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Recovery and separation technologies for selected elements and ashes - Report on experimental work

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Material Value Chains

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Recovery and separation technologies for selected elements and ashes
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Name of the report: Recovery and separation technologies for selected elements and ashes - Report on experimental work

Key words: ash, leaching, rear earth elements

Summary

The objective of this study was to determinate the contents of Antimony (Sb), Gallium (Ga), Germanium (Ge) and Rear Earth Elements (REEs) in a selected WtE ash sample and study their leaching behavior in acid conditions from the hydrometallurgical characterisation point of view. The study was conducted for a single fly ash sample from a bubbling fluidized bed boiler, where the main fuels are wood based solid biofuels, biosludge, peat and solid recovered fuel (SRF).

The major elements in “WtE fly ash” sample were silicon (Si), calcium (Ca), aluminium (Al), iron (Fe), magnesium (Mg), potassium (K) and sodium (Na), present typically in different silicates, oxides and carbonates. Additionally, the ash was characterised by elevated concentrations of phosphorus (P), antimony (Sb), zinc (Zn), copper (Cu) and lead (Pb), from which P and Sb being pointed out as CRMs. Analyses indicated that Sb and Ge are present in the ash in concentrations clearly higher than the average in the Earth crust.

The hydrometallurgical characterisation trials revealed that maximum leaching for the most of the elements of interest was achieved at pH 1 (Sb) or pH 0.5 (REEs), main exception being Ge. For Germanium the maximum leaching was obtained at neutral and alkaline conditions. However, more trials at different pH-values and with a denser spacing of pH-values should be carried out in order to define the ideal pH-conditions for target elements. Sequential leaching experiments are also needed to avoid the effect of disturbing elements.

The work also showed that composition analysis of ashes is extremely challenging. Especially this is the case with new critical and valuable elements, with growing interest. The laboratories do not have the expertise neither routine methods to analyse them reliably and accurately enough. Also the mineralogical characterisation of waste materials, like ashes for hydrometallurgical purposes requires development.

Helsinki, October 2015

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1 Background and objectives

Knowing the contents of valuable elements and materials in waste-to-energy ashes is the first step towards being able to extract more resources from the ashes. A possible recovery of these materials from the ash may result in an income that can help to reduce the overall cost of management of combustible waste and as a side benefit, the remaining ashes may have lower concentrations of contaminants, thus being more appropriate for provisions such as construction material or easier to manage.

Data on valuables in the waste-to-energy ashes has been very limited and the same applies, for example, for the distribution of substances between the fly and bottom ash. Deep knowledge of the elemental composition of the ash is however a prerequisite for exploitation of the potential added value of these materials in ashes and development of innovative ash processing and recovery concepts and technologies. Therefore the starting point of the recovery development work in the context of ash theme in ARVI during FP1 was to review the current knowledge about critical materials in ashes, especially in Waste-to-Energy ashes. The outcome of this reviewing work is published as a separate report in ARVI Portal (Laine-Ylijoki et al. “Review on Elemental Recovery Potential of Ashes; ARVI Deliverable: D4.4-1, D4.4-2 & D2.5-1).

This report summarises the experimental work on hydrometallurgical characterisation of a selected ash sample done under Ashes theme during ARVI FP1. The objective of these investigations was to determine the contents of Antimony (Sb), Gallium (Ga), Germanium (Ge) and Rear Earth Elements (REEs) in a selected Waste-to-Energy ash sample and study their leaching behaviour in acid conditions from the hydrometallurgical characterisation point of view. The target elements (i.e. Sb, Ga, Ge and REEs) and potential leaching technologies for their separation were selected based on the above-mentioned review and discussions with involved organisations and companies in ARVI Ashes theme.

2 Materials and methods

2.1 Sample

A single fly ash sample from a bubbling fluidized bed boiler, in this report referred to as “W-to-E fly ash” was received for the study. Visually the ash sample was best described as brown greyish fine grained dry ash. The main fuels of the boiler are wood based solid biofuels. Additional fuels include biosludge, peat and solid recovered fuel (SRF).

2.2 Leaching tests

The leaching behaviour of the sample in terms of environmental acceptability (utilization, landfill disposal) were studied using the two stage batch leaching test EN 12457-3. In the test a solid sample with particle size below 4 mm is agitated with demineralised water for 6 hours first at a liquid-to-solid ratio (L/S) of 2. The eluate and the solid are separated by filtration (0.45 µm membrane). The solid is subsequently agitated for 18 hours with demineralized water at L/S 8 after which the eluate is again separated by filtration. The concentrations of leached components in both collected eluates are measured.

Acid leaching of valuable components from the ash sample was studied using the pH-dependence test (CEN/TS 14997). In the test a solid sample (15, 30 or 60 g) with particle size below 1 mm is mixed with distilled water for 48-hours at L/S ratio about 10. The pH-level of the mixture is kept at the predetermined pH-value (pH range 4-12) by using an automated pH-titrator. The eluate is separated by filtration. Constituents of interest are determined from the eluates.

2.3 Analytical methods

Elemental composition of the sample was determined by using Axios mAX 3 kV X-ray spectrometer and semi-quantitative fundamental parameters program (RRFPO). The method is applicable for fluorine and elements heavier than fluorine, and a typical detection limit is approximately 0.01 w-%.

XRD analysis was performed using Philips X’Pert MPD X-ray diffractometer and a powder methdod. With the method crystalline phases contained in a sample can be identified.

For elementary analysis the sample was grinded in carbon steel bowl and dissolved in accordance with SFS-EN 13656 by microwave assisted digestion with hydrofluoric, nitric and hydrochloric acid mixture. The produced eluate was analysed for Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Rb, S, Sb, Se, Si, Sr, Th, Tl, U, V, Zn, Ce, Dy, Er, Eu, Ga, Gd, Ge, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm, Y and Yb by ICP-MS.

Total organic carbon (TOC) was determined according to standard SFS-EN 13137 using an element analyser . In the method, solid sample is combusted in an oxygen flow (1400 ºC), and carbon dioxide formed in combustion is determined on an IR-detector. Before combustion, the sample is acidified with phosphoric acid to remove inorganic carbon.

Leaching test eluates were analysed for concentrations of elements as described above. Chloride, fluoride and sulphate concentrations were determined with ion chromatography (IC). Concentrations of dissolved organic carbon (DOC) were analysed using accredited method according to the standard SFS-EN1484:1997, the principle of the method being similar to the determination of TOC. The pH, conductivity and redox-potential of the eluates were also measured.

3 Results

3.1 Composition

3.1.1 XRF

Results from XRF-analysis are shown in

Element, %	"W-to-E fly ash"
Al	8.3
Ba	0.13
Ca	10
Cl	0.25
Co	0.02
Cr	0.03
Cu	0.05
Fe	5.6
K	1.7
Mg	1.3
Mn	0.37
Na	1.6
Ni	0.01
P	2.0
Pb	0.04
Rb	0.01
S	0.71
Sb	0.01
Si	21
Sr	0.03
Ti	0.49
Zn	0.18
Zr	0.02

. Indicative results from elementary analysis are shown in Appendix 1.

Table 1. Semi-quantitative elemental composition of the ash sample (XRF). Concentrations of elements are expressed in percentages of weight (%). Elements heavier than fluorine withy concentrations ≥0.01% are shown.

Element, %	"W-to-E fly ash"
Al	8.3
Ba	0.13
Ca	10
Cl	0.25

Co	0.02
Cr	0.03
Cu	0.05
Fe	5.6
K	1.7
Mg	1.3
Mn	0.37
Na	1.6
Ni	0.01
P	2.0
Pb	0.04
Rb	0.01
S	0.71
Sb	0.01
Si	21
Sr	0.03
Ti	0.49
Zn	0.18
Zr	0.02

3.1.2 XRD

The diffractogram obtained in XRD analysis is shown in Figure 1.

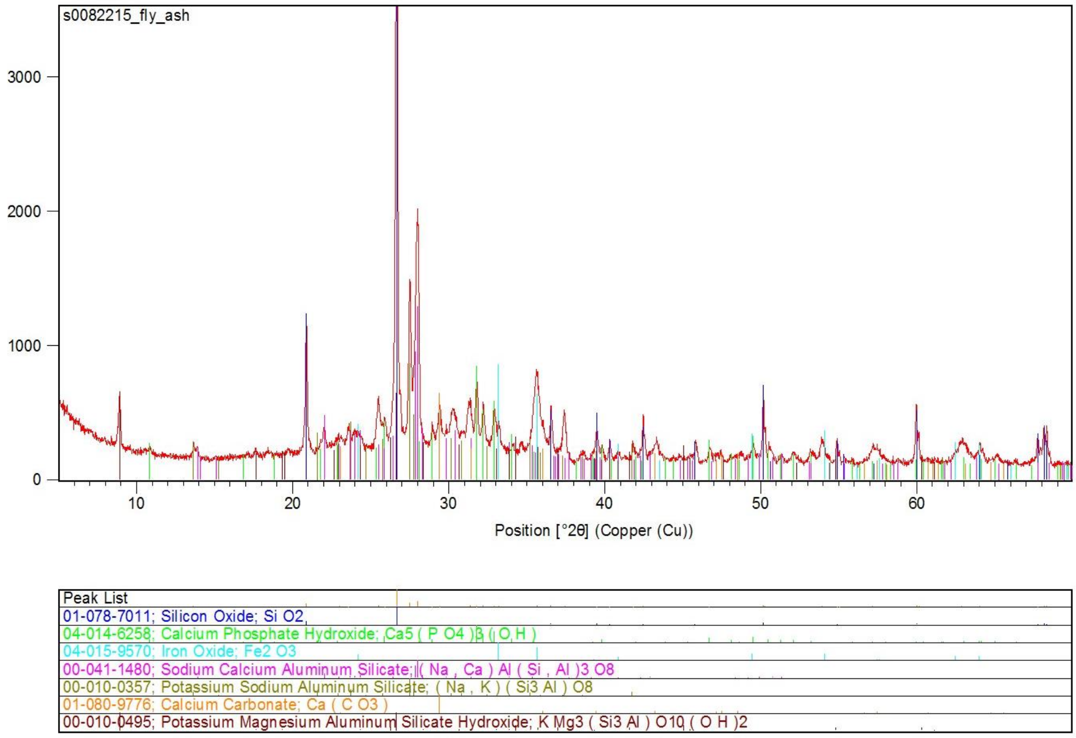

Figure 1. Diffractogram of the fly ash sample "W-to-E fly ash".

Based on elemental composition (see 3.1.1) and diffractogram (Figure 1) the following crystalline phases were identified in the fly ash sample:

- Silicon Oxide, SiO_2
- Calsium Phosphate Hydroxide, $Ca_5(PO_4)_3(OH)$
- Iron Oxide, Fe_2O_3
- Sodium Calcium Aluminum Silicate, $(Na, Ca)Al(Si, Al)_3O_8$
- Potassium Sodium Aluminum Silicate, $(Na, K)Al(Si_3, Al)_3O_8$
- Calcium Carbonate, $CaCO_3$
- Potassium Magnesium Aluminum Silicate Hydroxide, $KMg_3(Si_3Al)O_{10}(OH)_2$

3.2 Environmental leaching behaviour

Table 2 shows the results from two stage batch leaching test EN 12457-3. For comparison, landfill acceptability criteria for an EU landfill receiving non hazardous waste are also shown together with leaching criteria for ashes included in the Finnish Government Decree concerning the recovery of certain wastes in earth construction (1825/2009). It is to be noted, that the decree does not cover ashes that are generated with fuels containing waste, e.g. SRF.

Table 2. Leaching of contaminants from the ash sample in the two stage batch leaching test EN 12457-3 in cumulative L/S ratio 10 and corresponding limit values for landfill disposal and earth construction. The amounts of leached elements and limit values are expressed in mg/kg dry matter.

Parameter	**"W-to-E fly ash"**	**EU landfill for non hazardous waste**	**Finnish government decree (1825/2009) for ashes in earth construction, covered by bituminous coating***
pH (L/S 8 eluate)	12.5	-	-
Leached substances, mg/kg dry matter			
As	0.03	2	1,5
Ba	5.5	100	60
Cd	<0.01	1	0.04
Cr	1.5	10	3
Cu	0.12	50	6
Hg	<0.0002	0,2	0.01
Mo	1.6	10	6
Ni	<0.01	10	1.2
Pb	2.3	10	1.5
Sb	0.02	0.7	0.18
Se	0.02	0.5	0.5
V	0.02	-	3,0
Zn	4.8	50	12
Cl^-	1 700	15 000	2 400
F^-	17	150	50
SO_4^{2-}	3 600	20 000	10 000
DOC	9.7	800	500

*Note: the decree does not cover ashes that are generated with fuels containing waste, e.g. SRF.

3.3 Acid leaching of target elements

Table 3 shows the leached amounts of target elements in the pH-dependence test (CEN/TS 14997). The results for all studied components are shown in Appendix 2.

Table 3. Leaching of target elements as a function of pH in acid leaching experiments. The amounts of leached elements are expressed in mg/kg dry matter.

Element	**“W-to-E fly ash”**			
Target-pH	***pH 0.5***	***pH 1.0***	***pH 4.0***	***pH 11.3***
H^+ consumption, mol/kg	13	10	2.4	no pH adjustment
Leached elements, mg/kg dry matter				
Sb	6.8	11	0,38	0.11
Ce	46	0.07	0.09	0.11
Dy	1.6	0.21	0.18	0.13
Er	0.85	0.08	0.12	0.17
Eu	0.59	0.10	0.11	0.14
Ga	8.1	0.62	0.57	0.54
Gd	2,8	0.12	0.21	0.14
Ge	0.16	2.5	3.1	3.4
Ho	0,35	0.04	0.05	0.05
La	21	0.11	0.15	0.15
Lu	0.09	0.07	0.08	0.09
Nd	18	0.25	0.29	0.25
Pr	6.0	0.07	0.08	0.08
Sm	2.9	0.33	0.26	0.36
Tb	0.51	0.05	0.06	0.07
Tm	0.11	0.05	0.05	0.07
Y	8.4	0.12	0.15	0.17
Yb	0.58	0.10	0.19	0.22

4 Conclusions and insights for further work

Based on composition determinations done in this study the major elements in "W-to-E fly ash" sample, as typical for these types of fly ashes (see also Laine-Ylijoki et al. 2014), were silicon (Si), calcium (Ca), aluminium (Al), iron (Fe), magnesium (Mg), potassium (K) and sodium (Na). These compounds were mostly present as different silicates, oxides and carbonates. Additionally, the fly ash sample was characterised by elevated concentrations of phosphorus (P), antimony (Sb), zinc (Zn), copper (Cu) and lead (Pb), from which P and Sb being pointed out as critical elements. Sb is however from the environmental point problematic as leaching of it increases in aged ashes limiting often the utilisation of ashes in earth constraction. Environmentally harmful Pb on the other hand brings up challenges being very leachable in high pH-values typical for fresh wood-based ashes (see table 2).

Analyses indicate that Sb and Ge are present in the ash sample in concentrations clearly higher than the average in the Earth crust. For example the average antimony content has been estimated to be less than 1 ppm. The most part of the economic potential have been estimated to magnesium, present in ashes in large volumes. On the other hand, the others have a remarkably higher market prices (in pure metallic form).

Hydrometallurgical characterisation trials revealed that maximum leaching for the most of the elements of interest was achieved at pH 1 (Sb) or pH 0.5 (REEs), main exception being Ge. For Germanium the maximum leaching was obtained at neutral and alkaline conditions. Examples of observed leaching behaviour are shown in Figure 2. However, more trials at different pH-values and with a denser spacing of pH-values should be carried out in order to define the ideal pH-conditions for target elements. Sequential leaching experiments are also needed to avoid the effect of disturbing elements.

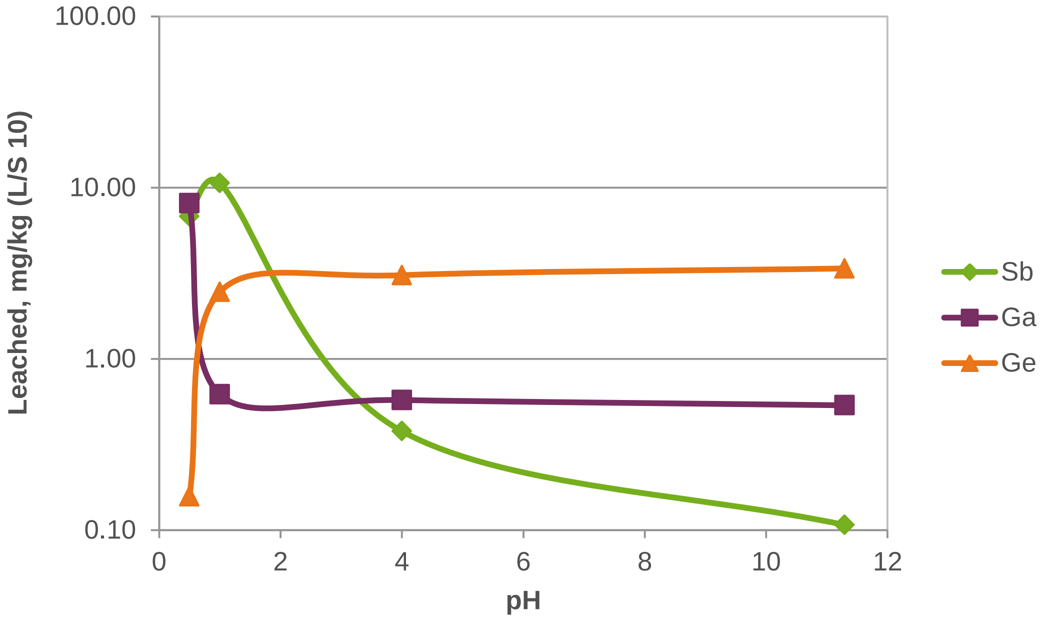

Figure 2. Leaching of Sb, Ga and Ge as a functin of pH in acid leaching experiments.

The work showed that composition analysis of ashes is extremely challenging. Especially this is the case with these new critical and valuable elements, with growing interest. The laboratories do not have the expertise neither routine methods to analyse them reliably and accurate enough. Also the mineralogical characterisation of waste materials, like ashes for hydrometallurgical purposes reguires development.

5 References

Laine-Ylijoki, J., Bacher, J., Kaartinen,T., Korpijärvi, K., Wahlström, M. & zu Castell-Rüdenhausen, M., (2014). Review on Elemental Recovery Potential of Ashes, ARVI DeliverableD4.4-1 (D4.4-1, D4.4-2 & D2.5-1).

Concentrations of elements in the ash sample determined by acid digestion according to EN 13656 and ICP-MS analysis. Concentrations of elements are expressed in mg/kg dry matter.

Element, mg/kg	**“ W-to-E fly ash”**
Sb	36
Ce	16.4
Dy	0.28
Er	0.17
Eu	0.24
Ga	22.6
Gd	0.46
Ge	16.3
Ho	0.07
La	6.24
Lu	<0.05
Nd	2.83
Pr	1.13
Sm	0.39
Tb	<0.1
Tm	<0.1
Y	1.35
Yb	0.11
Ag	2.53
Al	10800
As	<50
B	229
Ba	885
Be	3.23
Bi	4.44
Ca	27000
Cd	5.15
Co	22.3
Cr	245
Cu	583
Fe	61800
K	18600
Li	45.8
Mg	5070
Mn	4340
Mo	10.6
Na	12800
Ni	136
P	20600
Pb	398
Rb	76.5
S	<5000
Se	<5.0
Si	203000
Sr	221
Th	1.52
Tl	1.62
U	2.91
V	60.4
Zn	2080

Results from pH-dependence tests CEN/TS 14997 at L/S 10 l/kg dry matter. Amounts of leached substances are expressed in mg/kg dry matter.

Element	**"W-to-E fly ash"**			
Target-pH	0.5	1.0	4.0	11.3
H^+ consumption. mol/kg	13	10	2.4	no pH adjustment
Leached elements. mg/kg dry matter				
Ag	0.01	0.01	<0.01	<0.01
Al	36000	9700	810	2400
As	13.8	19	0.16	0.01
B	140	130	65	<0.50
Ba	24	26	5.8	38
Be	0.78	1.0	0.08	<0.01
Bi	0.37	0.42	0.01	<0.01
Ca	87000	86000	46000	2400
Cd	1.6	2.3	1.4	<0.01
Co	4.9	6.5	3.3	0.01
Cr	29	38	0.22	0.18
Cu	64	56	5.1	0.27
Fe	12000	10000	8.9	1.5
K	11000	11000	2700	830
Li	20	24	3.3	0.55
Mg	4400	4300	2200	1.0
Mn	1400	1800	480	0.09
Mo	1.8	1.6	0.11	1.0
Na	7800	7500	1500	520
Ni	22	32	20	0.01
P	16000	16000	5.3	1.4
Pb	72	85	1.2	0.04
Rb	46	61	8.1	4.2
S	4900	5300	4700	49
Se	0.42	0.53	0.10	0.01
Si	27000	29000	1600	6.2
Th	0.91	1.2	<0.01	<0.02
Tl	0.23	0.34	0.13	0.01
U	0.98	1.2	0.04	<0.01
V	28	37	0.09	0.04
Zn	450	640	580	2.7