



Prospects for cleaning ash in the acidic effluent from bioleaching of sulfidic concentrates

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Abstract

Leaching of ashes in sulfuric acid (pH 1.0, liquid-to-solid (L/S) ratio 10:1, 25 °C) has been characterized with respect to the neutralizing capacity and the dissolution of dominant ions and trace elements. The conditions mimic the oxidation stage of a biohydrometallurgical process for base metal production from sulfidic mineral concentrates. Direct acid leaching of ash, integrated with this metallurgical process, offers a feasible route to the sustainable handling of metal-rich ashes. The treated ash will be deposited together with the inert mineral residue. Cd, Co, Cu, Ni and Zn are effectively leached and can be recovered utilizing existing hydrometallurgical technology, but the recovery of other readily dissolved metals, notably Mn, U and V, requires that additional steps are implemented. We make two recommendations for industrial processes. The first is to replace limestone with ash from biofuels, except peat, for pH control in biohydrometallurgical processing. This requires a modest increase of fresh alkali compared with limestone. The second is to implement sulfuric acid leaching of fly ash from the combustion of solid waste and other metal-rich fuels (used wood, tires), thereby avoiding costly ash-deposits. There is a significant economic incentive for these changes, since no costly ash-deposits and less limestone will be needed.

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1. Introduction

Iron and sulfur oxidizing bacteria derive their energy from the reactions of ferrous iron and sulfidic sulfur oxidation. During the last four decades this has been exploited in extractive

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biohydrometallurgy [1]. Bioleaching, i.e., the biocatalyzed oxidation of mineral sulfides, is applied in heap and dump processes for copper recovery. It is also used as pretreatment for gold recovery from refractory concentrates containing arsenopyrite and pyrite. Since the early 1990s there has been an increased interest in stirred tank bioleaching of base metal sulfides containing nickel, cobalt, copper and zinc. Many of these new processes have been tested in pilot or demonstration plants and a full-scale cobalt plant is in operation in Uganda. Much of the current research is focused on chalcopyrite leaching, since it is the mineral that holds the main copper reserves in the world and the economic prospect for bioleaching is promising.

The microorganisms are autotrophic, i.e., CO_2 is the carbon source, and acidophilic, with an optimal pH in the range 1–2. Bioleaching of mineral sulfides, notably pyrite (FeS_2) and arsenopyrite (FeAsS), produces sulfuric acid and requires alkali for pH control and metal precipitation. The need for limestone is equal to 50–100% of the amount of mineral concentrate. The range corresponds to different concentrate mineralogy. We suggest that limestone can be replaced by limestone/ash mixtures. The kinetics of acid leaching also appear in line with typical residence times of processes based on the biocatalyzed oxidation of sulfidic concentrates [2], so ash may replace limestone in biohydrometallurgical processing [3,4].

Fig. 1 outlines a tentative process for base metal recovery (adapted from an original idea by Jan-Erik Sundqvist). pH adjustment is needed in the bioleaching stage as well as for precipitation, first at pH 2.5–3.0 ($\text{Fe}^{3+}/\text{As}^{5+}$) and later, for final precipitation, at pH 7.0–8.0 ($\text{Zn}^{2+}/\text{Cu}^{2+}$). Metal ions in the ash may carry nutritional value [3,5], but may also be toxic to the bacteria in the biocatalyzed oxidation stage or difficult to separate from the commercially viable metals in the effluent or the precipitate. We suggest that dubious ashes are treated in a separate leaching stage, fed by external H_2SO_4 or excess acid from the main process.

The concept of Fig. 1 recycles metals from the solid waste. The environmental incentive is to deplete the ashes of metal ions and terminate the release from deposits [6–8]. Quenching in natural water will only marginally affect the metal content of the ash [9], but acid rain triggers the release of metal ions [10,11]. pH 1–2 is lower than the pH of any conceivable natural water, but extended times at too low pH should also be avoided, since it may destabilize components which preferably should remain in the residue [12].

We do acknowledge that some processes for metal recovery, including selective adsorbents [13,14], need to be improved to materialize the concept of Fig. 1 [15,16]. Acid leaching processes have been simulated [17,18], including full-scale plants [19] and metal recovery stages [20]. Leaching in HCl [21], HNO_3 [22] or acids derived from ample crops [23] is an alternative. More elaborate schemes, for metal recovery or analysis [22,24–26], contain several acid leaching stages, with increasingly stronger acids [27,28], acid leaching followed by alkaline leaching [29] or acid leaching followed by chelation for Cr, Cu, Pb and Zn adsorption [30]. Cd, Cr, Hg, Pb and Zn are elements not (always) well handled by sulfuric acid leaching alone. We consider organic compounds in the ash, including dioxines [31,32], mainly a combustion problem.

Well established and most valuable stabilization methods are an alternative to the process in Fig. 1, albeit not part of a sustainable society. The obvious third alternative, deposits for untreated ash from solid waste incineration, using external diffusion barriers to meet regulations, are quoted at around 100 US\$/t ash. Deposits of untreated ash rely on the large buffering capacity of the ash [33].

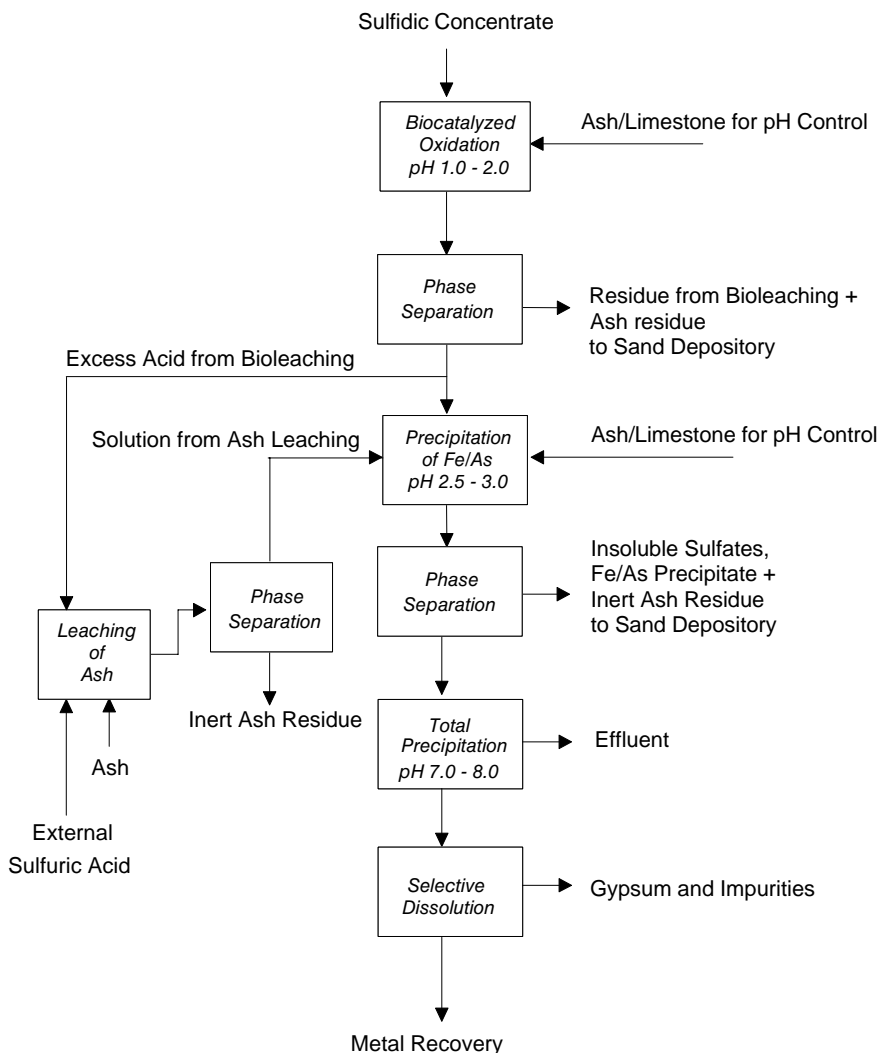


Fig. 1. Process combining biobleaching of sulfidic concentrates and acid leaching of ash.

The current work screens 26 ashes from commercial power plants in Sweden and serves to support literature data on acid leaching [7,34]. Ongoing work addresses metal recovery from the effluent, in connection with biohydrometallurgical processing [15]. We suggest that the concept may also be used for advanced chemical treatment of whole coals of low rank and a screening study of 13 lignites and asphaltites have been completed [16]. Coarsely ground lignites (18–50 mm) are used for heating and acid pretreatment is a sensible way to reduce the negative environmental impact from domestic stoves. Biondesulphurization is a combination of acid leaching and biocatalyzed oxidation of metal sulfides.

Table 1
Ash samples

Sample	Comments	Neutralizing capacity (l/kg) ^a	Weight change and acid leaching (g/kg) ^b
1	Fly ash from waste and chip of wood/mixed ash (from two separate units)	7.9	−119.1
2	Mixed fly and bottom ash from peat (from the same unit as sample 3)	6.0	−59.4
3	Fly ash from peat (from the same unit as sample 2)	5.3	−22.6
4	Bottom slag from waste	11.4	−67.4
5	Fly ash from waste (from the same unit as sample 6)	10.9	−0.2
6	Bottom slag from waste (from the same unit as sample 5)	9.2	−47.0
7	Mixed fly and bottom ash from bark and wood chips (0–20%) (from the same unit as sample 26)	7.6	−81.5
8	Ash from wood/domestic glazed stove/Cs-137 contaminated	13.2	−76.3
9	Fly ash from waste/fluidized bed (from the same unit as sample 10)	12.5	−0.5
10	Bottom slag from waste/fluidized bed (from the same unit as sample 9)	5.7	−61.7
11	Fly ash from waste/fluidized bed (from the same unit as sample 12)	8.7	−18.4
12	Bottom slag from waste/fluidized bed (from the same unit as sample 11)	6.2	−90.9
13	Mixed fly and bottom ash from wood/briquettes of softwood sawmill residues/Cs-137 contaminated	14.9	−0.6
14	Fly ash from the co-combustion of coal (50%), tires (40%) and wood (10%)/after desulfurization/stabilization (from the same unit as samples 15 and 16)	7.6	−0.5
15	Bottom ash from the co-combustion of coal (50%), tires (40%) and wood (10%) (from the same unit as samples 14 and 16)	12.7	−136.4
16	Fly ash from the co-combustion of coal (50%), tires (40%) and wood (10%)/before desulfurization/stabilization (from the same unit as samples 14 and 15)	10.3	−44.1
17	Fly ash (fine mesh) from the imported chips of used wood (from the same unit as samples 18 and 19)	8.2	−10.1
18	Fly ash (electrostatic filter) from the imported chips of used wood (from the same unit as samples 17 and 19)	8.1	−55.1
19	Bottom ash from the imported chips of used wood (from the same unit as samples 17 and 18)	8.3	−71.8
20	Fly ash from waste/polymer stabilized (from the same unit as sample 22)	6.7	−152.5
21	Fly ash from waste (from the same unit as sample 23)	8.9	−51.5
22	Bottom slag from waste (from the same unit as sample 20)	10.2	−95.8
23	Bottom slag from waste (from the same unit as sample 21)	9.7	−136.0
24	Fly ash from bark + chips (maximum 20%)/fluidized bed (from the same unit as sample 25)	8.8	−3.1
25	Bottom ash from bark + chips (maximum 20%)/fluidized bed (from the same unit as sample 24)	4.8	−23.3
26	Fly ash from bark and wood chips (0–20%)/electrostatic filter (from the same unit as sample 7)	14.6	−0.2

^a Neutralizing capacity, volume of H₂SO₄ (1 M) per kg dry ash, initial S/L ratio 1:10.

^b From untreated ash to dry solid residue.

2. Experimental

2.1. Ashes

Fly ashes and bottom ashes/slugs were collected from a series of Swedish power plants (Table 1). The ashes represent waste incineration and the combustion of wood chips and used wood, peat and tires. Waste was combusted in roaster or fluidized bed units (CFB). One unit uses fuel mixed with a Polish coal (50%). Ash from a domestic glazed wood stove completes the list. Two samples contain high levels of Cs-137 (ca. 4000 Bq/kg), but this will not alter the chemistry and is part of a separate study of radioactive ashes. All ashes were obtained as spot samples and represent the qualities from outgoing feeders.

Each sample was dried for more than 24 h at 105 °C in air and then sieved through a 4 mesh grid. Larger hard particles (>6.70 mm) were discarded. The relatively small surface area of large particles means this fraction will contribute marginally to the neutralization capacity, for any reasonable contact time. The sieved samples were divided, further dried in air at 105 °C, and ground in a ring mill pulverizer. The resulting fine powders were analyzed by ICP-AES/MS/SMS (SGAB-Analytica; <http://www.sgab.se>; procedure MG-2 plus additional elements) and stored, until used, in sealed plastic bags at room temperature. These powders constitute our untreated materials.

Twenty grams of powder was stirred with 200 ml deionized water (Millipore Milli-Q, >18 MΩ cm) overnight (>12 h), giving a liquid-to-solid (L/S) ratio of 10:1. Subsequently, 1 M H₂SO₄ was added to obtain and maintain pH 1.00 ± 0.005, throughout the leaching. This was done manually every 30 min during the initial rapid acid consumption, and later at longer intervals [16]. The maximum deviation from pH 1.0 was 0.1 pH unit. The total amount, initial plus additions, gives the neutralizing capacity, quoted as liters of 1 M H₂SO₄ per kg dry powder, at pH 1.0. Stirring was continuous and the temperature kept at 25 °C. The Erlenmeyer flasks were sealed by plastic film, to limit air access and avoid artifacts from the uptake of CO₂ [34], though less likely at pH 1.

Gas evolution from some samples is caused by carbonatization of the untreated ashes. Carbonatization scales with the surface area and is promoted by alkali metal ions. As a consequence gas evolution was merely observed for ashes from biofuels, particularly samples 8 and 13.

Stirring was discontinued after ca. 10 days and the solid phase allowed to settle. Following sedimentation, the aqueous phase was filtered (Munktell OOH) and the filter rinsed by an additional 200 ml sulfuric acid (pH 1.0). All liquids were mixed and measured and a sample was left for ICP-AES/MS/SMS analysis (SGAB-Analytica; <http://www.sgab.se>; procedure V3a plus additional elements). The solid residue was heated in air at 105 °C for 3 days or until stable weight was achieved. The sample was then weighed and a sample left for ICP-AES/MS/SMS analysis (SGAB-Analytica; <http://www.sgab.se>; procedure MG-2 plus additional elements).

The percent recovered (balance) was calculated from the mass of the untreated material, the solid residue and the volume of the liquid phase. The percent removed was calculated from the effluent as well as the solid residue, if both numbers were available. The reported numbers are the average of the percent calculated from the aqueous phase and the percent calculated from the solid residue.

3. Results and discussion

3.1. Neutralizing capacity

Fig. 2 shows the volume of 1 M H₂SO₄ required to establish a stable pH 1.0, when 1 kg dry ash is stirred with 10l of deionized water. All values represent long-term conditions, approaching equilibrium after more than 10 days at 25 °C. We give the value of CaO for comparison.

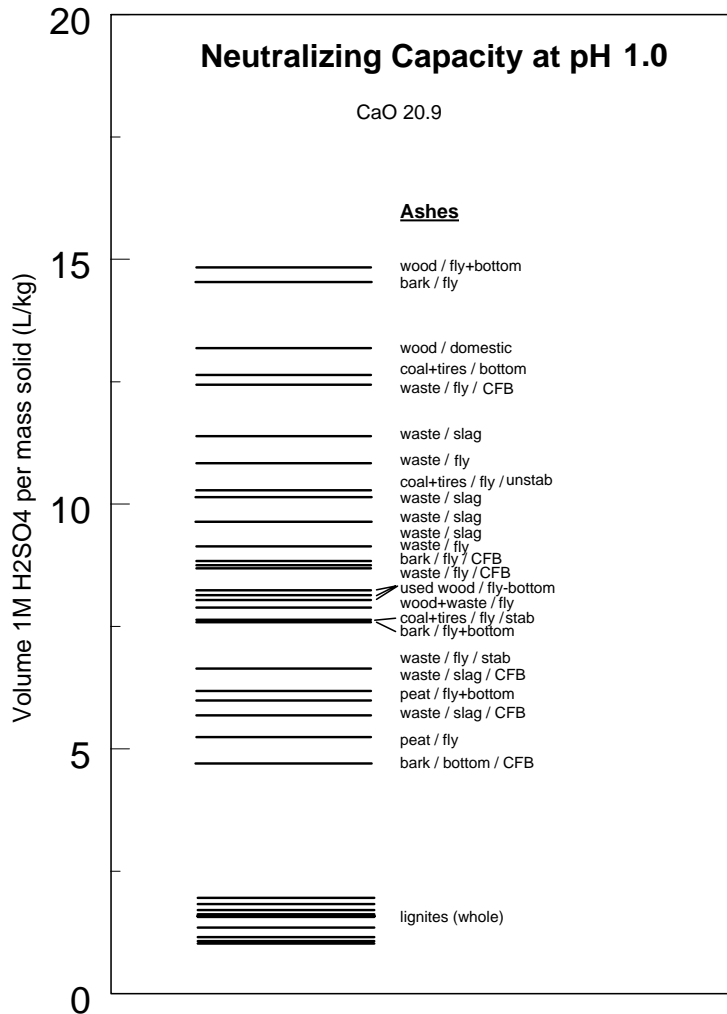


Fig. 2. Neutralizing capacity of miscellaneous ashes, CaO and whole ground lignites. The lignite data was taken from literature [16].

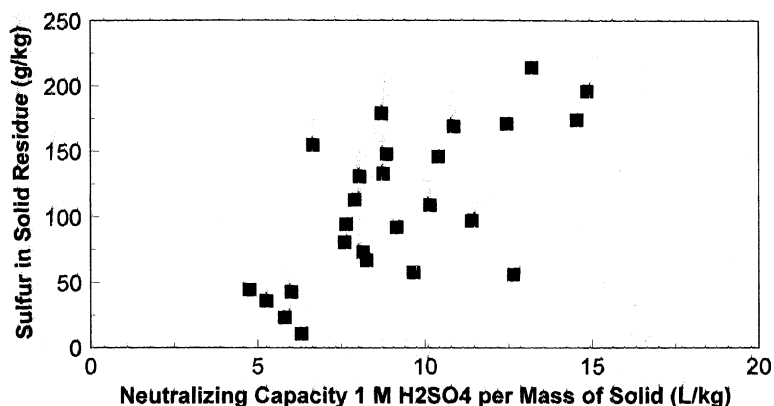


Fig. 3. Sulfur concentration in the solid residue vs. the neutralizing capacity.

Fig. 2 shows the high neutralizing capacity of bioashes from bark and wood chips, and the opposite low capacity of peat ashes. This is known to the power plant operators and one reason why blends of wood chips and peat are a preferred fuel. The acidity of peat ashes prevents the growth of solid phases of potassium-rich silicates on heat exchangers [35–37].

The neutralizing capacity of waste residues varies with the fuel and is therefore difficult to predict [38], but the fly ashes have, in general, higher neutralizing capacity than the bottom slags. This effect is further examined when comparing pairs of ashes. Samples 5, 6 and 9, 10 illustrate the regular situation, and samples 20 and 22 show that after-treatment, in this case fly ash polymer stabilization, will drastically affect the basicity.

The bottom slags of CFB units are diluted with sand, which reduces the neutralizing capacity [39], but no such effect is traceable in the fly ashes of CFB units (Fig. 2, samples 9 and 10). Chemical analyses show a corresponding high silica concentration in the bottom slags, but no enhanced level in the fly ashes. The simple conclusion is that the sand is not further ground in the swirling combustion bed and therefore will not rise with the flue gases.

3.2. Sulfates in solid residue

The neutralizing capacity shows the consumption of protons from the addition of sulfuric acid, but Fig. 3 reveals no simple relation between sulfur in the solid residue and the ash basicity. A positive slope is presented in Fig. 3, but the variations, due to the different solubility of metal sulfates, are considerable.

Ca, Ti, Ba, Hg, Pb and Sr form insoluble sulfates [40] and Fig. 4 shows that the sulfur level in the solid residues agrees well with the assumption that sulfur is present as CaSO_4 (gypsum), $\text{Ti}(\text{SO}_4)_2$, BaSO_4 (barite), HgSO_4 , PbSO_4 (anglesite) and SrSO_4 (celestite).

Chemical analysis reveals that the sulfur level increases during ash leaching and we can safely assume that the formation of gypsum and other insoluble sulfates is the main addition to the solid phase, but Fig. 5 shows that other components are affected, as well. The sulfate increase in Fig. 5 was calculated from the sulfur concentration, assuming CaSO_4 formation, and normalized to the weight of the untreated ash. A negative trend can be

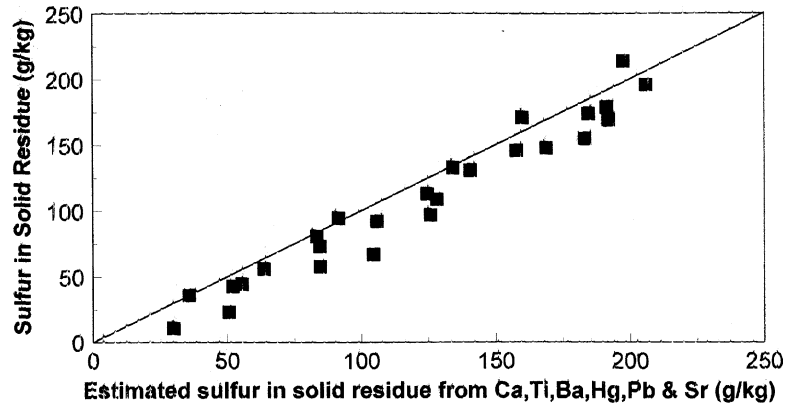


Fig. 4. Sulfur in solid residue as determined by chemical analysis vs. the predicted sulfur concentration, from the concentration of Ca, Ti, Ba, Hg, Pb and Sr.

observed, revealing that, as sulfate precipitation builds the mass of the solid phase, other phases are dissolved. Moreover, high levels of sulfur in the untreated ash lead to larger weight losses. This arises from the absence of suitable oxides, notably CaO, for the formation of insoluble sulfates, and from the dissolution of water soluble sulfates, in particular $ZnSO_4$. Zn is abundant in some waste residues and in samples 16 and 18, i.e., the fly ashes from tires and used wood. Extracted zinc ions are an asset in the effluent [41–43], if the ash is used in connection with zinc production from mineral sulfides (sphalerite). Zinc production from complex ores, rich in zinc, along with copper production from chalcopyrite, would be an additional monetary reward from this process.

Fig. 6 presents the total weight changes of the individual solid phases in g/kg. The values were calculated as the mass of the solid residue minus the mass of the untreated ash, divided by the mass of the untreated material. Fig. 6 also gives the exceptional weight increase for $CaSO_4$ (gypsum) formation from CaO, neglecting crystal coordinated water. Please note that the bar for this reaction is well out of scale.

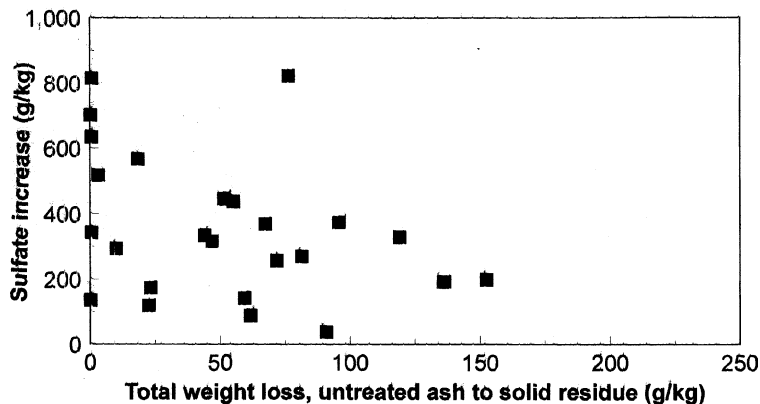


Fig. 5. Sulfate increase in the solid phase vs. total weight loss, from untreated samples to solid residue.

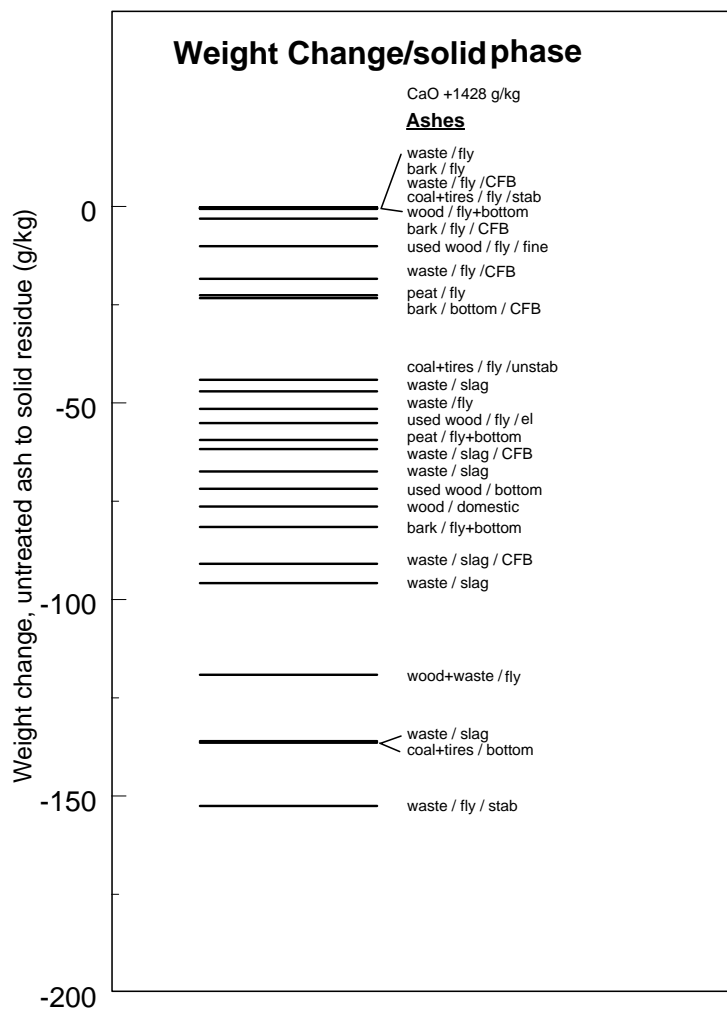


Fig. 6. Weight changes of miscellaneous ashes. Note that the figure for CaO is only given as a numerical value, since the corresponding bar is out of scale.

There is no strong correlation between the neutralizing capacity (Fig. 2) and total weight change (Fig. 6), but we would like to draw attention to sample 13. This ash represents common softwood sawmill residues and maintains a stable quality with 71% of the neutralizing capacity of CaO, at no weight change. This is a valuable by-product with low hazardous metal content.

3.3. Trace elements in effluent and solid residue

The untreated ashes were obtained as spotsamples and the individual concentrations might be of limited interest, but we wish to display the range by quoting maximum and minimum

values (and sample numbers) for some elements of interest: Ni, 14 (25)–356 (6) mg/kg; Co, 3.9 (7)–160 (16) mg/kg; Cu, 55 (14)–16,200 (22) mg/kg; and Zn, 62 (3)–47,500 (16) mg/kg.

Ni, Co, Cu and Zn are of interest for biohydrometallurgical metal production and we note that ashes with concentrations in the higher range give a contribution to the metal ion concentrations from dissolved minerals. Unfortunately, high concentrations of valuable metals coincide with high molybdenum concentrations. Mo, in concentrations above 50–90 mg/l, is poisonous to the bacteria/archaea used for biocatalyzed oxidation [1,44]. The present levels, from below 6 mg/kg (2–4, 7, 8, 10, 12–17, 25, 26) to 31 mg/kg (20), are below this range, but transients may threaten the entire process and we cannot recommend the use of waste ashes for pH control in the biocatalyzed oxidation stage (Fig. 1).

Cadmium, 0.2 (15)–297 (22) mg/kg; chromium, 36 (8)–812 (17) mg/kg; mercury, from below 0.1 mg/kg (4, 8, 10, 12, 13, 19, 22, 25, 26) to 20 mg/kg (20); and lead, 18 (26)–8130 (18) mg/kg are environmentally ominous. Waste ashes are notoriously suspicious and ashes from used wood and stabilized ash qualities may release high amounts of these. U, 0.18 (26)–4.3 (15) mg/kg, is not uncommon in coal combustion and we find the highest concentration in ash from the co-combustion of coal and tires, but note that other coals have considerably higher amounts of uranium [16].

Na, 138 (26)–48,000 (20) mg/kg, is commonly quoted for diffusion studies from landfills. Sodium in sample 20 comes from aftertreatment at the incineration station. Finally, chlorine and fluorine are found in the effluent and the corresponding values were: Cl, from below 35 mg/l (25)–4100 mg/l (20); and F, from below 0.1 mg/l (2–4, 15, 17, 19, 23, 26)–25 mg/l (1). Again waste ashes carry the highest concentrations.

Table 2 gives the leaching results for all elements in the study. Only results with better than 90% recovery of an individual element are reported and the errors are as a consequence small.

Si is stable, and present as SiO_2 , silicates, complex minerals or $\text{Si}(\text{OH})_4$. Ca, Ba, Ti and the trace elements Pb and Sr form insoluble sulfates. Hg forms insoluble sulfides or sulfates. Be, La, Nb, Sc, Sn, W, Y and Zr are not leached, with insignificant statistical variations. We note that the oxides TiO_2 , SnO_2 and ZrO_2 are stable under the present conditions.

Other elements are leached, but the percent removed varies considerably. The results are further analyzed with respect to the type of fuel. Table 3 presents data for (i) waste fly ash; (ii) waste slag; (iii) fly ash from waste, coal and used wood; (iv) bottom ash from waste, coal and used wood; (v) fly ash from coal and used wood; (vi) bottom ash from coal and used wood; and (vii) miscellaneous biofuels. Table 4 gives the corresponding average concentrations for individual elements.

The main elements, besides Si and Ca, are Al, Fe, K, Mg, Mn, Na, P and Ti. Potassium, Mg, Mn and Na are 70–80% dissolved in most fly ashes, but lower values are observed for the corresponding bottom ashes. The numbers for Al and K are further reduced for CFB slags, due to sands with unleachable silicates. Phosphorous is more effectively dissolved in bioashes, with high concentrations, than in other ashes, with lower concentrations. The percentages removed of other elements, from the above list, do not show any clear dependence either on the type of fuel nor the concentrations, but all fly ashes are more effectively leached than the corresponding bottom ashes. Calculations based on effluent concentrations and solid residues differ by less than 2%.

Table 2
Percent removed of miscellaneous elements

	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12	S13
Si		9	2							6		−8	
Al	57	53	58	68	76		57	77	68	20	75	18	
Ca	8	19	24	12	11		12	8	10	20	4	35	
Fe	23			20	43				40		57		81
K	91	41	51	52	81	32	82	99	63	7	79	8	95
Mg	54	40	46	63	85		88	96	83	49	76	33	98
Mn	52	37	44	62	88	72	90	99	77	45	80		100
Na	89	41	44	62	86	44	56	78			92		
P	85	89	87		71		99	98	76	91	61	46	97
Ti				9	3								
As		55	51	42	72	43							
Ba	−1	1	1	2		1	0		3	−2	−3		
Be							8	8					0
Cd	92	72	84	61	98		98		80	39	98		103
Co	42		30		49		64		54	41	65		86
Cr	16	10		20			41		39				
Cs			51	24		12				18		8	
Cu	81	34	37		92		73	97	75				98
Hg	−7	−1		7			−4	8		6		9	0
La								8					0
Mo		7	3				6				59		
Nb		6	2			−9	8	8		3	3	3	0
Ni	29	20	23		51			82	50		56		86
Pb	2	0	0	1						4		−1	
Sc								8					0
Sn			4				6	6					2
Sr													
U	62	65	63	50	72	37			58	23			81
V		52	54	51			60		69	48	92	41	
W		6	2	7	0	10	8	8	0	6	7	9	0
Y											7		
Zn	85				87		93	100	64	35		45	96
Zr	−6			2	−8	1	−8					4	
	S14	S15	S16	S17	S18	S19	S20	S21	S22	S23	S24	S25	S26
Si		7								6		7	
Al	32			65				59	63	61	47	25	93
Ca		26	6		6				11	17	9		
Fe			63			48			38	70		17	
K	48		66	40	83	31		84	36	24	48	19	95
Mg	78	52		68	78	56		67	67	51	86		98
Mn	83	74	86	74	86	66		76	76	79	91		100
Na		35		48	85	39		87	46	24	44	24	70
P	79	62		68	75	69		64	80	78		89	102
Ti		8		5						7			
As	58	58		58				69	31				
Ba				−3	−3	−3			2	0	1	3	
Be											9		0

Table 2 (Continued)

	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12	S13
Cd			96	76				100		80	96	19	100
Co			73	49	68				52	58			88
Cr						13			14	19			
Cs													
Cu			77	65				88			81	41	89
Hg	10		7		-2	7	-2		10			2	0
La	0		3										0
Mo						40		56				3	3
Nb	0		4	-5	5								0
Ni				37	47							23	73
Pb	3		4			1	1				6	5	
Sc													0
Sn	1			2					5			2	1
Sr				5	3	-2							
U			77	56	61	56		67				37	
V	49		73	54	77	38		72		54			
W	0		4	1		7		5	10	-4		2	0
Y													0
Zn	93		92	63	94	58		79			76	36	101
Zr		-2								-8		1	

The high recovery percentage is also true for trace elements, albeit many of these are present only in single digit ppm concentrations (Table 4). Trace metal leaching is most efficient for Cd, with 92% removed, Zn/85% and Cu/75%, followed by Co/65%, Ni/65%, U/59% and V/53%. Cesium/86%, arsenic/72%, molybdenum/65% and chromium/28% are also dissolved but the discrepancies between evaluations based on effluent and solid residue are more than 10%. Ba, Hg, Nb, Pb, Sr, W and Zr are not leached. The results for Be, Cs, La, Sc and Y were inconclusive.

4. Summary and recommendations for ash utilization and aftertreatment

The study embraced 26 samples, including fly ashes and bottom slags from the combustion of wood chips, used wood, bark, peat and waste. Different combustion forms and stabilized ashes were discussed. Results were based on the analyses of solution and solid residue, i.e., we calculated percent recovered as well as removed.

We observed a neutralizing capacity after 10 days, ranging from around 5 l H₂SO₄ (1 M) per kg dry peat fly ash or bottom ash from CFB units, to around 15 l/kg for fly and bottom ash from the combustion of wood chips or bark. The latter corresponded to 71% of the neutralizing capacity of CaO.

The main ash components were affected dissimilarly. Whereas Si was not transferred to the aqueous phase, K, Na, Mg, Mn, and P were almost completely dissolved. Al was dissolved to 50–70% and Fe to around 45%. Higher amounts of Al and K remained in the residue for CFB units than for roaster units. Ca, Ba, Ti and the trace elements Pb and

Table 3
Average percent removed, grouped by category

Element	Waste/fly (%)	Waste/slag (%)	Waste, coal, used wood/fly (%)	Waste, coal, used wood/bottom (%)	Coal, used wood/fly (%)	Coal, used wood/bottom (%)	Biofuels/fly and bottom (%)
Si	N/A	2	N/A	3	N/A	7	6
Al	67	46/CFB19	62	46	49	N/A	59/CFB25
Ca	8	19	7	20	6	27	15
Fe	41	43	45	44	63	48	49
K	80	27/CFB7	71	27	59	31	66/CFB19
Mg	73	53	74	53	75	54	79
Mn	75	67	78	68	82	70	80
Na	89	44	81	42	67	37	51
P	72	74	73	71	74	66	95
Ti	3	8	4	8	5	9	N/A
As	71	39	64	44	58	58	53
Ba	<1	1	-1	<1	-3	-3	1
Cd	94	60	91	60	86	N/A	82
Co	53	50	57	50	63	N/A	67
Cr	28	18	28	17	N/A	13	26
Cu	84	N/A	80	N/A	71	N/A	69
Hg	-5	8	1	8	5	7	1
Mo	58	N/A	58	41	N/A	41	5
Nb	3	-1	1	-1	1	N/A	4
Ni	46	N/A	45	N/A	42	N/A	51
Pb	2	1	3	1	4	1	3
Sn	N/A	5	2	5	2	N/A	4
Sr	N/A	N/A	4	-2	4	-2	N/A
U	65	36	65	41	65	56	62
V	78	49	70	46	63	38	56
W	3	6	3	6	2	7	4
Zn	79	40	82	46	86	58	84
Zr	-7	<1	-7	<1	N/A	-2	-4

N/A means that we have >10% unaccounted material when calculating balances.

Sr formed insoluble sulfates. Hg formed insoluble sulfides or sulfates and Ti, Sn and Zr unleachable oxides.

Trace metal leaching was most efficient for fly ashes from waste combustion and for all bioashes, due to high specific areas and complete combustion/oxidation. Cd was leached to 94%; Cu 84%; Zn 79%; V 78%; As 71%; U 65%; Co 53%; Ni 46%; and Cr 28%. The percentages appeared to be independent of the fractions in the ash, but slightly lower values were observed for slags and bottom ashes, due to incomplete combustion. Nb, W, Y and Zr were not leached. Mo was leached to 58% in waste fly ashes, but the results were inconclusive for Mo in bioashes due to low concentrations.

Ashes from biofuels, except peat, have great prospects to replace limestone for pH control and precipitation in biohydrometallurgical processing of mineral sulfides. This will require a modest (ca. 45%) increase in the mass of fresh alkali, but the mass of the corresponding solid residue will be reduced by as much as 60%. Bioashes have stable qualities and contain

Table 4
Average concentrations in the untreated ashes: grouped by category

Element	Waste/fly (mg/kg)	Waste/slag (mg/kg)	Waste, coal, used wood/ fly (mg/kg)	Waste, coal, used wood/ bottom (mg/kg)	Coal, used wood/fly (mg/kg)	Coal, used wood/bottom (mg/kg)	Biofuels/fly and bottom (mg/kg)
Si	(85200)	269000	(79800)	232000	(71600)	123000	139000
Al	52900	62500	49300	62500	41000	(93400)	34400
Ca	209000	106000	197000	99000	174000	63500	135000
Fe	51900	83700	45700	89200	20700	106000	11500
K	27100	16100	19900	16700	11000	20400	48400
Mg	20400	13300	16100	13900	9090	15500	22100
Mn	1970	1550	1790	1670	1550	1970	11400
Na	29600	26800	23500	20800	11300	8940	6950
P	5520	3370	4490	3000	2780	2240	13000
Ti	10400	7730	10600	7830	10900	8030	(779)
As	185	23	101	20	18	11	50
Ba	1952	1490	2790	2240	4060	5970	1110
Cd	145	5.0	105	5.0	5.8	(0.26)	7.9
Co	27	22	62	22	110	(50)	7.6
Cr	422	469	422	438	(250)	344	94
Cu	1760	(7080)	1280	(5570)	316	(1060)	128
Hg	14	0.11	7.2	0.10	2.5	0.10	0.24
Mo	21	(12)	21	8.9	(7.1)	8.9	6
Nb	12	9.4	7.1	9.4	6.0	(9.8)	6
Ni	117	(167)	105	(153)	81	(111)	33
Pb	4730	1140	2640	1090	561	967	81
Sn	(257)	134	20	134	20	(28)	20
Sr	(390)	(344)	440	512	440	512	(706)
U	2.2	2.4	2.2	2.6	2.2	3.3	0.82
V	54	42	48	49	44	76	51
W	61	58	61	59	60	60	60
Zn	13800	2970	19600	2790	25500	2540	1950
Zr	224	294	123	273	(112)	193	74
S	31200	4980	28600	4390	24800	2610	6830

Figures in parentheses show leaching resulted in >10% unaccounted material.

only small concentrations of environmentally hazardous or technically pesky elements. We note that the process water will contain high concentrations of Na^+/K^+ and SO_4^{2-} ions and that this issue has to be addressed in an environmental assessment plan.

Treacherous ashes from waste incineration or the combustion of used wood and other metal containing fuels, including low rank coals, are best treated in a separate, forced acid leaching process. This process can rely on surplus acid from bioleaching of sulfidic ores or other industrial processes.

Fly ashes contain fine particles with high specific area and completely oxidized metals. No grinding or sieving is needed and other aftertreatments (stabilization, etc.) should be avoided. Extended storage times are detrimental and lead to gas evolution, from carbonatization, during acid leaching.

Bottom ashes/slags can be treated in the same process as fly ashes, but metallic parts should be separated by sieving, magnetic separation or flotation before leaching. These

results also suggest that acid leaching can be part of a scheme to reduce the negative environmental impacts of ashes, deposited from the combustion of low rank coals.

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