the samples were centrifuged with a temperature-controlled bucket centrifuge ($r = 172$ mm) at 2500 rpm, 32 °C for 20 min. The pH was measured from the clear supernatant of the centrifuged samples by using a WTW pH 340i pH meter and a SenTix® 41 electrode. The clear supernatant was then carefully removed from the top of the settled solids, referred to as cake, and the masses of the solid and liquid fractions were measured. Finally the cake fractions were dried in the same plastic vessels at 60 °C to avoid loss of material, crushed manually, and analyzed for metals with ICP-MS.

The only exceptions to the above were Tests 4 and 8, where the pH of suspension was measured during the lime addition by using the above-mentioned pH meter. Analytical grade lime (J.T. Baker Chemicals B.V., Deventer, Holland) was slowly added into the pre-shaken turbid suspensions until the target pH of approx. 12.3 was reached. The pH-adjusted samples were stabilized and separated in the same way as the other samples.

3.2.2. Removal of non-process elements and recovery of process chemicals

Another test series was carried out to investigate the subsequent unit operation comprising the chemical recovery and removal of non-process elements. The crystallization experiments for the recovery of process chemicals, mainly in the form of sodium sulfate decahydrate, i.e. mirabilite $Na_2SO_4 \cdot 10H_2O$, were performed for the clear ash solution which was separated from the metal cake at the conditions of Tests 3 and 6 shown in Table 3. The concentration of dissolved solids in the liquid before crystallization was 33.3 wt.%, the initial temperature was 32 °C, and the duration of crystallization was 1 h. The experimental conditions used in the crystallization experiments are listed in Table 4.

Table 4. Experimental plan for the *second* part of the study (Step 2).

<i>Mill #</i>	<i>Test #</i>	<i>T_{end} (°C)</i>
1	9	22
1	10	22
1	11	11
1	12	0
1	13	0
1	14	0
2	15	22
2	16	22
2	17	11
2	18	0
2	19	0
2	20	0

4. Results and discussion

4.1. Removal of hazardous trace metals

Fig. 4 presents the main results of Step 1 with respect to the three target metals Cd, Pb, and Zn. The recoveries are plotted as a function of the pH of the salt liquid measured after the stabilization and settling of the suspensions overnight. As can be seen in Fig. 4, the dimensionless recoveries for all the target metals are within a narrow range in the case of Mill 1, ranging from approximately 0.8 to 0.9, and within a wider range for Mill 2, being generally over 0.95 at the natural pH of the suspension, and slightly lower at the lime-adjusted pH 12.35. The calculated recoveries in Fig. 4 are above 1 in some cases, due to the error arising primarily from the above-mentioned heterogeneity of the Mill 2 ash samples.

As Fig. 4 shows, the target metals were recovered efficiently without pH adjustment, and the favorable pH range was different between the mills. This observation could be due to two reasons: the target metals were either bound in different mineral structures, or the compounds were basically similar, but had different solubility properties in the differently composed solutions.

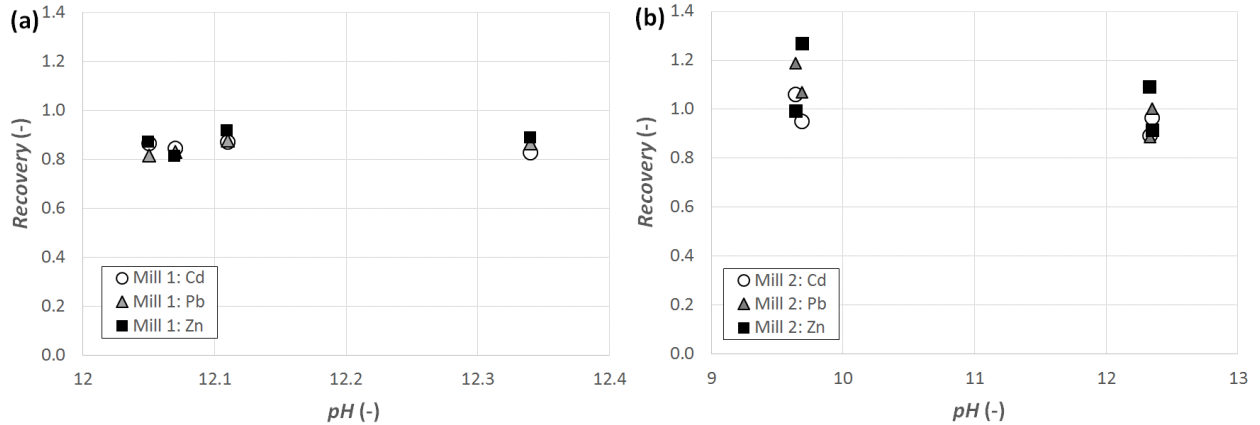


Fig. 4. Recovery of Cd, Pb and Zn in Step 1, calculated with relation to the metal contents of the ash samples for Mill 1 (a) and Mill 2 (b). Note that some of the calculated values are above 1 due to the heterogeneity of the Mill 2 sample.

4.2. Concentrations of metals and rare earth elements in the cakes

Fig. 5 summarizes the absolute concentrations of metals in the non-dissolved residual cakes separated from the aqueous ash suspensions by centrifugation for the experiments where the ash concentration was 33 wt.%. The most abundantly present metals in the cakes were Na, K, Mg, Zn, and Mn. The concentrations of Na and K were too high to be reported in Fig. 5: 350 g/kg (Mill 1) and 300 g/kg (Mill 2) for Na, and 28 g/kg (Mill 1) and 65 g/kg (Mill 2) for K. Iron was found to be present at concentrations above the detection limit only in the cake of Mill 2. The moisture contents of the cakes before drying were at the same level: 65 wt.% (Mill 1) and 64 wt.% (Mill 2).

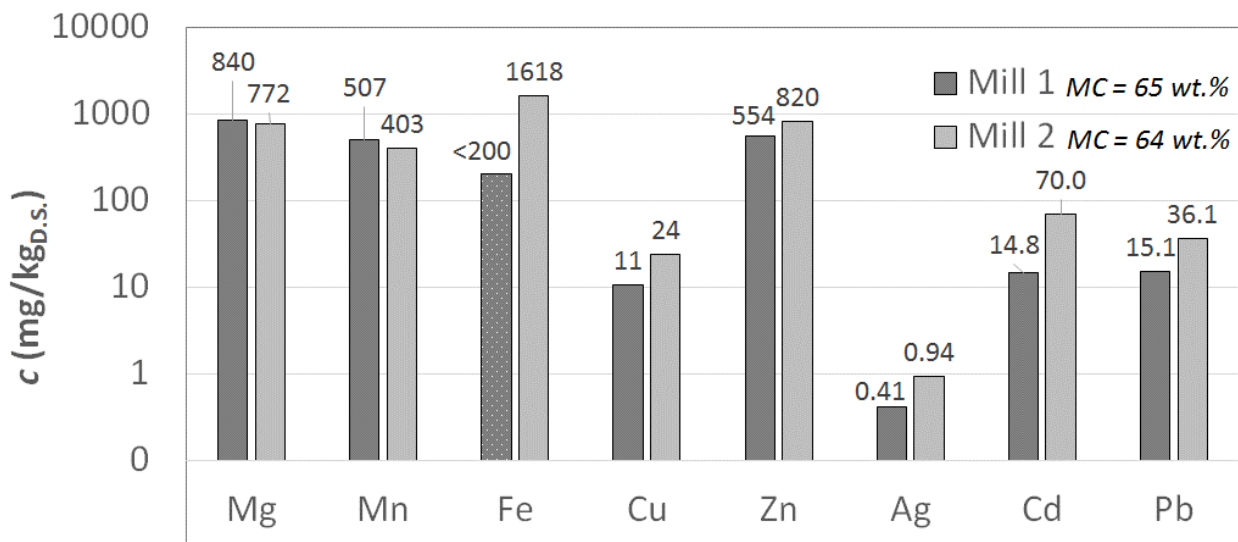


Fig. 5. Metal concentrations of oven-dried cakes with respect to dry solids (D.S.) analyzed with ICP-MS. The moisture contents (MC) of the centrifuged cakes before drying are also presented.

The concentrations of rare earth elements (REE) and several other elements in the same cakes, as shown above in Fig. 5, are presented in Table 5.

Table 5. Concentrations of elements in oven-dried cakes measured by ICP after digestion of the samples with four acids.

Sample	Element concentration (mg/kg _{D.S.})															
	As	Sb	U	Al	Ba	Ca	Fe	Mo	Ni	P	Rb	S	Sr	Ti	V	Y
Mill 1 cake	<2	0.5	0.2	124	15	480	124	<2	<2	59.6	211	166·10 ³	3.37	4.13	2.28	<0.2
Mill 2 cake	5.3	2.1	0.1	340	10	325	2440	2.7	19	214	545	212·10 ³	2.07	6.57	3.53	0.24

The metals which were not found in the cakes of the Mills 1 and 2 at concentrations above the detection limit (mg/kg) included Bi (< 1), Ce (< 0.2), Dy (< 0.01), Er (< 0.01), Eu (< 0.01), Gd (< 0.01), Hf (< 0.05), Ho (< 0.01), La (< 0.5), Lu (< 0.01), Nd (< 0.1), Pr (< 0.05), Sm (< 0.01), Sn (< 2), Ta (< 0.5), Tb (< 0.01), Th (< 0.1), Tm (< 0.01), W (< 2), Yb (< 0.01), B (< 10), Be (< 0.5), Co (< 2), Li (< 2), Sc (< 1), and Zr (< 2). It can be concluded that the attempts made to find REE in the cakes did not result in promising findings. However, this does not mean that it is impossible to find REE in ashes of mills located in areas where REE are naturally present at higher concentrations.

4.3. Recovery of alkali and removal of Cl and K

Batch cooling crystallization experiments were performed in Step 2 to recover the cooking chemicals and to remove Cl and K from the recovery cycle. The ash concentration of the solutions used in these experiments was 33 wt.%. The starting temperature of crystallization was 32 °C and the end temperatures were 22, 11, and 0 °C. Crystallization was continued under static conditions for one hour. When the end temperature of crystallization was 22 °C, nucleation did not start spontaneously during the cooling time. In those cases, negligible amounts of previously formed crystals were added in the solution as seed crystals, which caused crystallization to occur immediately. The crystallization data was not recorded by on-line measurement techniques, but parallel trials (see Table 4) were performed to ensure the consistency of the data.

Fig. 6 summarizes the recovery of total solids, sodium and potassium obtained at different end temperatures. For Mill 1, it can be observed in Fig. 6a that over 80 % of Na is recovered when the end temperature of crystallization is 0 °C. However, the drawback of good sodium recovery is the correspondingly decreasing removal efficiency for potassium, as illustrated in Fig. 6b. The differences between Mills 1 and 2 can be seen by comparing Fig. 6a and 6b with Figs. 6c and 6d. The Na recoveries for the Mill 2 ash are high, varying from almost 90 % to closer to 100 %. An interesting characteristic of the Mill 2 crystals, compared to those of Mill 1, is their higher purity as regards their Na contents. This is clearly illustrated in Fig. 6c by the mostly overlapping solid recoveries, which are lower than the Na recoveries in all three temperatures. The potassium removal for Mill 2 was in accordance with the typical rule of thumb: the higher Na recovery was obtained, the lower was the corresponding K removal. The moisture contents of the crystal cakes after vacuum filtration varied between 49 to 62 wt.%, which is higher than in commercial and optimized plant-scale processes.

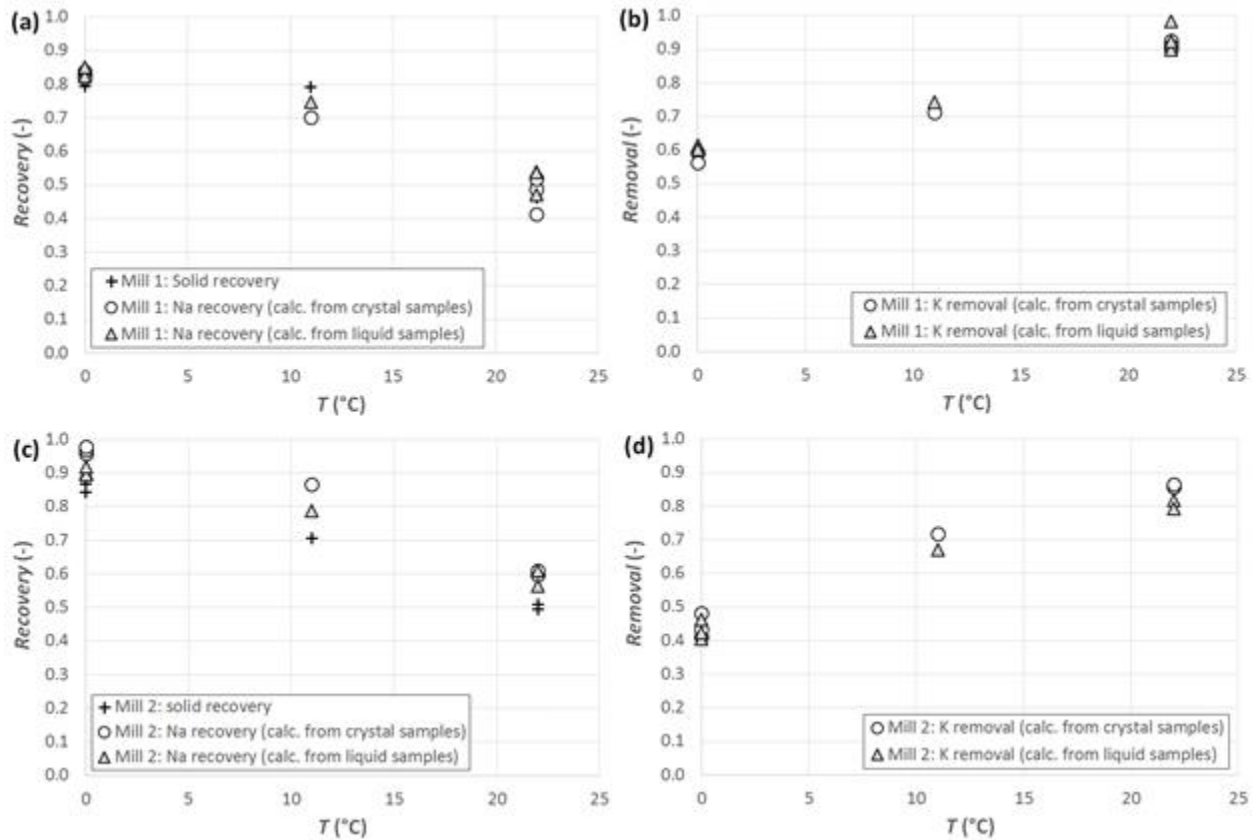


Fig. 6. Dependence of total solid recovery and sodium recovery on the end temperature used in the cooling crystallization in Step 2, calculated on the basis of crystal and liquid samples (a, c) and the corresponding degrees of potassium removal (b, d). The results for Mill 1 are shown in (a,b) and Mill 2 in (c,d). The starting temperature was 32 °C in all tests.

In order to illustrate the relationship between K removal and Na recovery, the potassium removal is presented as a function of the sodium recovery for both mills in Fig. 7. The results show that K appears to be consistently easier to remove with a high recovery of sodium from the Mill 1 solutions, although the highest Na recoveries of approx. 90 % obtained with Mill 2 samples, crystallized at 0 °C, were not reached with the Mill 1 experiments. The removal efficiencies for sulfate have been reported by Goncalves et al. [22] to be close to the Na recoveries for the reason that Na_2SO_4 is the main component in recovery boiler fly ashes. Most technology providers seem to report narrow ranges or only a single value for the removal of K corresponding to a certain level of Na recovery, as summarized in Johansson [23]. The results presented in Fig. 7 show that there may be clear differences in the K removal between the mills.

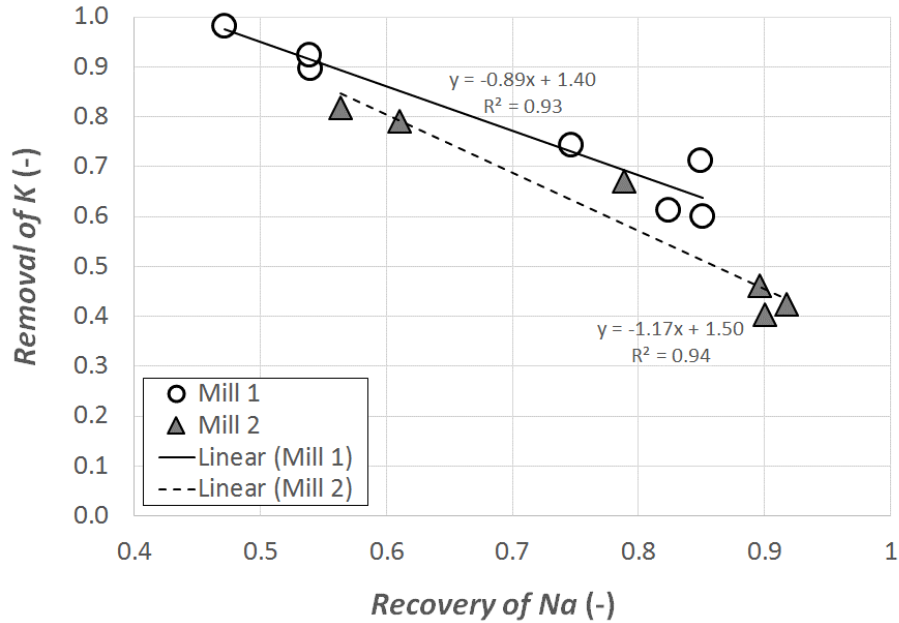


Fig. 7. Relationship between sodium recovery and the degree of potassium removal obtained by cooling crystallization in Step 2 of the treatment sequence.

Fig. 8 shows how the pH of the remaining salt liquid containing the removed K and Cl is related to sodium recovery. The pH measurements were carried out after separating the crystals from the salt liquid by vacuum filtration and after the liquids had reached a constant room temperature. The results presented in Fig. 8 give an impression that there are no dramatic changes in the pH of the salt liquid when there is a change in the sodium recovery. However, the pH is higher in the samples of both mills (Fig. 8) compared to the initial pH of the samples after forming the ash suspensions (Table 3). In other words, the recovery of process chemicals from the solution increases the pH slightly. This is not surprising, because Na_2SO_4 , which is the main component in the crystals recovered from the solution, is a neutral salt.

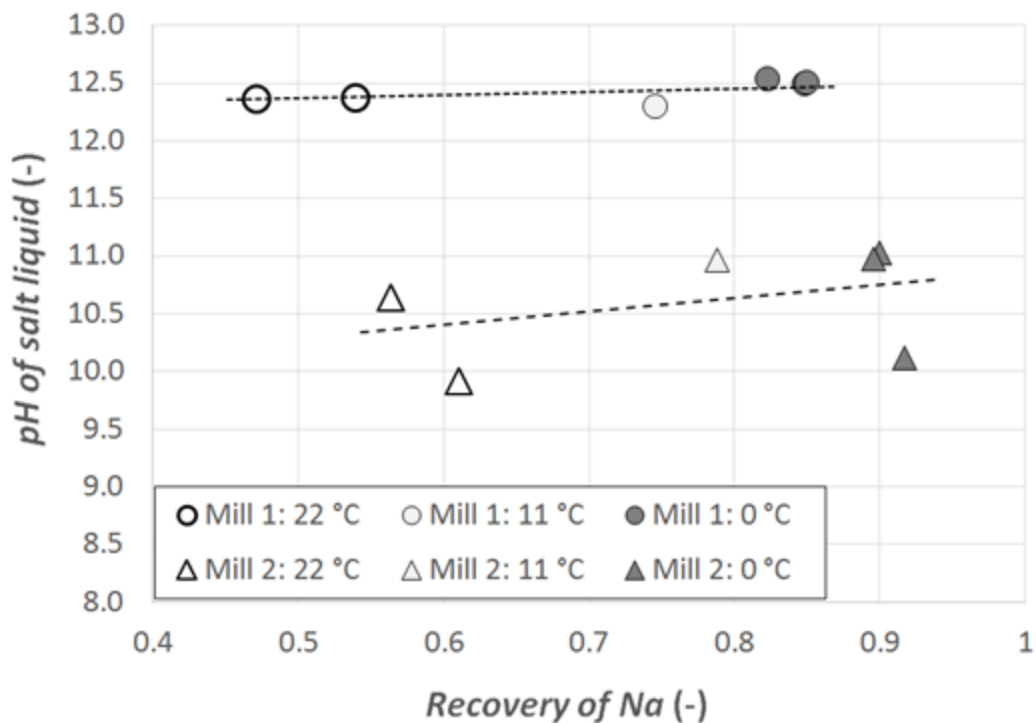


Fig. 8. The pH of the remaining salt liquid after cooling crystallization at 22, 11 and 0 °C (Step 2). Each pH measurement was performed at 22 °C after separating the crystals by vacuum filtration. The crystallization temperatures (22, 11 and 0 °C) of the samples are also presented.

The trace metal concentrations were also measured to double-check that the target metals were not present in the crystals which are mixed again with black liquor to recover the process chemicals at mills. The ICP-MS analyses confirmed that the metals had been adequately removed in Step 1. The only metals, except the already discussed Na and K, which remained in the salt crystals above the detection limit were magnesium (8-9 mg/kg in two samples of Mill 2), manganese (3-5 mg/kg in 6 samples of Mill 2), molybdenum (≤ 0.5 mg/kg, Mills 1 and 2), and thallium (≤ 0.3 mg/kg, Mills 1 and 2).

The chloride and sulfide contents of the clear salt liquids after the crystal separation were measured with ion chromatography. The removal of Cl^- and the recovery of SO_4^{2-} as a function of potassium removal are presented in Fig. 9. Only the results for Mill 1 are reported. These results are in good agreement with Fig. 7 regarding sulfate removal. However, chloride removal is slightly lower than it should be in such a crystallization process (see [15]), which may have been due to the high moisture content of the crystals or the long (2 months) storage time of the samples prior to the chloride analyses.

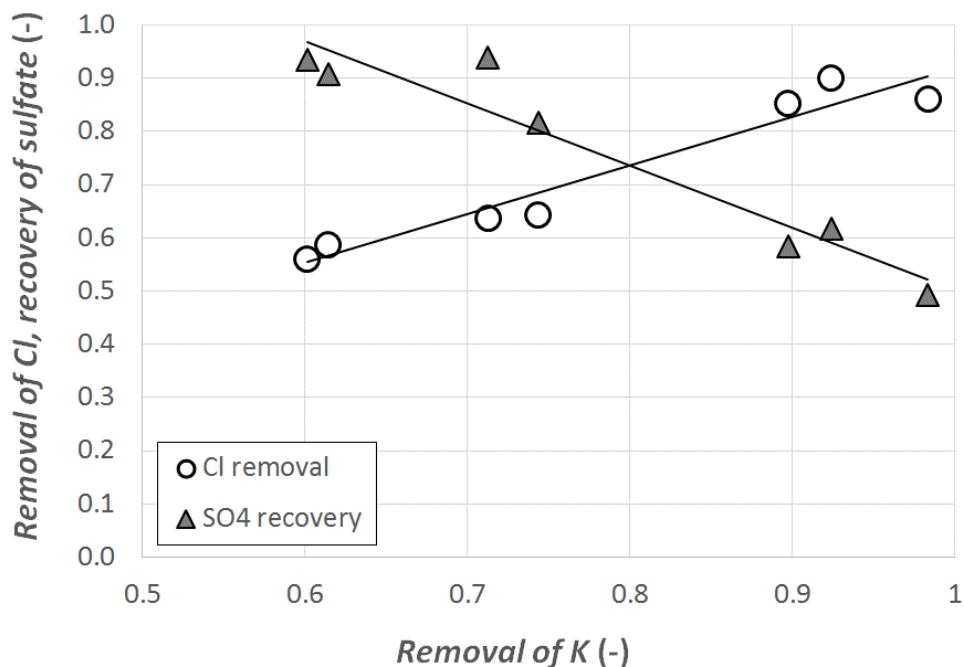


Fig. 9. Removal of Cl^- and recovery of SO_4^{2-} as a function of potassium removal for Mill 1.

4.4. Overall mass balance of the treatment sequence

An approximate mass balance of the treatment process for the treatment of 1000 kg recovery boiler ESP ash is presented illustratively in Fig. 10. The cake separation taking place in Step 1 can be implemented e.g. with a centrifuge, vacuum filter, or a filter press. In this study, separation aiming at maximizing the dryness of the cake was not performed due to the small volume of the suspensions.

The crystallization performed for chemical recovery and NPE removal in Step 2 removed 790 kg of clear solution from the recovery cycle and recovered 2150 kg of crystals with a moisture content of 60 %. In this study, the crystals were separated from the salt liquid by vacuum filtration, which is not a highly effective technique for obtaining high cake dryness.

To summarize the most important results, the removal of cadmium from the chemical recovery cycle can be implemented effectively with a small loss of the process chemicals. The amount of cadmium circulating in the fly ash loop is much larger than the amount of cadmium removed from the cycle with green liquor dregs, as reported in a master's thesis by Wikstedt [24]. Therefore, the removal of cadmium from the fly ash has the potential to reduce the cadmium content of the dregs significantly.

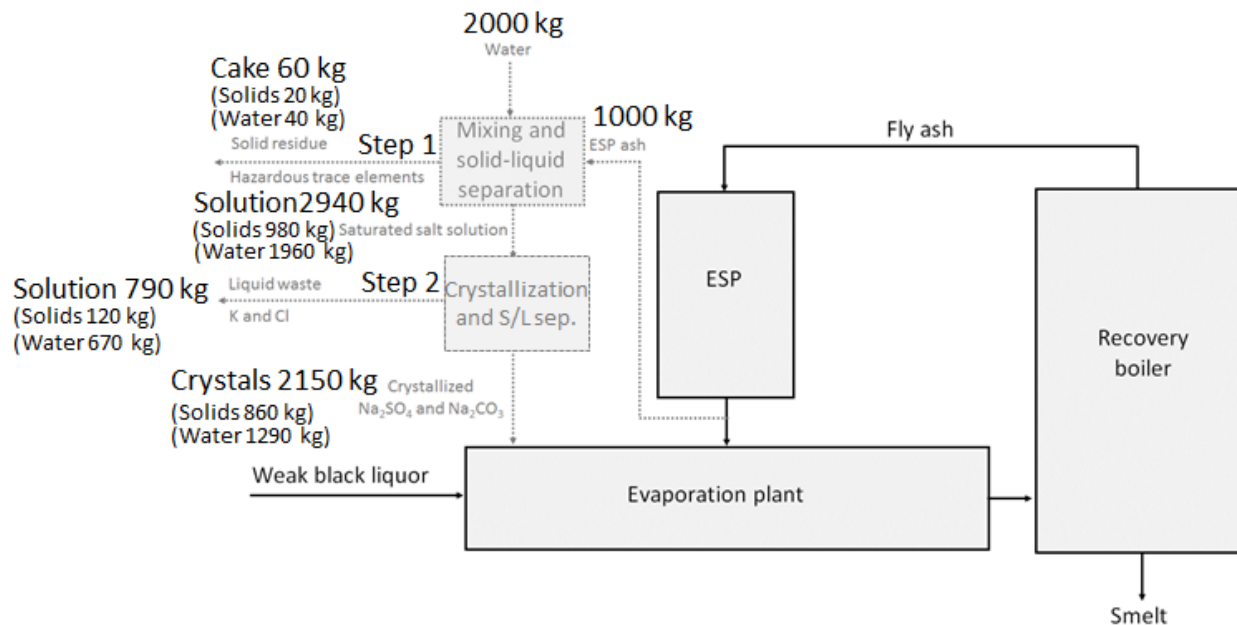


Fig. 10. Mass balance chart of the treatment sequence. Assumptions: 2 % of ash is lost with the cake in Step 1, and crystallization is performed by cooling from 32 to 0 °C in Step 2 to recover 88 % of the solids in the crystals and the associated liquid.

5. Conclusions

The aim of this study was to remove hazardous trace metals from the fly ashes of the recovery boilers of Kraft pulp mills by using a novel ash dissolution method, which can be integrated with existing ash treatment processes. The most noteworthy result was the high removal efficiency of the target metals in the first part of the study (Step 1), ranging from 80 to over 90 % for Mill 1 and from almost 90 % to roughly 100 % for Mill 2. The multimetal cake separated from the saturated salt liquid consisted of elements such as Mg, Mn, Fe, Cu, Zn, Cd, and Pb. The agglomerate size of Mill 2 ash was relatively large, which increased the variation in the analysis results, compared to Mill 1 ash. In order to separate the multimetal cake from the salt liquid, settling or centrifugation followed by pressure filtration should be tested in future studies. Further, stability of the separated multimetal cake should be investigated.

The purpose of the second part of the study (Step 2) was to demonstrate a cooling crystallization process for chemical recovery from the saturated salt liquid. The chemical recovery was found to work appropriately, although at a lower efficiency than tailored commercial solutions.

Owing to the large mass flow rates of recovery boiler fly ash incorporated in the material balance around the recovery boiler, the removal of hazardous trace elements even from a relatively low fraction of the total amount of fly ash could produce two main benefits: slightly reduced scaling of the recovery boiler, and reduction of the metal concentrations in the green liquor dregs. In other words, the metal removal from recovery boiler fly ash has great potential to enable the utilization of green liquor dregs. These issues should be investigated in mills aiming at reducing the disposal of dregs in the future.

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