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VTT Technical Research Centre of Finland Ltd.

Review on Elemental Recovery Potential of Ashes

ARVI Deliverable (D4.4-1, D4.4-2 & D2.5-1)



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Material Value Chains



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Key words: Ash, critical elements, waste-to-energy, recovery technologies

Summary

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

The European Commission has identified 20 critical raw materials or metal groups. These are those that are considered vital for development in areas such as computers, electronics and electric vehicles and where the use is expected to increase significantly in the coming decades. Furthermore, the known assets of several of these substances concentrated in individual countries outside the EU. Knowledge and information of these substances in the waste-to-energy ashes is very limited and the same applies, for example, for the distribution of substances between the fly and bottom ash. There are some values reported in the literature but no major review has been made to cover the critical metals in a number of plants. A better knowledge of the elemental composition of the ash is a prerequisite for exploitation of the potential added value of these materials in ashes and selection of further ash processing and recovery concepts and technologies.

Based on this review the concentrations of critical elements in waste-to-energy ashes are generally lower than the average concentration in the earth upper crust. The exceptions are antimony, cobalt, silver, thallium and tungsten. Antimony and silver occur in elevated concentrations in fly ashes from waste-to-energy grate-fired and fluidized-bed boilers. Fly ashes from grate-fired boilers may also contain higher concentrations of germanium. Furthermore, elevated concentrations of silver, gold and antimony occur in waste-to-energy bottom ashes, whereas coal fly ashes contain germanium and gallium. Despite the relative low content, the critical materials in the ashes may still represent a yearly value of 0.1 billion Euros.

A better knowledge of the composition and speciation in ashes is vital in the choosing of treatment methods for the ashes and also for the possibility to recover valuable resources from the ashes. It will also be necessary to evaluate and prioritize these resources to focus efforts on those ashes with the highest amounts of target elements and those that can be effectively extracted from the specific ash matrix. Information in the recovery of scarce metals concerning costs and revenues, operational costs and investment costs are not available. Generally, the economic feasibility of a recycling technology to recover scarce metals depends at most on the local disposal cost. However, the retrofitting of existing ash treatment plants to a state-of-the art level is technological possible and economical feasible. These technologies would allow an optimised separation of liberated metal particles and the production of a mineral fraction suited for the substitution as a construction material.



Although no suitable patents were found in the patent survey, several chemical extraction techniques have been applied for scarce elements in ashes. Generally, these processes usually include chemically induced leaching of the material, often employing the use of low-pH acids together with varying temperatures and leaching times, depending on the composition of the ash. When choosing technologies for recovery, it is crucial to distinguish the varieties of ashes and the differences in their chemical and mineralogical compositions by a detailed material characterisation. When new processes for ashes develop, it will also be important to consider potential environmental impacts.

Helsinki, December 2014



Contents

1	Introduction	7
2	Background	8
2.1	Defining 'critical' raw materials	8
2.2	Supply and occurrence	9
2.3	Demand and outlook	11
3	Ashes as a source for critical materials	14
3.1	General characteristics of ashes	14
3.1.1	Fly ash characteristics	15
3.1.2	Bottom ashes	16
3.2	Presence of valuable elements in ashes	17
3.2.1	Concentrations in waste-to-energy ashes	17
3.2.2	Concentrations in MSW melting ash	20
3.2.3	Concentrations in municipal solid waste (MSW)	22
3.2.4	REEs in coal and coal ashes	23
4	Enrichment and recovery technologies	27
4.1	Mechanical treatment of ashes	27
4.1.1	Bottom ash treatment	28
4.1.2	Fly ash treatment	29
4.2	Chemical leaching	30
4.2.1	Fundamentals	30
4.2.2	Examples of ash leaching	32
4.3	Thermal processes	34
4.4	Industrial scale processes for ashes	35
4.4.1	FLUWA process	35
4.4.2	Ash Dec.	36
4.5	Emerging technologies	37
4.6	REE processing from secondary resources	37
4.7	Economical aspects	40
5	Conclusions	41
	References	43

APPENDIX 1. REE Recycling Operations, Technologies Utilized, Current Status, and Benefits

APPENDIX 2. Mechanical treatment technologies



1 Introduction

Resource scarcity is a dynamic concept, depending on many factors and varying over time. Different industries will hold very different view on which is the most importance resource for their businesses and the concept of supply risk varies by region and so various lists of critical elements or resources exist. Recently, prices of certain minerals and elements have been rising dramatically due to global supply shortages and increasing demands. These elements are vital components of advanced technologies, such as cell-phones, wind turbines, permanent magnets, and semi-conductors. Due this supply risk and Europe's high dependence on imports, the EU published in 2010 a list of 14 critical raw materials, the so called EU-14, materials on which the European economy depends but which might be at risk of supply disruptions.

Supply disruption could be feared if one country exerts a monopoly of supply (e.g. China for Rare Earth Elements) or because the mineral is mainly produced in politically or economically unstable regions (e.g. tantalum from the Democratic Republic of Congo). The European Commission has this year presented a revised list of Critical Raw Materials including 20 raw materials which are now considered critical by the European Commission: antimony, beryllium, borates, cobalt, chromium, gallium, germanium, indium, coking coal, fluorspar, magnesite, magnesium, natural graphite, niobium, phosphate, platinum group metals, heavy rare earths, light rare earths, silicon metal and tungsten.

This relative scarcity of certain valuable elements has prompted many companies to search for new mineral sources. In addition to new mining ventures and recycling wastes, e.g. municipal solid waste (MSW), plastics, Waste of Electrical and Electronic Equipment (WEEE) and End of Life Vehicle (ELV) fractions and ashes have been suggested as possible untapped resources. Ashes contain many common metals (e.g. Al, As, Cr, Ni, Se, Cu), but some ashes also contain elevated concentrations of rare earth elements (e.g. Ce, La, Ga, Ge) and strategic metals (e.g. Sb, Co). Several companies are currently exploring methods to extract valuable elements from ashes and investigating whether ash processing can serve as an economical and environmentally friendly alternative to traditional mining.

There are varieties of methods in use for recovery of different elements and metals. These include pyrometallurgical, hydrometallurgical and bio-hydrometallurgical methods. Pyrometallurgical recovery is thermal treatment with material typical processes such as calcining, roasting, smelting and refining. Hydrometallurgical recovery uses mainly the leaching process, involving the use of aqueous solutions containing specific extraction agents, which is brought into contact with the material. Biohydrometallurgy is one of the most promising and revolutionary biotechnologies. This technique exploits microbiological processes for recovery of metal ions.

This document reviews the current knowledge of the elemental composition of ashes and gives a short summary on recovery of potentially ash related elements. The focus is on waste-to-energy ashes and critical raw materials. The review also includes a survey on recent patents regarding recovery of valuable elements from ashes. Using the key words ash, valuable metals, and scarce metals no suitable patents were unfortunately available.



2 Background

Extensive work over the last several years has attempted to cover which elements and materials should be deemed critical. Determining material criticality is very time dependent and hinges conceptually on the “eye of the beholder.” The novelty and fluid nature of the marketplace also intensifies the difficulty in assessing which materials should be deemed critical. The public conversation about critical materials has been dominated by certain stakeholders, thus creating a hype regarding this issue that is counter-productive to finding viable solutions. This review will follow the conventions of the previous ash related studies and broadly define a “critical material” in terms of its relevance from waste-to-energy ashes point of view.

2.1 Defining 'critical' raw materials

The European Commission presented 2014 a revised list of Critical Raw Materials. The 2014 list (Figure 1) includes 13 of the 14 materials identified in the previous list of 2011, with only tantalum moving out of the list (due to a lower supply risk). Six new materials appear on the list: borates, chromium, coking coal, magnesite, phosphate rock and silicon metal bringing the number up to 20 raw materials which are now considered critical by the European Commission. The other 14 raw materials are: antimony, beryllium, cobalt, fluorspar, gallium, germanium, indium, magnesium, natural graphite, niobium, platinum group metals, heavy rare earths, light rare earths and tungsten.

Antimony	Beryllium	Borates	Chromium	Cobalt	Coking coal	Fluorspar
Gallium	Germanium	Indium	Magnesite	Magnesium	Natural Graphite	Niobium
PGMs	Phosphate Rock	REEs (Heavy)	REEs (Light)	Silicon Metal	Tungsten	

Figure 1. The 20 Critical Raw Materials currently listed by EU. (http://ec.europa.eu/enterprise/policies/raw-materials/critical/index_en.htm)

The following assessment components have been used in defining critical raw materials (see also Figure 2 below):

- Economic importance: this analysis is achieved by assessing the proportion of each material associated with industrial megasectors at an EU level. These proportions are then combined with the megasectors’ gross value added (GVA) to the EU’s GDP. This total is then scaled according to the total EU GDP to define an overall economic importance for a material.
- Supply risk: in order to measure the supply risk of raw materials, the World Governance Indicator (WGI) is used. This indicator takes a variety of influences into account such as voice and accountability, political stability and absence of violence, government effectiveness, regulatory quality, rule of law or control of corruption. (http://ec.europa.eu/enterprise/policies/raw-materials/critical/index_en.htm)

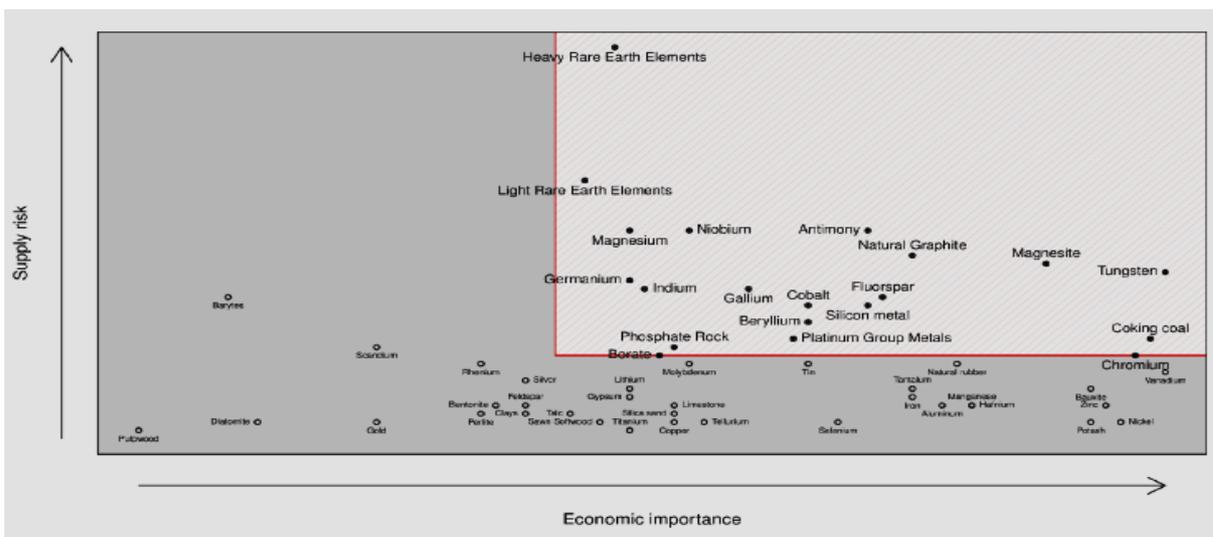


Figure 2. Assessment components in defining Critical Raw Materials.
(http://ec.europa.eu/enterprise/policies/raw-materials/critical/index_en.htm)

2.2 Supply and occurrence

Geological deposits and production through mining of certain elements are geographically highly concentrated in a small number of countries located outside the EU, such as Brazil, China, the DR Congo and South Africa. This means that about twenty countries supply approximately 80% of the critical materials when primary production is considered (Figure 3).

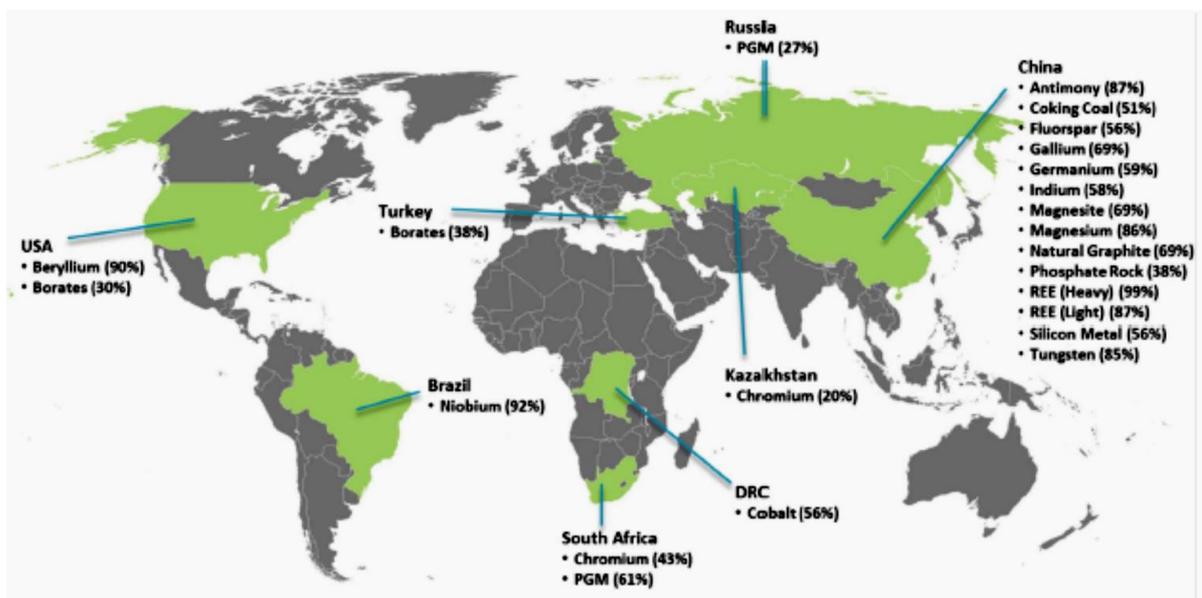


Figure 3. Major supplying countries of the EU Critical Raw Materials.
(http://ec.europa.eu/enterprise/policies/raw-materials/files/docs/crm-report-on-critical-raw-materials_en.pdf)

China holds the world's largest reserves of antimony (56%), tungsten (67%) and REEs (58%), and accounts for 91%, 75% and 97% of global production respectively. While the geological availability of most critical materials is potentially high, access to the critical materials' markets of exporting countries has nevertheless become increasingly difficult. (Grieger 2013)



There is also a big difference between how common the different critical materials are seen to the average content in the earth's crust. Figure 4 shows the average content of various elements in the upper crust.

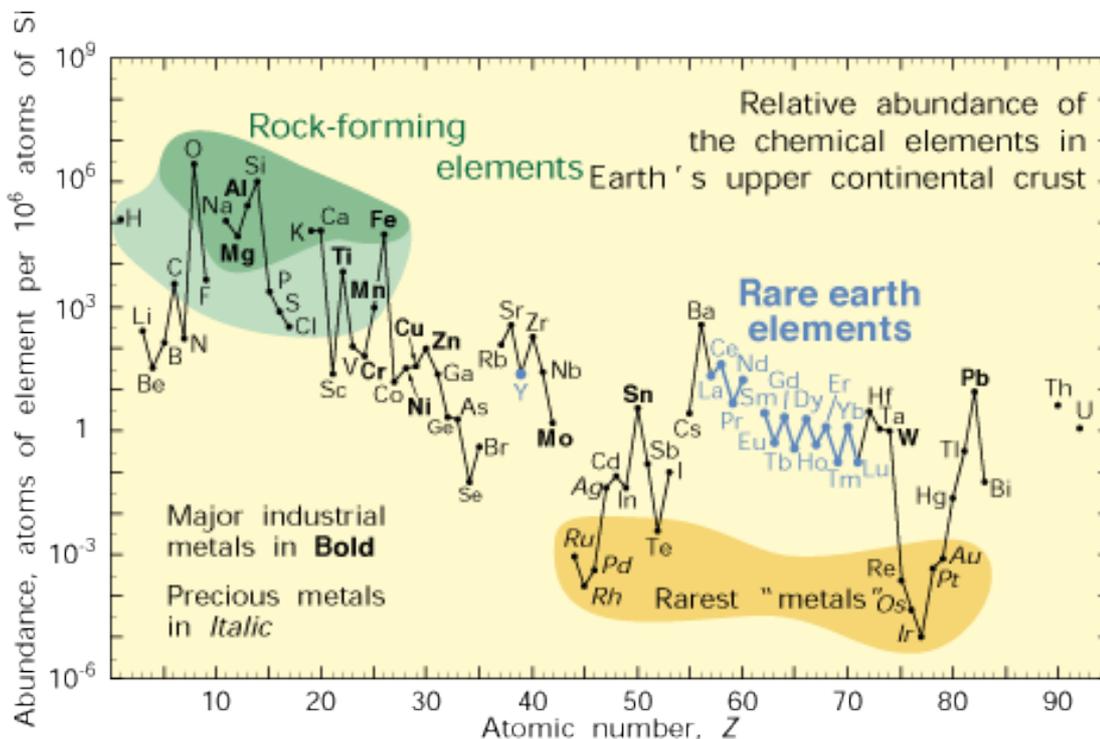


Figure 4. Abundance (atom fraction) of the chemical elements in Earth's upper continental crust as a function of atomic number. Many of the elements are classified into (partially overlapping) categories: (1) rock-forming elements (major elements in green field and minor elements in light green field); (2) rare earth elements (lanthanides, La–Lu, and Y; labeled in blue); (3) major industrial metals (global production >~3x10⁷ kg/year; labeled in bold); (4) precious metals (italics); and (5) the nine rarest “metals”—the six platinum group elements plus Au, Re, and Te (a metalloid). (U.S.G. Survey 2002)

The criticality of a material does not necessary mean, that a material or element is rare. For example the lanthanides, yttrium, and scandium are commonly referred to as REEs are common mineral constituents as compared with many other metal elements (Table 1). The term “rare” is a carryover from metallurgical chemists from around the 1940s. The metallurgical processes needed to isolate the individual metal species are complex, and early technology prevented commodity-level production. As a result, lanthanide metals or metal oxides (i.e., REOs) were difficult to obtain and thus are considered rare. (US EPA 2012)

On the other hand, for example, antimony is a rare element, belonging to the 7th tier (in decreasing order, out of 9) of the order of abundance of the elements. The average antimony content of the Earth's crust has been estimated at 0.20001% (i.e. 1 ppm (parts per million, equivalent to grams per metric tonne)). Most antimony lodes occur in volcanic and sedimentary rocks. Deposits have an average antimony content of between 0.1 and 2 wt.%. (http://ec.europa.eu/enterprise/policies/raw-materials/files/docs/crm-critical-material-profiles_en.pdf)



Table 1. Abundance of Elements in the Earth's Crust. (US EPA 2012).

Elements	Crustal Abundance (parts per million)
Nickel ($_{28}\text{Ni}$)	90
Zinc ($_{30}\text{Zn}$)	79
Copper ($_{29}\text{Cu}$)	68
Cerium ($_{58}\text{Ce}$)^a	60.0
Lanthanum ($_{57}\text{La}$)	30.0
Cobalt ($_{27}\text{Co}$)	30
Neodymium ($_{60}\text{Nd}$)	27.0
Yttrium ($_{39}\text{Y}$)	24.0
Scandium ($_{21}\text{Sc}$)	16.0
Lead ($_{82}\text{Pb}$)	10
Praseodymium ($_{59}\text{Pr}$)	6.7
Thorium ($_{90}\text{Th}$)	6
Samarium ($_{62}\text{Sm}$)	5.3
Gadolinium ($_{64}\text{Gd}$)	4.0
Dysprosium ($_{66}\text{Dy}$)	3.8
Tin ($_{50}\text{Tn}$)	2.2
Erbium ($_{68}\text{Er}$)	2.1
Ytterbium ($_{70}\text{Yb}$)	2.0
Europium ($_{63}\text{Eu}$)	1.3
Holmium ($_{67}\text{Ho}$)	0.8
Terbium ($_{65}\text{Tb}$)	0.7
Lutetium ($_{71}\text{Lu}$)	0.4
Thulium ($_{69}\text{Tm}$)	0.3
Silver ($_{47}\text{Ag}$)	0.08
Gold ($_{70}\text{Au}$)	0.0031
Promethium ($_{61}\text{Pm}$)	10^{-18}

^a Lanthanides (lanthanoids), scandium and yttrium are presented in boldface type

2.3 Demand and outlook

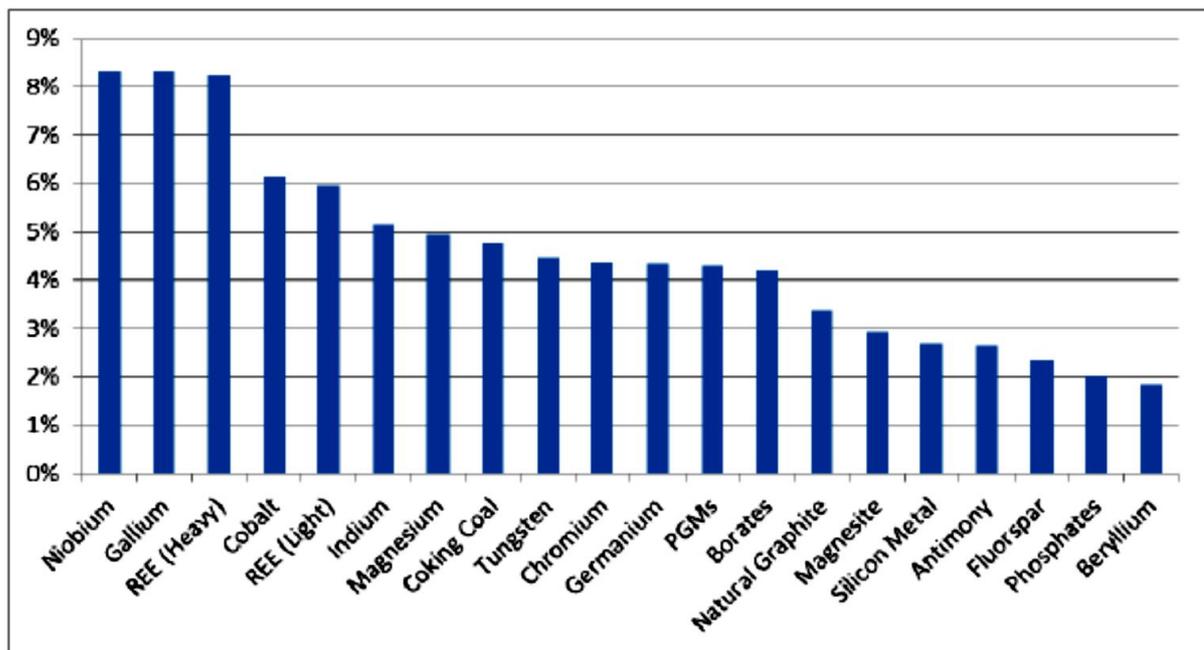
Our current society and industry is highly dependent on these critical high-tech materials, which are essential in the manufacture of advanced technological products, such as circuit boards, semiconductors, coatings, magnets, mobile phones, computers, home electronics, and solar panels (Table 2). The use of electronic products is increasing globally. The fastest growing sector globally is the advanced energy production. Furthermore the market of consumer electronics is growing especially in developing countries. Growth can be expected also in Western countries due to shorter product lifecycles and introduction of new products.



Table 2. The current main emerging technologies for the demand of certain critical raw materials. (http://ec.europa.eu/enterprise/policies/raw-materials/files/docs/crm-report-on-critical-raw-materials_en.pdf)

Antimony	Antimony tin oxide, micro capacitors
Lithium	Lithium-ion batteries
Cobalt	Synthetic fuels
REEs, e.g. Germanium, Gallium, Indium, Niobium, Tantalum	Fibre optic cables, IR optical technologies, thin layer photovoltaics, IC, WLED, displays and thin layer photovoltaics. micro capacitors and ferroalloys, permanent magnets, laser technology
PGMs, e.g. Platinum, Palladium	Fuel cells, catalysts, seawater desalination
Tantalum	Micro capacitors, medical technology

One further part of the extended analysis is to compile long-term forecasts for the supply and demand for each of the critical raw materials. It should be noted that a supply deficit/surplus does not necessarily imply a change in criticality of these materials. Figure 5 summarises the demand forecasts for each of the critical raw materials. All are predicted to experience demand growth, with lithium, niobium, gallium and heavy rare earth element forecast to have the strongest rates of demand growth, exceeding 8% per year for the rest of the decade. (Oakdene Hollins 2013)



Source: Roskill Information Services (September 2013) and other data in the extended profiles

Figure 5. Forecast average annual demand growth to 2020 for critical raw materials (% per year). (Oakdene Hollins 2013)



As the demand and use of these critical materials continuously increases, more and more of these materials end up into waste and therefore also into the combustion, although many of the uses of the critical metals are in products and applications that should not appear in the combustible waste in a large scale. For instance, there is already some indication of continuously increasing presence of e.g. magnesium, common in different packages; antimony, commonly used as plastic catalyst and fire retardant; and copper from electronic appliances in combustible waste. Naturally, waste-to-energy ashes will follow the same trend in the long run.



3 Ashes as a source for critical materials

The elemental composition and, thus, the properties of ashes are differing from a power plant to another depending on e.g. fuel, technology, boiler type and ash recovery system. Among different waste-to-energy technologies grate incinerators are dominating the sector. The installed waste-to-energy capacity of the largest waste management companies in the EU shows that fluidised bed combustion may have a share of 3–7 % of the treatment capacity (Vainikka 2011). Within fluidised bed combustion one can choose between two main types: bubbling fluidized bed (BFB) and circulating fluidized bed (CFB). Due to historic reasons Finland and Sweden have a higher proportion of fluidised beds. Here both fluidised bed combustion and gasification have been adopted.

Ash properties are also varying within a specific combustion plant in accordance with the output of the boiler, as well as the blend of fuels and their specific properties. The physical and chemical properties of ashes are determined by reactions that occur during the high-temperature combustion of fuel and the subsequent cooling of the flue gas. A considerable amount of research effort has been put into understanding how the ash is formed, its characteristics, and how it weathers in the environment.

3.1 General characteristics of ashes

Ash composition can be considered from two viewpoints: main components or minor substances (e.g. heavy and scarce metals). Usually research is focused on the concentration and leaching of harmful substances, which are usually used as basis for evaluation of the environmental acceptability of the ashes. Ashes (both fly and bottom ash) however also contain numerous compounds, such as Au, Ag, Pt, Pd, Sb, In, Co, Ga, Ge, Mg, Ta, W or REEs, with high strategic and economical value but existing at low concentration.

A variety of chemical analysis techniques are available for characterization of individual compounds and elements in such secondary waste materials as ashes. However, no analysis technique alone suffices to identify and analyse fully ashes. What appears to be a single phase under the optical microscope may turn out to be a mixture of several phases with different compositions when examined by scanning electron microscopy (SEM). The relative small grain size and complex intergrowths of secondary mineral assemblages, elements, precipitates and compounds can be extremely complicated to unravel.

Classical wet chemical analysis for determination of total content and composition is always important, because certain elements, such as arsenic, antimony, cadmium, selenium etc., are typically sequestered as minor constituent and their presence may not be apparent from a casual mineralogical examination. Many compounds in secondary materials also (1) occur as very fine-grained or poorly crystalline materials that can sorb and desorb metals, depending on local conditions, (2) form complex solid solutions that incorporate metals, and (3) are transient because they can precipitate and dissolve in a matter of hours depending on changes in the local environment. The most commonly used multi-element methods are inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and inductively coupled plasma-mass spectrometry (ICP-MS). Detection limits by ICP-MS are orders of magnitude lower than detection limits for other methods, so very low concentrations of elements can be measured by this method and it is increasingly becoming the method of



choice for trace element analysis of secondary material samples. (Hammarstrom & Smith 2002)

Mineralogical characterization of materials using instrumental analysis typically includes, besides rough microscopic examination, x-ray fluorescence (XRF), x-ray diffraction (XRD), scanning electron microscopy (SEM-EDS), and in some cases, electron probe microanalysis (EPMA). All these instrumental methods depend on fundamental principles involving interactions between electron beams and x-rays with samples. (Hammarstrom & Smith 2002)

3.1.1 Fly ash characteristics

Fly ashes (FA) are obtained from air pollution control (APC) systems and are often characterized by high concentrations of salts, heavy metals and organic trace-pollutants. A compilation of composition data of waste-to-energy fly ashes from the literature is shown in Tables 3 and 4. The Table 3 illustrates the major elements in fly ashes being typically: Si, Al, Fe, Ca, Mg, K and Na. These compounds are mostly present as oxide, chlorides, sulphates and carbonates. In practice, the most common options for the management of waste-to-energy fly ash/APC residues are the permanent storage in hazardous disposal site or treatment followed by disposal with less stringent requirements.

Table 3. Chemical composition of the major oxide on APC/fly ash residues in wt.%. (Quina et al. 2008)

	Auer et al, 1995		Alba et al, 1997		Romero et al, 2001	Li et al, 2003a	Piantone et al, 2003	Song et al, 2004		Cheng & Chen, 2004	Kim & Kim, 2004	
	ESP	FA	APC	FA	FA	FA+APC	APC	SDS	FF	FA	ESP	ESP_wash
CaO	19,3	24,3	27,7	29,34	13,9	24,2	52,9	25,2	19,7	19,5	26,2	
SiO ₂	20,2	18,8	15,0	11,47	8,57	33,6	5,8	4,7	19,4	7,3	21,9	
Al ₂ O ₃	12,3	12,7	7,1	5,75	3,9	11,6	2,8	1,8	10,1	3,2	9,97	
Fe ₂ O ₃	1,2	1,6	1,4	1,29	2,58	1,9	2,4	0,95	1,8	1,39	2,08	
MgO	2,5	2,6	1,9	3,02	3,16	2,2	2,6	1,3	2,8	2,61	8,32	
Na ₂ O	6,4	5,8	4,1	8,70	14,0	2,2	(a)	10,9	8,9	13,07	2,11	
K ₂ O	6,2	4,3	4,4	7,02	8,77	2,6	1,5	10,6	8,1	11,21	0,84	
TiO ₂	1,4	1,5	1,0	0,85	0,76	1,7	1,9	1,2	1,9	2,77	3,8	
SO ₃	8,3	6,4	8,2	(a)	15,36	(a)	6,7	8,0	(a)	9,76	11,93	
P ₂ O ₅	1,3	2,7	1,6	1,69	2,81	1,4	1,4	1,2	(a)	1,72	5,76	
MnO	(a)	0,12	0,06	0,18	0,12	0,06	(a)	(a)	(a)	(a)	(a)	
ZnO	3,0	(a)	(a)	(a)	(a)	(a)	(a)	(a)	(a)	3,02	4,72	

ESP – electrostatic precipitator, FA – fly ash, APC – air pollution control residues, SDS – semi-dry absorber, FF-bag filter, a – not indicated



Table 4. Composition data of APC/fly ash samples analysed with X-ray fluorescence (XRF). Results are expressed wt. %. (Kaartinen et al. 2007)

Ash type	Fuel	As	Cl	Cr	Cu	Ni	Pb	Sb	Zn
Fly ash	MSW	<0,01	14	0,04	0,07	<0,01	0,14	0,05	0,79
Fly ash	MSW	0,02	14	0,09	0,10	0,01	0,27	0,06	1,5
Fly ash	Industrial waste 70 %, MSW 30 %	<0,01	4,2	0,12	0,49	0,02	0,09	0,02	0,55
Fly ash	Biomass, waste wood	0,03	0,34	0,07	0,16	0,01	0,14	<0,01	1,1
Fly ash	Bark, peat, sawdust, SRF (25 %), fibre pulp	<0,01	0,55	0,04	0,09	0,03	0,03	0,01	0,22
Fly ash/ APC	MSW	0,02	18	0,03	0,07	<0,01	0,33	0,06	1,7
APC	MSW	<0,01	27	0,01	0,02	<0,01	0,05	0,01	0,22
APC	Industrial waste 70 %, MSW 30 %	<0,01	17	0,11	0,79	<0,01	0,55	0,03	0,50
APC	Biomass, waste wood	0,08	3,1	0,09	0,14	0,01	0,16	0,01	1,2

3.1.2 Bottom ashes

During fluidized bed combustion the bottom ash is formed by the deposition of ash particles on quartz sand particles. The deposited particles are mainly non-volatile, Ca- and Si-rich particles. In addition, volatilised K and Zn diffuse into and react with the bed sand. Bottom ash is depleted of volatile Cl, S and Cd. Approximately 25 % of the ash-forming species originating from the fuel are removed from the furnace with the bottom ash. (Lind 1999)

Bottom ash (BA) from municipal solid waste (MSW) incineration contains elements, such as calcium, silicon, aluminum and sulfur; which can be used as secondary raw materials for special cements containing hydraulic materials. The composition of the bottom ash, generated 20-35 wt. % per each incinerated waste ton is typically:

- Slag, glass, ceramics, rock: 80 - 85 %:
- SiO₂: 32 - 48 % (from glass)
- CaO 16 - 23 % (from paper)
- Organics: 1 - 3 % organics
- Ferrous metals: 4 - 15 %
- Non-ferrous metals 0.2 - 3 %.

A compilation of composition data of waste-to-energy bottom ashes from the literature is showed in the Table 5.



Table 5. Composition data of bottom ash samples analysed with X-ray fluorescence (XRF). Results are expressed as wt. %. (Kartinen et al. 2007)

	Bottom ash (MSWI)	Bottom ash (MSWI)	Boiler ash (BFB)	Bottom ash (BFB)	Bottom ash (BFB)
Element, %					
Arsenic, As	<0,01	<0,01	<0,01	<0,01	0,02
Chromium, Cr	0,04	0,04	0,05	0,03	0,06
Copper, Cu	0,08	0,21	0,51	1,0	0,13
Lead, Pb	0,23	0,21	0,06	0,10	0,02
Antimony, Sb	0,005	<0,01	0,01	0,01	<0,01
Zinc, Zn	0,16	0,29	0,29	0,34	0,49

3.2 Presence of valuable elements in ashes

3.2.1 Concentrations in waste-to-energy ashes

There is surprisingly little information available on the content of possible valuable elements in waste-to-energy ashes. Most of the information in the literature refers to residues from municipal solid waste incineration and especially to fly ash. Some information about composition of medical waste incineration containing rare earths also exists. In older literature this type of content data is almost totally lacking, as it has not been of special interest. Furthermore, the results are often presented in an inapplicable form e.g. graphically or as ratios of reference data and lack information about elemental speciation. The information comes mainly from Japan or China. There are a few references with European data for Sb, Co and Mo. Generally, the quality of data is not possible to evaluate with exception for the Swedish study by Johansson et al. 2014.

3.2.1.1 The Swedish study

The metal concentration in waste-to-energy ashes is highly dependent on the input material (e.g. WEEE, medical waste). The Table 5 summaries data on scarce element concentrations in bottom and fly ash from different waste-to-energy plants comprised in the Swedish study. (Johansson et al. 2014)



Table 6. Summary of concentrations of critical materials in waste-to-energy ashes. (Johansson et al. 2014)

	Bottenaska, mg/kg				Flygaska, mg/kg			
	Medel	Min	Max	Antal	Medel	Min	Max	Antal
Antimon (Sb)	44	7,6	110	4	680	73	2100	14
Indium (In)	0,95	0,2	1,7	2	2,4	2,0	2,8	2
Beryllium (Be)					1,3	0,75	1,5	3
Kobolt (Co)	27	2,8	55	4	25	0,60	79	17
Gallium (Ga)	21	17	24	2	18	4,1	22	4
Germanium (Ge)	1,5	1,5	1,5	1	5,7	4,4	6,9	2
Magnesium (Mg)	8800	4100	12000	4	12000	3900	22000	11
Niob (Nb)					11	0,40	11	1
Tantal (Ta)	3,0	2,5	3,4	2	16	0,90	43	3
Volfram (W)	13	11	14	2	71	6,2	230	7
Guld (Au)								
Silver (Ag)	9,8	5,7	17	3	61	12	190	7
Palladium (Pd)	0,03	0,03	0,03	2	4,1	3,6	4,5	2
Sällsynta jordartsmetaller (Σ)	83	83	83	1				
Cerium (Ce)	25	25	25	1	31	30	31	2
Dysprosium (Dy)	1,3	1,3	1,3	1				
Europium (Eu)	1,5	1,5	1,5	1				
Erbium (Er)	0,74	0,74	0,74	1				
Gadolinium (Gd)	2,0	2,0	2,0	1				
Holmium (Ho)	0,24	0,24	0,24	1				
Lanthanum (La)	15	15	15	1	16	14	18	3
Lutetium (Lu)	0,13	0,13	0,13	1				
Neodym (Nd)	9,3	9,3	9,3	1	11	11	11	1
Praseodym (Pr)	2,5	2,5	2,5	1				
Samarium (Sm)	2,3	2,3	2,3	1				
Skandium (Sc)	6,5	6,5	6,5	1				
Terbium (Tb)	0,64	0,64	0,64	1				
Thulium (Tm)	0,09	0,09	0,9	1				
Ytterbium (Yb)	0,70	0,70	0,70	1				
Yttrium (Y)	16	16	16	1	16	8	21	3

The results from the Swedish analysis (Table 6) show that the concentration levels of most of the critical elements in ashes are below the average concentration in the upper earth crust. Indium and the platinum metals are present in concentrations lower than the report limit of the used method. In the case of gold, there are some results above the determination limit, but most are below. Antimony and silver are the elements present in concentrations significantly higher than the average in the earth crust. Despite the low content, the critical



metals in the residues still represent a value of 1.3 billion SEK each year. The most part of the economic potential comes from a limited number of metals; these are lutetium, magnesium, scandium and thulium. Magnesium is present in large volumes while the others have a very high market price (in pure metallic form). (Johansson et al. 2014)

The Swedish study (Johansson et al. 2014) comprises also a comparison between the levels of critical metals in fly and bottom ashes from the grate furnaces and fluidised bed (FB) boilers (Figures 6 and 7, Note: the logarithmic scale). For the fly ash there is a clear tendency that the levels of FB boilers are higher than in grate furnaces. The exceptions are antimony, germanium and tungsten. For the bottom ash one can see the same trend but the differences are much less.

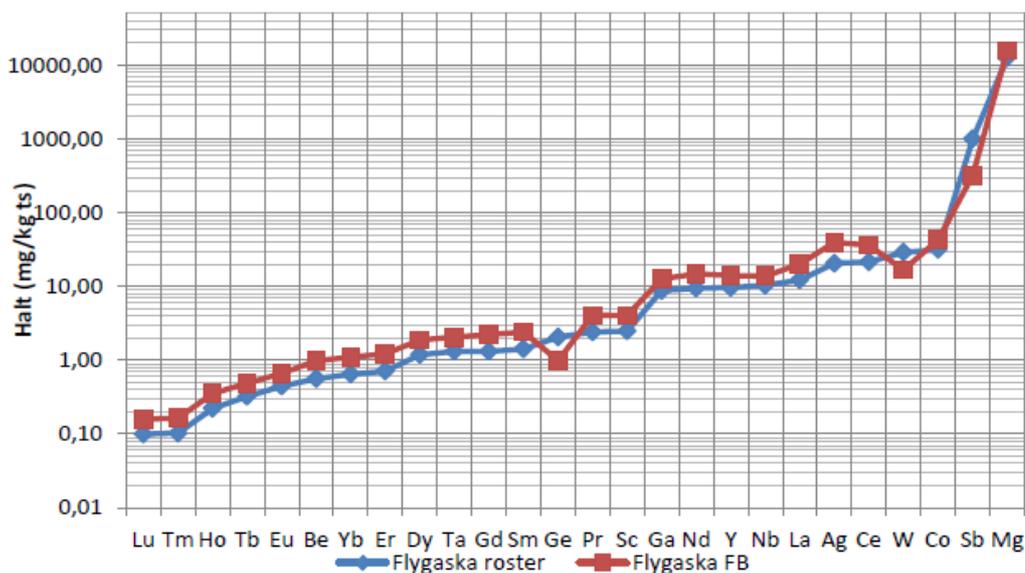


Figure 6. Comparison between the levels of critical metals in fly ash from grate furnaces and fluidised bed boilers. (Johansson et al. 2014)

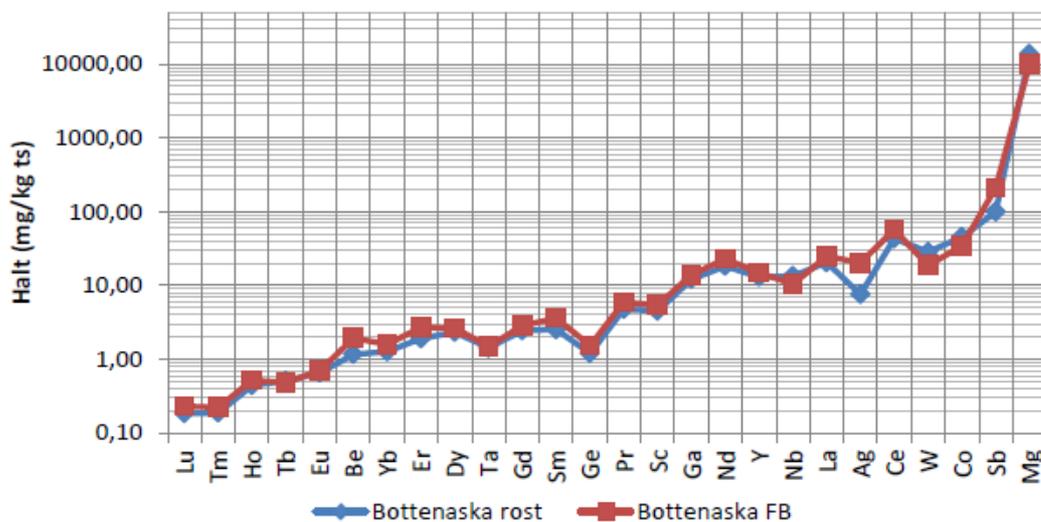


Figure 7. Comparison between the levels of critical metals in bottom ash from grate furnaces and fluidised bed boilers. (Johansson et al. 2014)



3.2.1.2 Other studies

Examples of single literature references for concentrations of ashes from incineration of municipal solid waste and hospital waste are compiled below:

- In Japan, studies developed by Chang-Hwuan Jung showed that several rare elements were present in both bottom and fly ashes from municipal waste residue incineration. Japanese target rare metal (including European scarce metals as Sb, In, Co, Ga, Ge, Mg, Ta, W, Ag, Pt and Pd) was ranged from 0.2 to 0.4% in total ashes. Most of the Co, Cr, Mn, Ni and V were found in bottom ash while high concentration of Ag, Pd and Sb were found in fly ash. Studies showed that rare metal elements are transferred to fly or bottom ash according to the physical/chemical characteristics of each rare metal element. (Jung 2007)
 - Analysis of typical Chinese medical waste incinerators ashes showed that REE content in the ash residues ranged from 10.2 to 78.9 mg/kg. REE content in bottom ash was apparently higher than those in fly ash, which can be attributed to the high boiling points of REE elements (1194 – 3426 °C). Ce was the most abundant of the whole REEs (range 1.6-31.52 mg/kg) and it was apparent that the content of total light REEs (LREEs, including La, Ce, Pr, Nd, Sm, Eu) was much higher than that of heavy REEs (HREEs, including Y, Gd, Dy, Er, Yb, Ho, Tb, Lu, Tm). (Zhao et al. 2006)
 - Research carried out on Creek medical waste incinerator bottom and fly ash samples showed the presence of several scarce metals e.g. Sb, Ga, Nb, Ta, W, REEs and precious metals as Au, Ag in both residues. These compounds were found in both bottom and fly ash with significant amounts. Wolfram concentrations were for fly ash 185 mg/kg and for bottom 498 mg/kg. The total REE content was 415 mg/kg, Ce being the most important component. The scarce metal concentration in fly ash was significantly lower than in bottom ash in most elements, excluding Sb, W, and Ag. (Kougemitrou et al 2011)
 - Fu-Shen Zhang studied REE content in different waste ashes and noted sewage sludge ashes (SSA) and incinerator bottom ashes (IBA) may cause some REEs (Sc, Sm o Eu) accumulation in some soils. The sums of REE concentrations in SSA and IBA ranged 80-130 mg/kg and total LREEs was relatively higher than total HREEs concentration. (Zhang et al 2001)

3.2.2 Concentrations in MSW melting ash

As an urban mine for metal resources, the residues of municipal solid waste (MSW) melting plants such as fly ash and molten metal are attracting considerable attention due to the high metal content. They are generated when MSW and/or MSW incineration residues are treated at 1300–1800 °C. Metal elements with low boiling point are volatilized and concentrated in fly ash, while elementary Fe, Ni, and Cu, etc. with high specific gravity remain in the furnace, separated from molten slag by the gravity difference, and discharged as molten metal (Figure 8). Particularly, Zn and Pb are highly concentrated in fly ash. In addition, it is found that not only Zn and Pb but also rare metals such as Ag, Bi, Ga, Ge, Pd, In, Sb, Sn, Te, and Tl are volatilized and highly concentrated in fly ash during the melting process. The high metal content in fly ash is preferred for metal recovery. (Jung & Osato 2009)

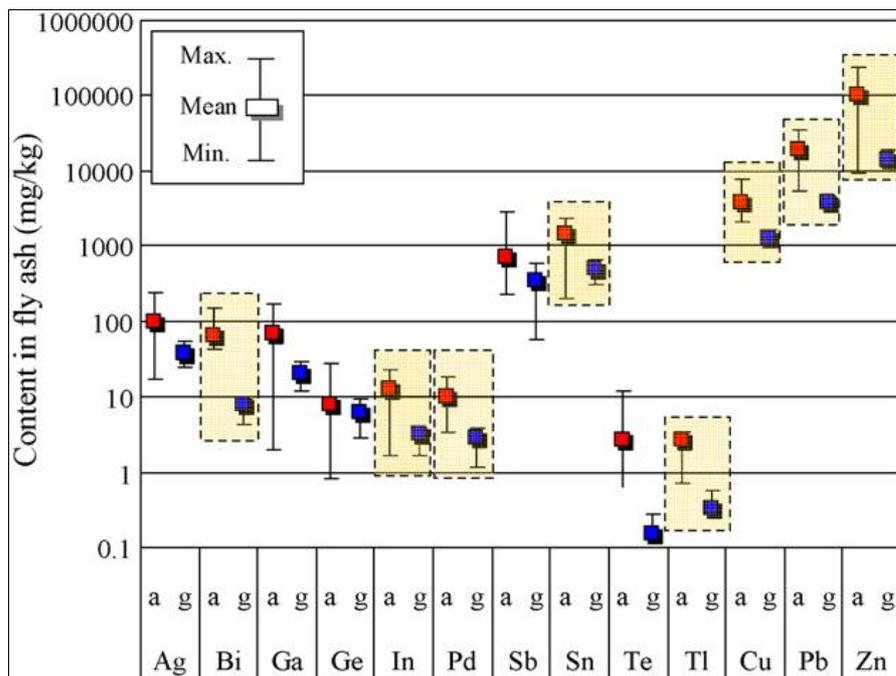


Figure 8. Comparison between ash melting and gasification/melting for metal content in fly ash. a: ash melting and g: gasification/melting. (Jung & Osato 2009)

Metal content in incineration residues such as fly ash (IFA) and bottom ash (IBA) is much higher than that in feed MSW since the low level of metal in end-of-life products (waste) is concentrated in residues by incineration (see also Figure 9). Thus, for the most metal elements including rare metals, the content in fly ash from incineration residues treated by ash melting is higher than that in fly ash from MSW treated by gasification/melting. Also, fly ash from plants receiving waste plastics show a higher content of Sb than that in fly ash from other plants. This might be caused by antimony trioxide (Sb_2O_3) often used as flame retardant in plastic products. The content of Cu is remarkably high in fly ash from plant treating ASR. This is because Cu is highly included in ASR, ranging from 23,000 to 88,000 mg/kg. In addition, Jung et al. (2005) indicated that Cu in fly ash was affected by Cl content in feedstock since thermally mobile $CuCl_2$ is formed with sufficient Cl and volatilized during the melting process. (Jung & Osako 2009)

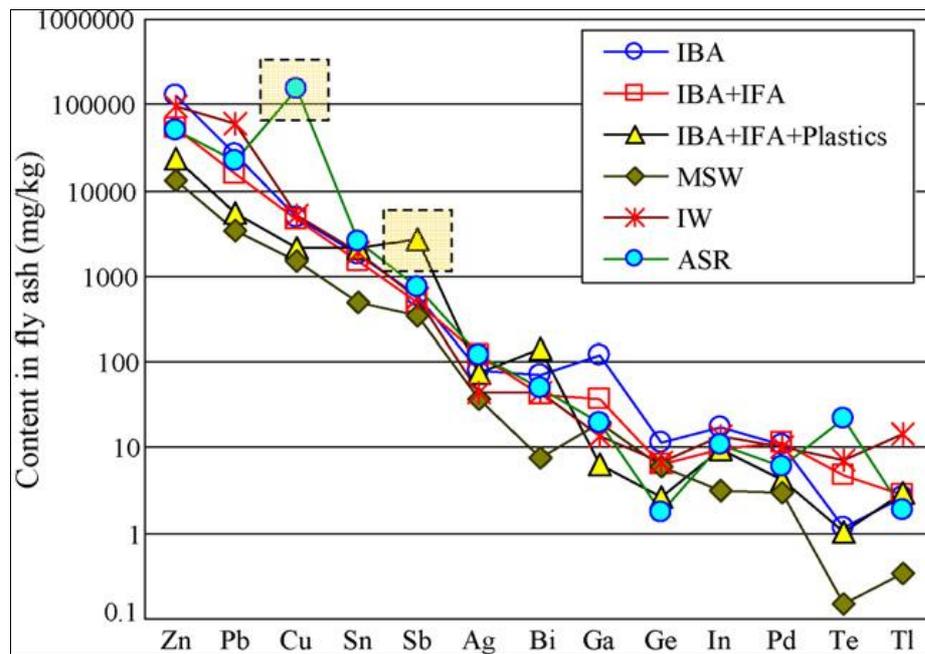


Figure 9. Metal content in fly ash with feedstock of melting plants. MSW: municipal solid waste, IBA: bottom ash from MSW incinerator, IFA: fly ash from MSW incinerator, IW: illegal dumping waste and ASR: automobile shredder residue. (Jung & Osato 2009)

3.2.3 Concentrations in municipal solid waste (MSW)

In a Swiss study precious metals, REE, and other metals in input waste from a Swiss municipal solid waste (MSW) incineration plant with a total capacity of 25 t per hour were analyzed. The analyzed compounds were precious metals (Au, Ag), the critical resource (Be, Co, Ga, Ge, In, Nb, Ta, W, PGM -Pt, Pd, Rh, Ru-, including the group of REE -Gd, Nd, Pr, Sc and Y-) and other metals such as Ba, Bi, Pd, Hf, Li, Mo, Rb, Se, Sr, Te, Tl, V and Zr. In the article the annual flows for the precious metals gold and silver in the solid waste incineration input were determined to be approximately 81 kg/a (Au) and 1070 kg/a (Ag) respectively. For PGM, the annual flow was estimated at 12 kg/a for Pt. REE as Nd and Y was ranged until 1.5 t/a and 1.6 t/a respectively (see Table 7). Also, transfer coefficients for selected metals into different outputs of the solid waste incineration were presented. (Morf et al. 2012)

*Table 7. Annual flow of precious metals, REE and other metals in the waste input of a Swiss incineration plant (Morf et al. 2012).*

	Annual flow (kg/a) ± uncertainty (sd)
Iron	6,300,000 ± 309,000
Aluminum	3,400,000 ± 191,000
Copper	440,000 ± 44,000
Zinc	320,000 ± 60,000
Barium	150,000 ± 12,000
Lead	110,000 ± 9800
Chromium	36,000 ± 2800
Strontium	26,000 ± 1800
Nickel	24,000 ± 2300
Zirconium	23,000 ± 8400
Tin	15,000 ± 1400
Wolfram	11,000 ± 9600
Vanadium	2200 ± 150
Cobalt	2100 ± 160
Lithium	1800 ± 120
Cadmium	1800 ± 110
Molybdenum	1700 ± 180
Rubidium	1700 ± 90
Yttrium	1600 ± 710
Neodymium	1500 ± 590
Silver	1100 ± 140
Bismuth	570 ± 31
Hafnium	530 ± 187
Niobium	500 ± 19
Gallium	440 ± 27
Praseodymium	380 ± 170
Tantalum	250 ± 110
Scandium	190 ± 16
Gadolinium	150 ± 35
Selenium	89 ± 4.1
Gold	81 ± 40
Indium	58 ± 4.4
Beryllium	56 ± 6.2
Germanium	41 ± 2.8
Tellurium	17 ± 2.2
Thallium	16 ± 4.1
Platinum	12 ± 4.4
Ruthenium	0.10 ± 0.033
Rhodium	0.018 ± 0.010

3.2.4 REEs in coal and coal ashes

Rare earth elements (REEs) are a group of chemically similar metals including the fifteen elements with atomic numbers 57 through 71, plus scandium and yttrium. Together, the lanthanides, yttrium, and scandium are commonly referred to as REEs or REMs, although this is a misnomer since most of the REEs are common mineral constituents as compared with other metal elements. The metallurgical processes needed to isolate the individual metal species are complex, and early technology prevented commodity-level production. As a result, lanthanide metals or metal oxides (i.e. REOs) were difficult to obtain and were thus considered rare.



The average sum REE content of world coals, based on calculation of average individual lanthanide and Y concentration is estimated to be 68.5 ppm, about 2.5 times lower than that in the rocks of the upper continental crust (UCC, 168.4 ppm). The average REE including Y (REY) content of USA coals (62.1 ppm) is close to that of world coals. The average REY content of Chinese coals (137.9 ppm) is two times higher than that of world and USA coals. The distribution plots of REY averages for both Chinese and USA coals are similar to those of the UCC (Figure 10). (Seredin & Dai 2012)

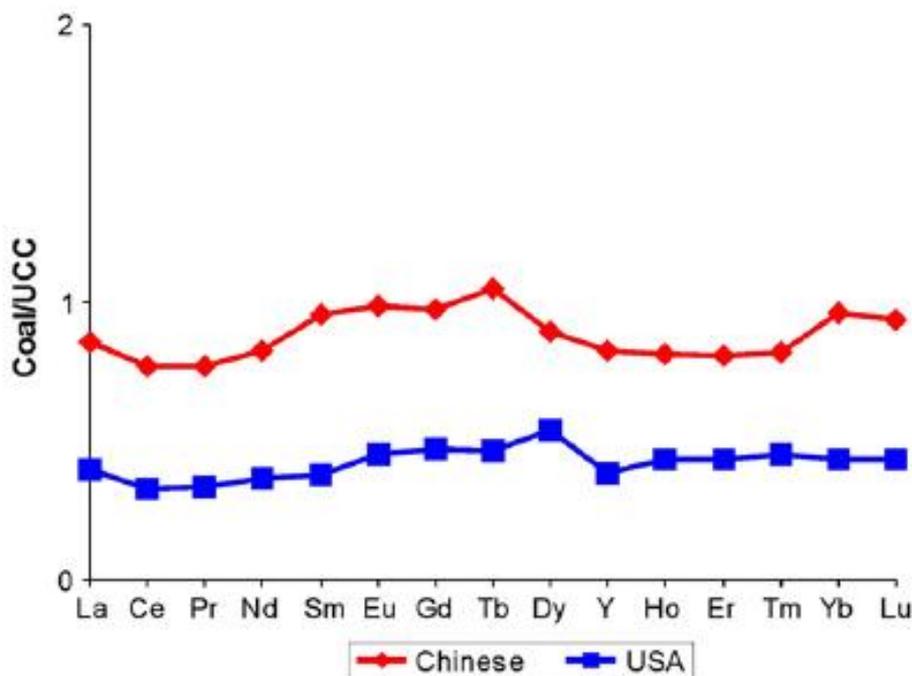


Figure 10. REE including Y (REY) plots for average Chinese and USA coals. Normalized by average REY content of Upper Continental Crust (UCC). (Seredin & Dai 2012)

The average REY content in world (404 ppm) and USA (517 ppm) coal ashes is approximately 3 times higher than that in the upper continental crust (UCC). The REY oxides (REO), which are generally used to estimate the abundance of the metals in ores, are 483 and 621 ppm, respectively, after recalculation from the content of single elementary substance. These values are close to the REO content of some ion-adsorbed deposits (Longnan — 840 ppm and Huashan — 700 ppm) and large-tonnage and low-grade ores of hydrothermal origin (Round Top Mountain, USA — 690 ppm; <http://www.trer>). Hence, if the average REY content in coal ashes, based on analyses of numerous samples, is comparable to some conventional ores, the ashes of coal combustion could and should be considered as possible sources of these metals. As REE are non-volatile elements, their distribution patterns in an average coal ash should be the same as those in an average coal. (Seredin & Dai 2012)



Table 8. The main genetic types of high REY accumulation in coals. (Seredin & Dai 2012)

Type	REO content in ash, %	Associated elements
Terrigenous	0.1 – 0.4	Al, Ga, Ba, Sr
Tuffaceous	0.1 – 0.5	Zr, Hf, Nb, Ta, Ca
Infiltrational	0.1 – 1.2	U, Mo, Se, Re
Hydrothermal	0.1 – 1.5	As, Sb, Hg, Ag, Au, etc.

Table 9. REE content (ppm) in coal samples. (Seredin & Dai 2012)

Index	R14		R2		R3		C6		M1	
Sample no	R-IIIb/3		P5-93		P1/2-93		sh-11-8		A-ch-6	
Thickness, cm	20		20		20		3		5	
Ad, %	6,7		14,5		16,1		43,0		37,7	
Materials	Coal	Ash	Coal	Ash	Coal	Ash	Coal	Ash	Coal	Ash
• La	91	1360	371	2557	224	1390	498	1158	598	1586
• Ce	247	3680	240	1654	256	1590	1132	2631	1280	3392
• Pr	41	609	31	211	50	311	113	263	169	447
• Nd	204	3040	104	719	208	1290	366	851	829	2197
• Sm	60	899	29	202	60	372	60	139	188	498
• Eu	15	277	2	12	4	23	6	14	46	123
• Gd	78	1160	38	261	113	701	56	129	279	740
• Tb	12	182	8	58	20	124	6	14	40	106
• Dy	77	1150	57	393	139	865	31	72	237	619
• Ho	16	246	12	81	31	192	6	13	49	131
• Er	49	732	36	246	93	580	17	39	144	381
• Tm	7	107	5	33	14	85	2	6	19	51
• Yb	51	755	30	205	91	564	16	38	127	337
• Lu	7	109	5	33	13	79	2	5	20	53
• Y	186	2770	507	3499	1138	7067	135	313	1156	3063
• REY, ppm	1141	17,026	1474	10,164	2453	15,233	2446	5686	5178	13,723
• REO, %	0,14	2,03	0,18	1,23	0,30	1,85	0,29	0,68	0,62	1,65

Limited information exists on concentrations of strategic elements in U.S. coal ash storage facilities. One detailed assessment of rare earth elements in coal ash from a Kentucky power plant reported a range of 1213.6 – 1667.6 mg/kg total rare earth elements (TREE) in fly ash and 1202.5 mg/kg TREE in bottom ash. It is also estimated that the rare earth ash content from the Kentucky plant and other international coal ashes contained concentrations within the range of mineral ore deposits. Thus, the potential for utilizing coal combustion products as a source for strategic elements is evident. (Mayfield & Lewis 2013)



Table 10. Mean and range of concentrations (mg/kg) in coal and coal ashes. (Mayfield & Lewis 2013)

Element	Raw coal ^a	Coal ash ^b	Coal fly ash ^c
Ce	20.9 (0.79-790)	468.78 (151-1784)	--(405-565)
Dy	2.09 (0.11-28)	61.54 (18-527)	--(32.1-50.3)
Eu	0.28 (0.025-5.8)	7.64 (2-31)	-- (3.9-5.9)
La	9.09 (0.07-230)	259.85 (60-839)	-- (206-286)
Nd	8.48 (0.47-230)	236.02 (70-967)	-- (183-256)
Pr	4.81 (0.17-65)	59.02 (17-239)	-- (49-68)
Tb	0.54 (0.01-21)	10.29 (3-80)	-- (4.9-7.3)
Y	8.18 (0.10-100)	408.34 (94-3540)	-- (191-259)
Total REE	54.9 (0.20-1031)	1723 (721-8426)	-- (1213-1667)
Ga	5.24 (0.044-41)	Limited data	-- (212-229)
Ge	4.23 (0.007-220)	-- (<10-1841)	-- (1-356)
In	0.71 (0.025-23)	Limited data	Limited data
Te	1.82 (8.8-510)	Limited data	-- (0.14-2.7)

- (a) [a] Data represents detectable concentrations from unprocessed coal samples collected throughout the U.S. from 1973 to 1989 as summarized in the USGS COALQUAL;
- (b) [b] Rare earth metal content estimated (from laboratory analyses) for ashes from coal deposits in the U.S., Russia, China, and the Middle East summarized by Seredin and Dai (2012);
- (c) [c] Range of concentrations measured from coal and coal fly ashes collected from power facilities in the U.S., Europe, Mexico and Spain.



4 Enrichment and recovery technologies

The recovery of metals from mineral ores, particularly critical elements, is a complicated multi-step process that consumes energy and results in a variety of waste products. This beneficiation process for ores includes initial crushing and grinding of the ores to smaller particles, filtration and flotation to remove undesired minerals, and further conditioning prior to final metal purification. By contrast, initial metal recovery from secondary resources and waste, e.g. ash may be more efficient than ore processing since the physical form is more amenable to processing (i.e., with limited initial conditioning).

Waste treatment and material recycling processes can be divided into mechanical, thermal and chemical treatment steps. Mechanical treatment processes are a combination of sorting, comminution and classifying steps and present often a necessary pre-treatment prior to chemical or hydrometallurgical recycling steps. Hydrometallurgical and pyrometallurgical processes represent then a crucial step to recover valuable metals with a sufficient quality from complex waste and material streams. In the following chapters the state-of-the-art of different processes also feasible for ashes are described.

4.1 Mechanical treatment of ashes

Mechanical treatment of ashes is usually carried out to separate valuable material for further material or energy recovery or to increase the quality of feed by removing impurities. The processing consists mainly of different mechanical unit processes which are usually implemented in a row. In the list below, common process steps in the processing are presented:

- size reduction
- size controlling
- separation of desired material or contaminant

The unit processes should be optimized over the whole process chain in order to avoid losses and to achieve as high as possible recovery rate without decreasing the quality of the products. This is essential for the further processing of the separated materials. Each unit process has its own limitations and requirements which must be considered when a process chain is designed for the feed. It should be noticed that due to the physical boundary conditions in mechanical processing, 100 % recovery with good quality is not achievable (Reuter et al. 2005). Therefore, the product from mechanical treatment is usually a concentrate. A more detailed description of mechanical treatment technologies has been presented in Appendix 2.

The treatment structure and equipment varies from case to case depending on the target of the treatment and on feed materials. For example the bottom ash treatment utilizes different equipment than fly ash treatment, since i.e. the particle size of the feed is different. However, prior to the treatment, feed material needs to be well characterized in order to develop suitable treatment method. Important characteristics of the feed (considering mechanical treatment) are: particle size (distribution), chemical composition and liberation. (Gupta 2013)



4.1.1 Bottom ash treatment

The mechanical treatment of bottom ash has focused mostly on the recovery of ferrous and non-ferrous (Cu, Al) metals. In some cases, the beneficiation of the residual mineral fraction has also been executed. The metal recovery from bottom ash is conventionally carried out by dry mechanical methods such as magnetic and eddy current separators. However, the equipment limit the recovery usually only to particle sizes above 4 mm. Wet physical processes needed if metal recovery and organic removal is applied to particle sizes down to 0.3 mm. As a result, higher metal recovery rates and better quality mineral fraction can be achieved. For example the recovery of ferrous metals (>80 %) are similar for both wet and dry process, but for non-ferrous metals the recovery is significantly higher for wet process (>80 %) than for the dry process (10-30 %) (Muchova 2010). On the other hand, investment costs and treatment costs increase when process method shifts from dry to wet. Flowsheets for dry and wet treatment processes are presented in Figures 11 and 12.

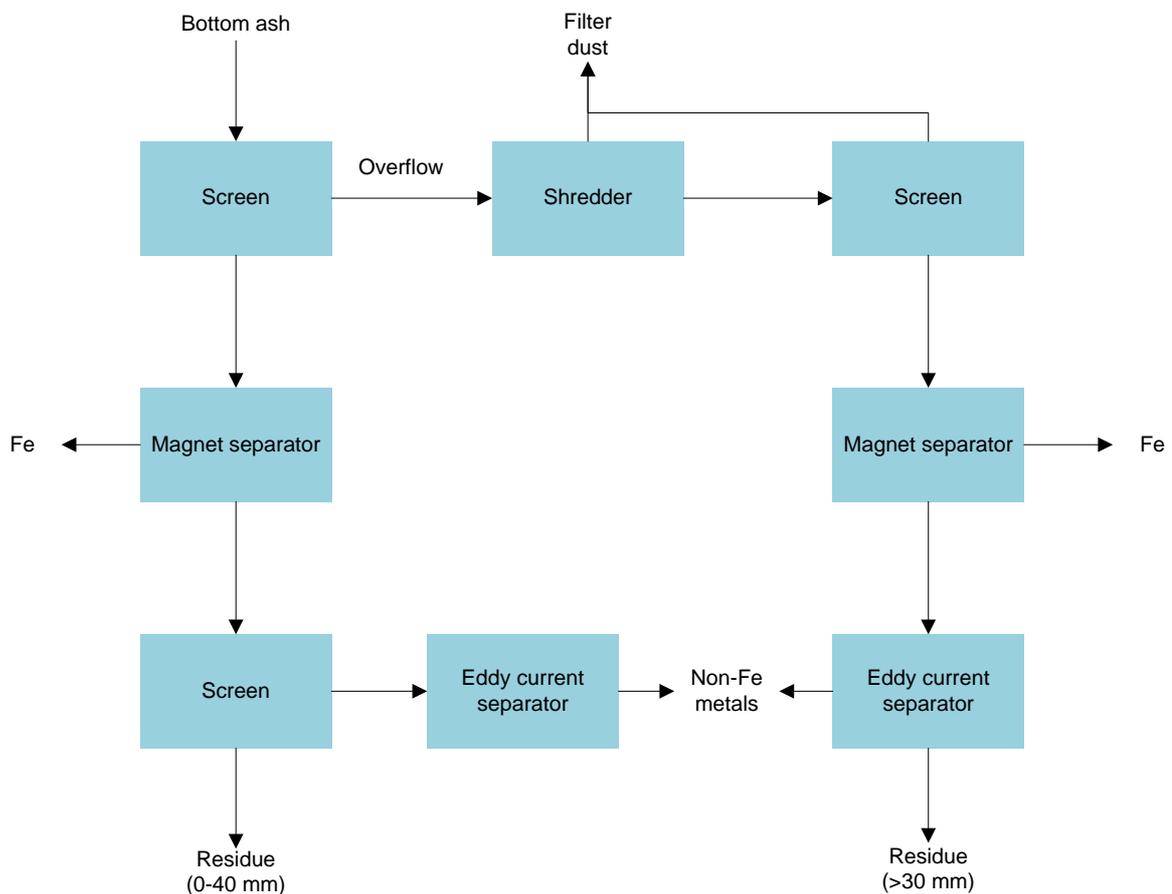


Figure 11. Typical dry treatment process to recover coarser metal particles. (Muchova, 2010)

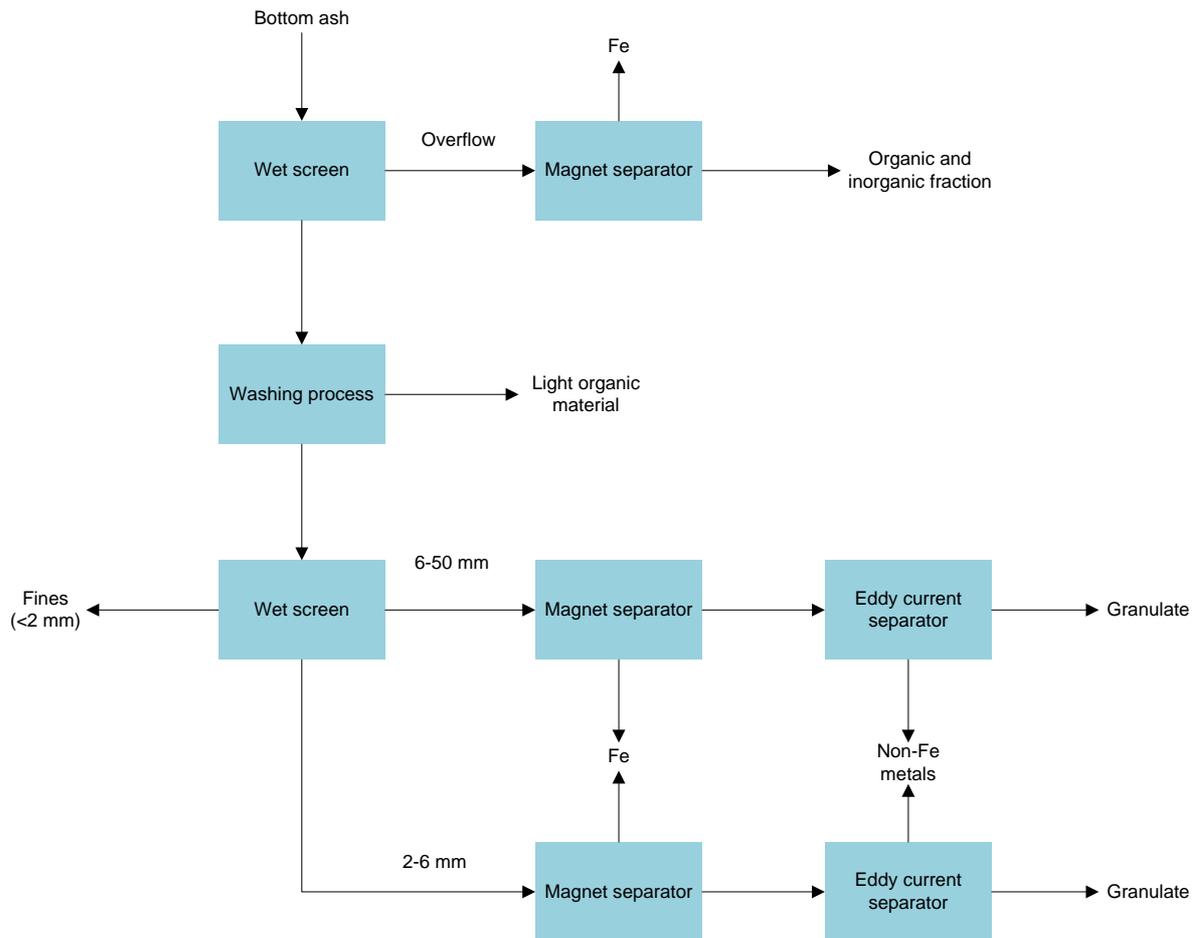


Figure 12. A wet treatment process to recover metals and granulates (Vandecasteele et al. 2007).

Current research in mechanical bottom ash treatment has focused on wet processes such as density separators (magnetic, shaking tables, jigs) and flotation to increase metal (valuable and precious) recovery and to improve the quality of mineral fraction for further utilization. (Berkhout et al. 2011; Holm and Simon, 2014; Kaartinen et al. 2010; Muchova 2010) In addition, new size reduction processes such as electrodynamic fragmentation has been studied lately (Thome 2012).

4.1.2 Fly ash treatment

The mechanical treatment of fly ash has emphasized on separation of unburnt organic matter from other materials such as cenospheres and on mechanical activation (Blisett and Rowson, 2012; Hirajima et al. 2013; Hela and Orsakova, 2013). The separated unburned organic matter can be used as a fuel whereas the inorganic matter is a potential raw material for cement industry (Blisett and Rowson 2012). The typical particle size of fly ash is below 300 µm (Blisett and Rowson 2012) which reduces significantly the separation efficiency of traditional over belt magnetic separators and eddy current separators. Therefore separation processes such as density separation and flotation are usually applied on fly ash. Even though no effective size reduction is required on the fly ash, mechanical activation by abrasion to increase its reactivity can be carried out (Hela and Orsakova 2013; Fu et al. 2008). A schematic description of a mechanical treatment process for fly ash has been presented in the Figure 13.

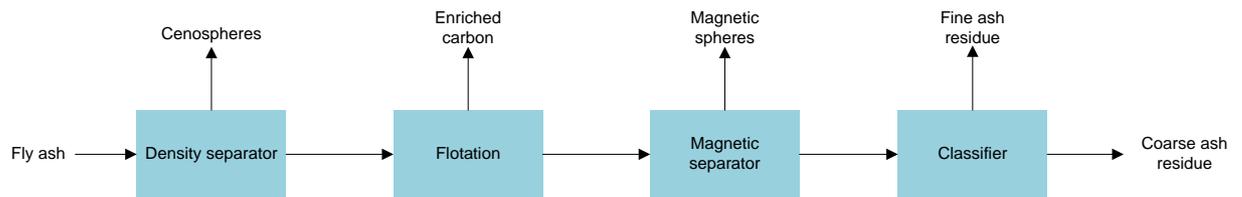


Figure 13. A schematic description of fly ash treatment. (Blissett and Rowson, 2012)

4.2 Chemical leaching

4.2.1 Fundamentals

Hydrometallurgical processes usually include initial chemically induced leaching of the material, often employing the use of low-pH acids (e.g. hydrochloric, nitric, sulfuric, or oxalic acid) together with varying temperatures and leaching times, depending on the composition of the ash. After leaching, removal of non-target minerals (e.g., silicates, iron, calcium) by solution purification by e.g. ion exchange, adsorption or solvent extraction. Finally, recovery of the desired metal takes place by e.g. chemical precipitation. Chemical separation of critical metals can be cumbersome. Therefore, it is necessary to optimize the extraction technique for each material and element. (Gupta 2003)

Aims of a leaching procedure can be 1) a metal or salt laden solution for further processing to recover valuables or 2) remove impurities that are otherwise not removable from a matrix or 3) both of these. The general conditions likely to favor dissolution may be derived from the thermodynamic data presented in the form of Pourbaix diagrams. These diagrams have gained widespread acceptance in various disciplines concerning the thermodynamics of aqueous systems. Two independent variables, pH and redox-potential, form the basis of Pourbaix diagrams. Figure 14 shows an example of a Pourbaix diagram. It can be seen from the figure, that favourable conditions for the solubilisation of Zinc can be reached below pH of about 7 with the production of Zn^{2+} ions and above 13 with the production ZnO_2^{2-} ions. (Gupta 2003)

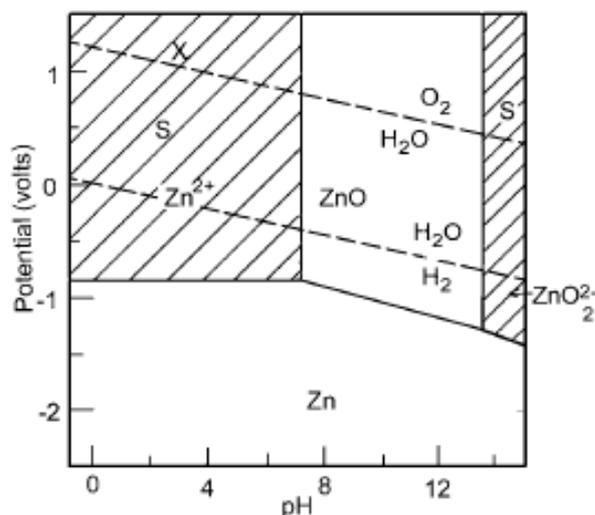


Figure 14. Example of a Pourbaix diagram.



In practise these types of diagrams give the starting points for leaching conditions, which then have to be tailored for each case. They do not provide information of the reaction kinetics. Furthermore, the regions of stability of the various species in a Pourbaix diagram shift as the temperature is changed, providing a third variable that may be manipulated to achieve the desired effect. Yet another variable that can be manipulated is the concentration of the complexing agents (particularly CN^- , NH_3 , and Cl^-) that can stabilize ions in solution. Table 11 shows what is usually wanted from a leaching process.

Table 11. Some of the most essential and desirable features of a leaching process.

Essential feature	Desirable features
1. The valuable metal must be soluble in an economically usable solvent	1. The gangue minerals should not consume excessive amounts of solvents
2. The metal must be economically recoverable from solution	2. The solvent should be recoverable (or capable of regeneration) for recycle
3. The impurities that are co-extracted during leaching must be capable of further separation from solution	3. The feed should be free of clay materials, as they make separation of leach liquor from the treated solids difficult
	4. The feed material should be porous to the solution allowing direct contact between the solvent and the phase to be dissolved, and providing a high liquid/solid area for reaction for a given mass of material
	5. The solvent should preferably be noncorrosive to materials used in plant equipment to minimize capital and maintenance costs, and should be non-toxic

Leaching characteristics of a target element is strongly related to the nature of the element to be leached as well as its mineral phase(s). Three main typical leaching behaviours for solubility-controlled leaching have been identified: (1) cation-forming species and non-amphoteric metal ions (e.g. Cd) that display fairly constant high values at $\text{pH} < 4$ and decreases strongly up to $\text{pH} 8-9$, remaining approximately constant or slightly increasing for higher pH values; (2) amphoteric metals (including Al, Pb, Zn) increase solubility under both strongly acidic and strongly alkaline conditions and (3) oxyanion-forming elements (e.g. As, Cr, Mo, V, B, Sb) whose solubility decreases in alkaline ranges ($\text{pH} > 10$) (Sabbas et al. 2003).

Several chemical extraction techniques have been applied for metals in ashes. Methods for extraction and separation of individual strategic metals from ashes are emerging and becoming more efficient as chemical engineering techniques are improved. Chemical leaching processes can be used not only to concentrate valuable elements but also to remove undesirable substances such as chlorine and sulphate.



4.2.2 Examples of ash leaching

The extraction of Pb and Zn from fly ash from MSWI incineration using different acidic liquors such as H_2SO_4 , HCl, acetic acid and water as well as alkaline leaching solution such as NaOH has been studied (Nagib & Inoue 2000). Acid leaching was found to be more effective than alkaline leaching. However, the acids dissolve also some impurities together with Pb and Zn from the fly ash. Therefore, alkaline leaching using NaOH as leachate was also carried out. The alkaline leaching suffered from low solubility of Zn. In order to improve Zn solubility, washing the solid residue from alkaline leaching using HCl was carried out. It was found that almost all Pb (more than 97 wt.%) and about 68 wt.% Zn were leached from secondary fly ash by this method. The study showed that hydrometallurgical treatment of fly ash by means of alkaline leaching followed by dilute acid washing is a potentially feasible method.

In a study by Gutierrez et al. (1997) the recovery of gallium from coal fly ash by a dual reactive extraction process was investigated. Hydrochloric acid (6 M) in contact with Amberlite LA-2 was used to extract the gallium and iron. The iron was then precipitated with sodium hydroxide, while 83% of gallium remained in solution and was extracted selectively from the base solution with LIX 54, an extractant developed for copper.

The extraction of gallium from coal fly ash was studied by a hydrometallurgical process by Fang & Gesser (1997) which included acid leaching, impurity removal, foam extraction of gallium and its purification. The extraction was carried out at different acid concentration, temperature, L/S ratio, extraction time, and particle size of fly ash to determine the highest extraction yield. The results showed that high acid concentration, low temperature, high L/S ratio, short extraction time and small particle size formed a combination of suitable conditions for extraction of gallium. They also proposed a flowsheet for the treatment of coal fly ash with recovery of gallium (Figure 15).

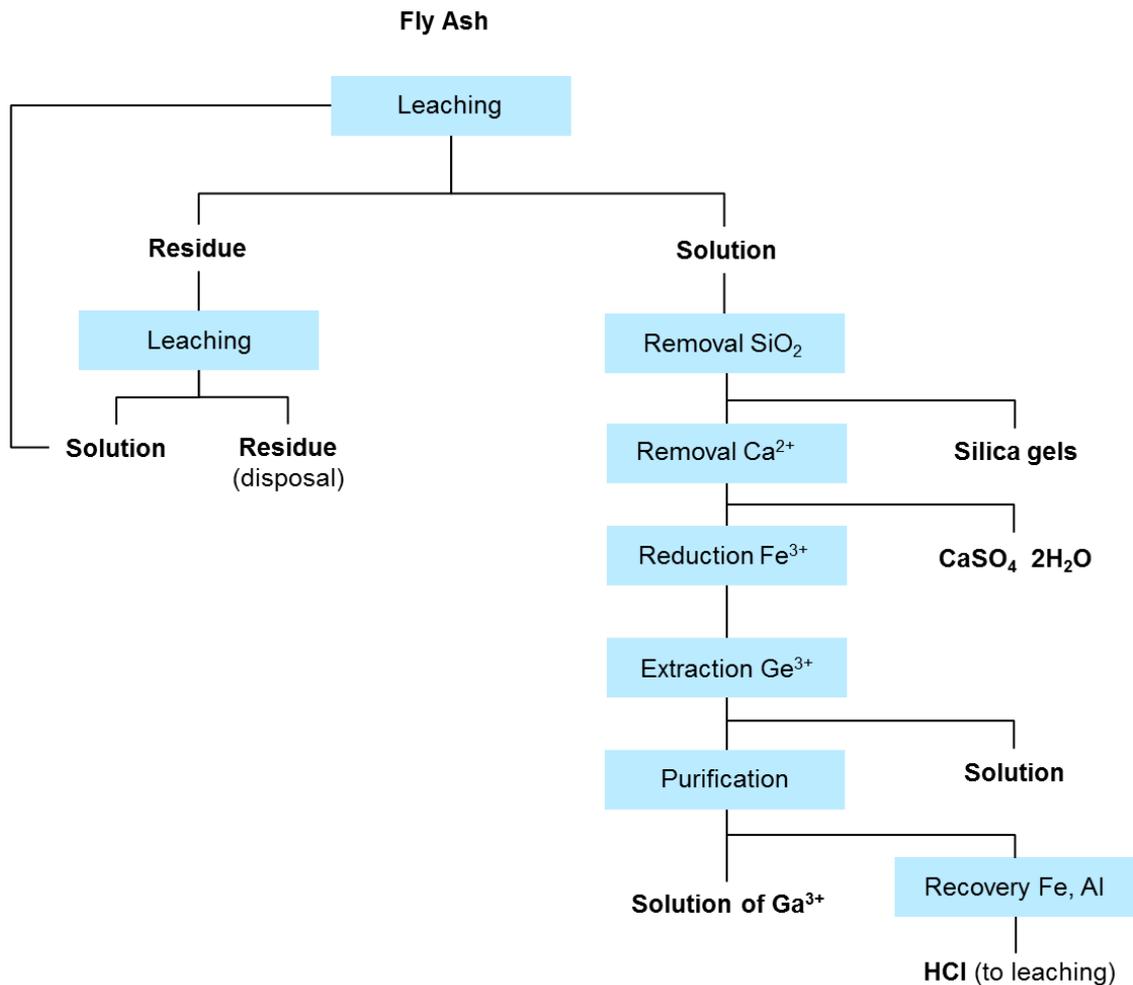


Figure 15. Proposed flowsheet for coal fly ash treatment. (Fang & Gesser, 1997)

Font et al. (2005) used only water in an attempt to develop a low cost, environmentally friendly process to obtain a commercial Ge product from gasification fly ash. The fly ash samples were extracted at different temperatures, fly ash/water ratios and extraction times to determine the highest extraction yield. High Ge extraction yields (up to 84%) were obtained at room temperature (25 °C) but also high proportions of other trace elements (impurities) were simultaneously extracted. Increasing the extraction temperature to 50, 90 and 150 °C, Ge extraction yields were kept at similar levels, while reducing the content of impurities, the water/fly ash ratio and extraction time. The experimental data also pointed out the influence of chloride, calcium and sulphide dissolutions on the Ge extraction.

Supercritical fluid extraction (SFE) with CO₂ has become a promising method for extraction a range of metals from ashes such as Sb, Cr, and Mo (Meawad et al. 2010). Compared with conventional solvent extraction, SFE is relatively fast and its selectivity can be controlled. When combined with an appropriate complexing agent, supercritical CO₂ is a strong solvent with a high diffusivity and a low viscosity. Furthermore, because it can be recycled easily, the absence of solvent waste is a major advantage. In order for heavy metals to be dissolved in CO₂, the metals must be present as electrically neutral complexes. Therefore, organic ligands are added to form metal complexes.



4.3 Thermal processes

In Japan, ash melting plants treat fly ash and bottom ash residues from incineration. Around 10% of total generated ashes are processed at 1300-1700°C to form molten fly ash (≈13%) and molten slag (≈88%) containing molten metal in a concentration around 4%. Currently the majority of all of the thermally treated residues are either sent to landfill or used for construction, while some of the molten metal is recycled. During the melting of incineration residues, metal separation occurs by volatilization in the melting furnace and/or by the physical characteristic of the metal elements. Elementary Fe, Ni, and Cu, etc. remain in the furnace and the metal fraction separates by gravity. (Jung et al. 2009)

Metal elements with a low boiling point and metal chlorides evaporate and accumulate in the fly ash confined in the APC system. Thus, Zn and Pb are highly concentrated in molten fly ashes reaching concentrations nearly equal to the quality of raw ores. These fly ashes are supplied to some non-ferrous metal smelting plants and the main metals recovered but the critical metals containing are not taken into account. Nowadays it is necessary a modern technology and possibly concentrate the scarce metals in melting fly ash to recover the containing critical compounds.

Following are some of the current studies aimed to concentrate rare metal containing in the ash (Jung et al. 2009):

Melting conditions: The thermodynamic behaviour of rare metals can change the ratio distribution in molten fly ash and molten slag. Thus, experimental and thermodynamic equilibrium calculations have revealed that Ag, Bi, Ga, Ge, In, Pd, Sb, Te and Tl are readily volatilized as chloride and/or gaseous form and then condensed in melting furnace fly ash. Also, Cr, Ni, Ta, V and Zr tend to mostly remain in molten slag (Figure 16). Similarly, the calculations suggest that compounds such as Co, Mo and W, without volatilization in actual plants, can volatilize in chloride form.

Water extraction methods: They can be used not only to concentrate valuable rare metals but also to remove undesirable substances such as chlorine for their recovery from melting fly ash. Figure 16 shows the composition change in melting fly ash before water washing.

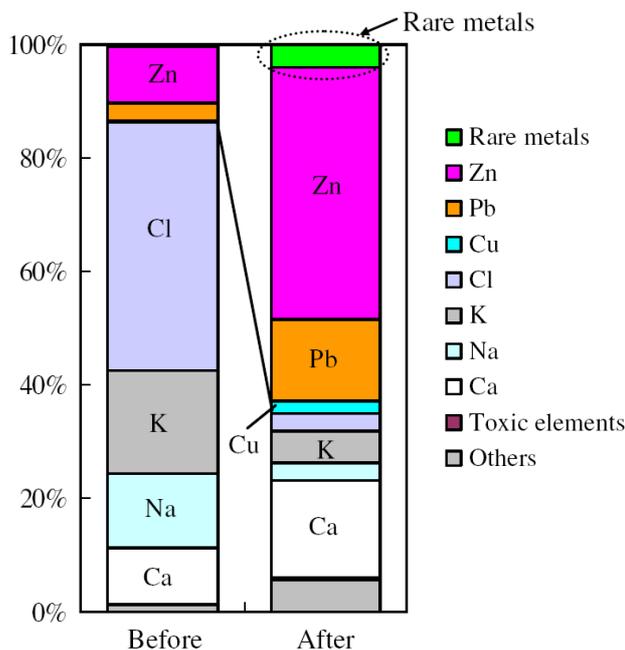


Figure 16. Composition change in MFA before water washing at pH10 (Jung et al. 2009)

4.4 Industrial scale processes for ashes

4.4.1 FLUWA process

About half of waste-to-energy (WTE) plants with wet flue gas cleaning process in Switzerland are using the FLUWA process to separate heavy metals from filter ash. The processed heavy-metal-free filter ash cake is recycled together with the bottom ash. The downstream FLUREC process extracts high-purity zinc from the heavy-metal-filtrate out of the FLUWA process - direct on site. The FLUWA process (Figure 17) uses the acid in the scrub water, mobilizes and extracts the heavy metals contained in the filter ash. At the same time, the excess acidic content of the scrub water is neutralized by the alkalinity of the filter ash. The downstream FLUREC process separates cadmium, lead and copper, and recovers zinc, a valuable metal that is present in high concentrations in the filter ash, as a high-purity metal (Zn > 99.99 %). (Schlumberger & Bühler 2012)

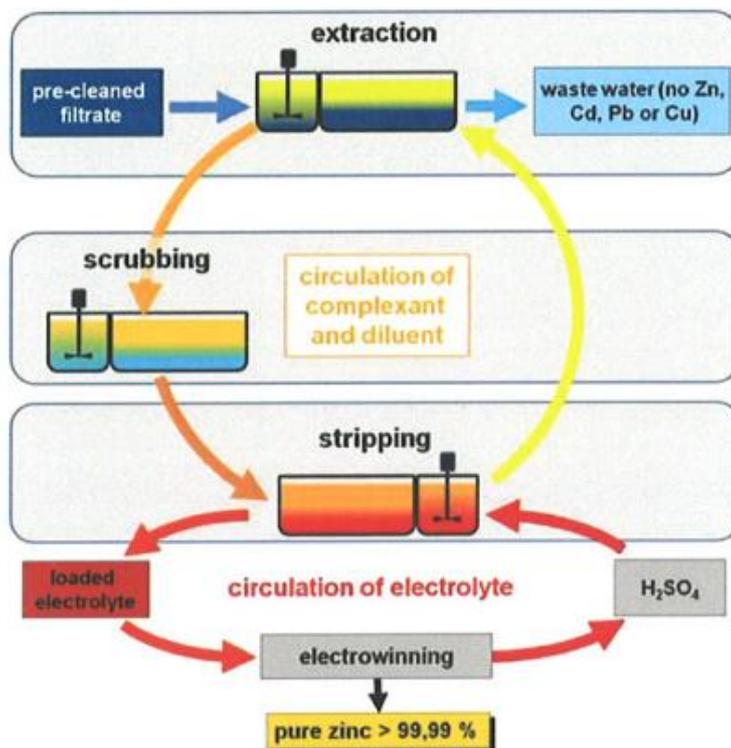


Figure 17. Schematic diagram of the solvent extraction and zinc electrowinning cycles (Schlumberger & Bühler 2012).

The FLUREC process steps have proven their value in long-term piloting projects at various industrial sites. Heavy metal recovery will be implemented on a large scale (FLUREC) during process technology replacement at the Zuchwil WTE plant in Switzerland and will go into operation in 2012. It is planned to recover approx. 350 tonnes of zinc per annum. (Schlumberger & Bühler 2012)

4.4.2 Ash Dec

Thermochemical processes use ash or solid wastes and high temperatures to separate heavy metals from phosphorus as the heavy metals are the main obstacle in using sewage ash directly in fertilizer industry.

In the Ash Dec process, high phosphorus concentration ashes are mixed with a molar surplus of chloride donor such as CaCl_2 , KCl or MgCl_2 . Fillers such as coal, aluminium, wood or paper waste can also be added to affect the properties and structure of the end product. The mixture should contain about 55 – 90% of ash, 5 – 40% metal chlorides and 2 – 30% fillers which are pelletized. The pellets are then dried and heated in around 300°C after which the temperature is raised into $900 - 1100^\circ\text{C}$ causing the gasification of heavy metal chlorides that are removed with the flue gases. The flue gases are washed and the heavy metal waste is disposed. The process removes 99% of Cd, Hg and Pb and over 90% of Cu and Zn rendering the end product (registered as PhosKraft) feasible for fertilizer use. Ash Dec flowsheet is presented in Figure 18. (Nieminen 2010)

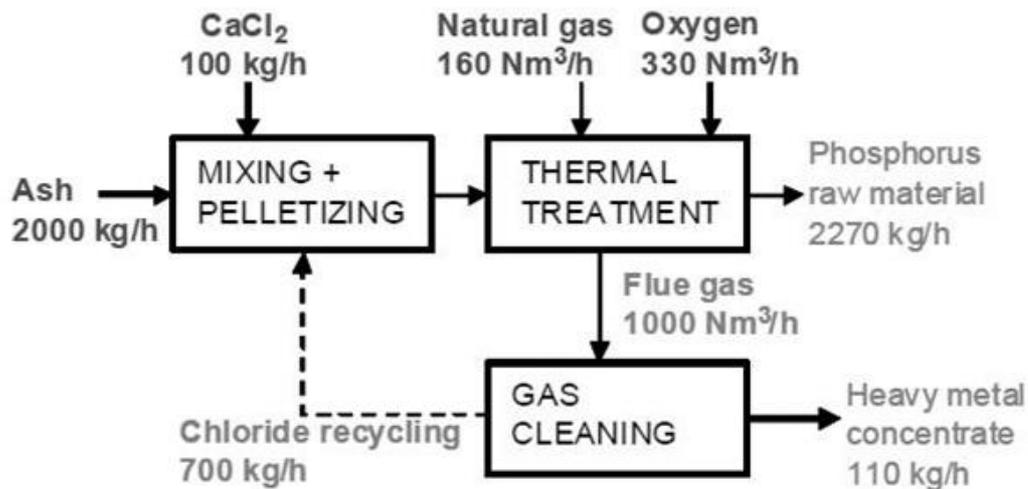


Figure 18. Ash Dec flowsheet (Nieminen 2010)

Ash Dec was started already in 2002 and completed as a part of EU project SUSAN in 2008 when a 10 t/a pilot scale plant was built in Leoben. The process is ready for full scale implementation and plans were underway to construct a full scale plant but the company went bankrupt and the process was sold to Finnish company Outotec spring 2011. (Nieminen 2010).

4.5 Emerging technologies

Use of hyper-accumulating plants, biosorption using biomass and bacterial leaching are methods in initial steps but with a great potential of development. Also, integration these novel methods with existing metallurgical recovery process may be beneficial and necessary for the purification, concentration and separation of the value/targeted metals from impurities. The use of existing technologies could include:

- Separation and concentration: solvent extraction, ion-exchange, membrane technology, supercritical fluid treatment, precipitation and crystallization.
- Metal extraction and precipitation: electro-winning and/or electro-refining, cementation, gas reduction.

Therefore, new technologies to initial metal extraction should be developed which combining with existing metallurgical operations allow treating each individual waste stream for different targeted metals.

4.6 REE processing from secondary resources

The physical advantage of REE recycling is the REE extraction process. Much of the difficulty of extracting REEs from virgin ores results from them occurring intermixed in ores. Extraction methods separate elements by the differences in their properties, which are minimal between REEs. Some of these characteristics include: reactivity, electrical conductivity, and melting points along with ionic and strongly paramagnetic properties which are common for all REEs; solubility and complex formation which only have very small



differences between REEs; and basicity and density which undergo size induced variations. The REEs are essential for their unique chemical, magnetic, electrical, and luminescence characteristics, but the minute differences in characteristics between the rare earths make it difficult for them to be separate from each other. When rare earths are separated from waste products, they are intermixed with fewer rare earths and sometimes occur in higher concentrations than in ores. There is also the possibility of eliminating the complications of extracting intermixed rare earths by extracting the mixture, then refurbishing the mixture to be placed back in its original supply chain. (Meyer & Bras 2011)

In order to extract REEs, current best mining practices use a mix of primarily solvent extraction and ion exchange, with more specific methods sometimes integrating solid phase extraction, supercritical extraction, electro slag refining, electrowinning, and electrorefining processes. These processes fall into three main categories: hydrometallurgy, which is variations of aqueous chemistry; electrometallurgy, which is variations of electrolysis; and pyrometallurgy, which is variations of thermal treatments. (Meyer & Bras 2011)

Processing technologies that are currently used, or are in the research stage, for the recovery of REEs are discussed in several references and can be grouped into the following general categories as presented in Table 12.



Table 12. Current processing technologies for the recovery of REEs. (US EPA 2012)

Process	Description and stage
Pyrometallurgy processes	Pyrometallurgy processes are energy intensive, using high temperatures to chemically convert feed materials and separate them so that the valuable metals can be recovered. It should be noted that rare earths can oxidize easily in these types of processes, making recovery difficult. While one recycling facility in Japan reportedly is recovering REEs using this type of process, others companies such as Umicore and Alcoa are conducting research that will enable wider use of this type of technology for REE recycling. During smelting, volatile organic compounds (VOCs) and dioxins could be generated and would need to be managed.
Hydrometallurgy processes	Hydrometallurgy processes use strong acidic or basic solutions to selectively dissolve and then precipitate metals of interest from a preprocessed powder form. The specific process used will vary depending on the metal to be recovered, but options could include solvent extraction, leaching, and selective precipitation, among others. Variations of this type of technology are frequently reported in the literature, and a recent summary is provided by. The fundamental processes used for recycling REEs are the same as those utilized for raw ore. Accordingly, the waste streams and pollutants of concern are the same as in those. In short, chemical and particulate air emissions, as well as slag material from the smelting process are all potential pollutant sources.
Electrometallurgy processes	Electrometallurgy processes such as electrowinning (where a current is passed from an inert anode through a liquid leaching solution containing the metal; the metal is extracted by an electroplating process, which deposits the rare earths onto the cathode), and electrorefining (where the anode is composed of the recycled material--when the current passes from the anode to the cathode through the acidic electrolyte, the anode corrodes, releasing the rare earth ions into the solution, then electrowinning occurs). No specific information was located on environmental impacts from these processes when they are used to recycle REEs; however, they are expected to be similar to those identified for primary processing operations.
Dry processes	Dry processes (research stage) use hydrogen gas at atmospheric pressure to turn neodymium-containing magnets to a powder that can then be re-formed into new magnets under heat and pressure. This research is being conducted at the University of Birmingham in the United Kingdom, and while the newly produced magnets are not of the same quality as the originals, they are suitable for use in motors.
Tailings recycling	Tailings recycling involves reprocessing of existing tailings to recover the remaining amounts of REEs they contain. Recycling of tailings generally will occur at the same location as the mining operation using existing processes and equipment and resulting in the same contaminants as when processing the original ore. As reported, the economic benefit, energy savings, and environmental benefits can be significant.
Microbe-filled capsule technology	Microbe-filled capsule technology (research stage) has been recently reported in the literature as being developed jointly by Morishita Jintan Co. and Osaka Prefecture University. With this technology, capsules are reportedly placed in a medium containing rare metals, and the microbes then absorb the metals. While the research to date has focused on rare metals (not specifically rare earths), it is thought to be transferable. If this is in fact proven to be true, an official at the Japan Society of Newer Metals has indicated that it could help to make REE recycling more cost-effective.
Titanium dioxide process	Titanium dioxide process (research stage): While evaluating a process to develop methods for extracting higher yields of titanium dioxide, researchers from the University of Leeds, Faculty of Engineering discovered how to recover significant quantities of REOs present in titanium dioxide mineral. While the original benefits of this technology were thought to be that it could improve purity, eliminate hazardous wastes, and cut costs and CO ₂ emissions, the team also discovered that they could extract significant quantities of REM oxides as co-products of the refining process. Current recovery rates of oxides of neodymium, cerium, and lanthanum vary between 60 percent and 80 percent and are thought to be able to be increased in the future.



Significant amount of research into the recycling of REEs has on the other hand been undertaken, most notably in Japan. The result of the research activities is that there are potentially a number of extraction processes but none of them has been developed commercially due to drawbacks on yields and cost. The most attractive appears to be treatment with liquid metals. The only patents appear to be from the early 1990s. Little progress has been made in 15 years or so. (Oakdene Hollins 2010)

Currently the number of commercial REE recycling operations is limited and recycling plants and technologies are quite rare. However, this is likely to change in the near future due to the number of operations under development and the extent of ongoing research. Appendix 1 provides a summary of commercial, or soon-to-be-commercial, operations by selected companies and includes the information that is known on the target item to be recycled, the materials being recovered, the technology to be used, the anticipated time frame until commercial application; notes with respect to cost or environmental benefits; and the source of information. The literature indicates that the focus of REE-recycling research and commercialization efforts has been on magnets, batteries, lighting and luminescence, and catalysts. It should be noted that in many cases, the companies that are in the process of developing or deploying recycling technologies have not published reports or papers with the details of their individual processes, as these are generally a competitive advantage and considered proprietary. (US EPA 2012)

4.7 Economical aspects

Information concerning the recovery of scarce metals concerning costs and revenues, operational costs and investment costs are not available. If the implementation of a recycling technology to recover scarce metals will be economical feasible, depends among others on the quality and amount of secondary scarce metal products and the prices available for primary and secondary products and at most on the local disposal cost. For disposal cost under 20 Euro further treatment of ash is difficult.



5 Conclusions

The European Commission has identified 20 critical raw materials or metal groups. These are those that are considered vital for development in areas such as computers, electronics and electric vehicles and where the use is expected to increase significantly in the coming decades. Furthermore, the known assets of several of these substances concentrated in individual countries outside the EU. Knowledge of these substances in waste-to-energy ashes is very limited and the same applies, for example, the distribution of substances between the fly and bottom ash. There are some values reported in the literature but no major review has been made to cover the critical metals in a number of plants. A better knowledge of the elemental composition of the ash is a prerequisite for selection of further treatment of ashes and for exploitation of the potential added value of these substances.

Metal mine development, particularly for critical elements, requires extensive capital investments and complicated regulatory oversight. Several companies are therefore currently exploring methods to extract critical metals from different secondary materials e.g. ashes. However, the knowledge of the presence of valuable elements in ashes is limited. There are concentration values available, but no comprehensive studies have been made to systematically investigate the elemental composition of ashes. Due to the lack of elemental data, there is a further need to characterize strategic element content in different ashes.

Based on this review the concentrations of critical metals in waste-to-energy ashes are generally lower than the average concentration in the earth upper crust. The exceptions are antimony, cobalt, silver, thallium and tungsten. Antimony and silver occur in elevated concentrations in fly ashes from waste-to-energy grate-fired and fluidized-bed boilers. Fly ashes from grate-fired boilers may also contain higher concentrations of germanium. Furthermore, elevated concentrations of silver, gold and antimony occur in MSWI bottom ashes, whereas coal fly ashes contain germanium and gallium.

A better knowledge of the composition and speciation in ashes is vital in the choosing of treatment methods for the ashes and also for the possibility to recover valuable resources from the ashes. It will also be necessary to evaluate and prioritize these resources to focus efforts on those ashes with the highest amounts of target elements and those that can be effectively extracted from the specific ash matrix. Information concerning the recovery of scarce metals concerning costs and revenues, operational costs and investment costs are not available. Generally, the economic feasibility of a recycling technology to recover scarce metals depends in practice at most on the local disposal cost. However, the retrofitting of existing ash treatment plants to a state-of-the art level is technological possible and economical feasible. These technologies would allow an optimised separation of liberated metal particles and the production of a mineral fraction suited for the substation construction material.

Although no suitable patents were found in the patent survey, several chemical extraction techniques have been applied for metals in ashes. Generally, these processes usually include initial chemically induced leaching of the material, often employing the use of low-pH acids (e.g. hydrochloric, nitric, sulfuric, or oxalic acid) together with varying temperatures and leaching times, depending on the composition of the ash. When choosing technologies for



recovery, it is crucial to distinguish the varieties of ashes and the differences in their chemical and mineralogical compositions. When new uses for ashes develop, it will also be important to consider potential environmental impacts.

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REE Recycling Operations, Technologies Utilized, Current Status, and Benefits (1/2)

Company	Target Feedstock/ Element	Technology to Be Used	Anticipated Time to Commercialization	Benefits (Cost and Environmental)	Source
Hitachi	Rare earth magnets from air conditioner compressors and hard disk drives	Automated separation process and dry extraction process	Anticipates recycling will meet 10% of its need by 2013 when facility goes online	Dry extraction method that allows processing without acids; resulting waste water problem. Automated separation process is faster than manual. Cost savings anticipated.	http://www.hitachi.com/New/cnews/101208.pdf
Toyota	Hybrid car batteries	Unknown	Ongoing	Main driver is supply concerns	http://shanghaiscrap.com/?p=5854
Japan's Shin-Etsu Chemical	Air conditioners	Plans to recycle recovered REEs into magnets	2011	No information readily available.	http://www.matternetwork.com/2011/3/new-push-recycle-rare-earth.cfm
Showa Denko KK	Dysprosium and didymium (a mixture of praseodymium and neodymium)	No information readily available.	Estimated output of 800 tons from recycling facility	No information readily available.	http://www.bloombergonline.com/news/2010-12-08/hitachi-recycles-rare-earth-as-china-crimps-supply.html



REE Recycling Operations, Technologies Utilized, Current Status, and Benefits (2/2)

Mitsubishi (with Panasonic and Sharp)	Neodymium and dysprosium, washing machines and air conditioners	No information readily available.	Currently in research stage. Anticipated production stage by 2014	No information readily available.	http://www.bloomberg.com/news/2010-12-08/hitachi-recycles-rare-earth-as-china-crimps-supply.html
Kosaka, Dowa Holdings	Existing electronics recycling plant—future processing of neodymium.	Smelter—300 tons of material per day are processed, resulting in 150 grams of rare metals	Research being conducted to develop technologies for REE recovery	Factory is making money. Process for neodymium extraction is estimated to be costly.	http://www.nytimes.com/2010/10/05/business/global/05recycle.html?emc=eta1
Raptor Technology Group	Mine tailings (from hardrock ore deposits from Washoe mine).	"Advanced chromatography and innovative separation technologies"	2,000 tons of ore per year, currently. New facility being built with capacity of over 10,000 tons of ore per year.	Cost savings; reclaimed mine wastes; chemical recycling and water savings.	http://www.raptortechnologygroup.com/general.php_category=Raptor+Technologies=metal.php
Creative Recycling Systems/ GreenRock Rare Earth Recovery Corporation	Electronics	"Closed loop" process. Details not available	By end of 2011, estimated to have four processing facilities with a capacity to process 500 million pounds of electronics per year.	No information readily available.	http://www.sustainablebusiness.com/index.cfm/go/news.display/id/21900
Wings Enterprises Inc.	Tailings from previous mining at Pea Ridge, Missouri	No information readily available.	Within 12 months.	No information readily available.	http://www.raremetalblog.com/2011/01/rare-earths-producer-molycorp-rivals-seek-us-aid-as-china-chops-exports.html
Umicore and Rhodia	Nickel Metal Hydride (NiMH) rechargeable batteries	Umicore's proprietary Ultra High Temperature (UHT) battery recycling process in combination with Rhodia's rare earth refining processes	First production expected by end of 2011.	This is the first known technology for recycling rare earths from NiMH batteries. "A typical NiMH battery will contain some 7% of rare earth elements including cerium, lanthanum, neodymium and praseodymium. This equates to 1 gram of rare earth for a AAA battery, 60 gram for a household power tool and 2 kilograms for a hybrid electric vehicle battery."	http://www.euronext.com/fic/000/064/994/849944.pdf

Mechanical treatment technologies

In the following sub chapters the common mechanical process steps (size reduction; size controlling; separation of desired material or contaminant) are presented in more detail.

Size reduction

In order to achieve sufficient separation efficiency, the particle size distribution of the feed must be optimized for the separation process. Fly ash is composed of small sized particles and therefore seldom requires any size reduction. In some cases dry agglomerates can be crushed in a light milling process. As for bottom ash, the particle size rarely fulfils the particle size requirements of the separation processes at which time particle size reduction is required. In addition, ash particles or agglomerates may consist of several different materials in which case these needs to be crushed and detached before the separation can take place. In other words the liberation degree of the feed can be increased by crushing at which time the separation processes becomes more efficient (Reuter et al. 2005).

The size reduction equipment differ in technologies and therefore on the target of application. Brittle material breaks up by compression and impact whereas ductile material requires shear force for breaking (Worrell and Reuter, 2014). Considering bottom ash that consists mostly of brittle material jaw-, cone-, impact- and roll crushers are commonly used for the size reduction process. If the target particle size of the feed for further treatment is below 2.5 cm grinding mills such as ball- and tumbling mills are preferable (Wills and Napier-Munn, 2006). However, energy consumption of the process increases when grinders are used. Recently study on applying electrodynamic fragmentation to crush and break agglomerates in bottom ash has been carried out (Thome, 2012). Within this method ultrashort flashes are used under water to separate materials from each other.

Beside size reduction, milling and grinding can be used for activation. In these cases the ash is mechanically activated by abrasion to increase its reactivity and consequently the behaviour and handling in further utilization schemes (Hela and Orsakova, 2013; Fu et al. 2008).

Size controlling

Size controlling is precondition for several mechanical separation processes. In the control solids are separated into two or more products on the basis of their size and/or gravity/density. The process can be wet or dry. In the coarser end (> 250 µm) screening is used for the controlling while for the fines dynamic size separation (classification) such as cyclones are utilized (Gupta, 2003; Wills and Napier-Munn, 2006).

Screening is carried out for numerous reasons, depending on the application: (Wills and Napier-Munn, 2006)

- *Sizing* to split in several size classes, each intended for a process optimized for that particular size class
- *Grading* to classify into sizes as required by the market
- *Scalping* to remove coarsest size fractions in the feed material, commonly carried out to be crushed or removed from the process
- *Desliming or de-dusting* to remove fine material (generally below 0,5 mm)



- *Dewatering* to drain free moisture from a wet slurry
- *Trash removal* usually to remove wood fibres from fine slurry

In screening particles are presented on a surface that has uniform holes and either pass through or be retained according to whether the particles are smaller or larger than the governing dimensions of the hole. The screening efficiency is determined by the degree of perfection of separation of the material into size fractions above or below the hole size. (Wills and Napier-Munn, 2006) Common screening equipment are trommel, vibrating deck, roller and gyratory screens.

In classification, a material aggregate of mixed sizes and different gravities is allowed to settle through a medium, which may be either in motion or at rest. As a result, the material is separated into two or more fractions. The separation is caused by the differential settling. The used medium is commonly water, though other liquids and gases including air may also be used. The efficiency of a classifier is presented by a performance partition curve, which relates to the particle size to the percentage of each size in the feed that reports to the underflow. (Gupta, 2003) The most commonly used device is the hydrocyclone, but other devices such as mechanical- and hydraulic classifiers may also be used.

Separation and enrichment

Enrichment can be considered either as a washing process which removes impurities from the feed to improve the value of the waste stream or as a separation process in which valuable materials are separated from material matrix. Usually both size reduction and – controlling is required before separation processes to ensure sufficient separation efficiency. In Figure the relation between reject and valuable product in a washing and separation process is presented.

Separation processes are often in series to improve the yield of the valuable target material. In such situation the waste in Figure 1 continues to further processing. Separation processes set stricter requirements for the feed than washing processes.

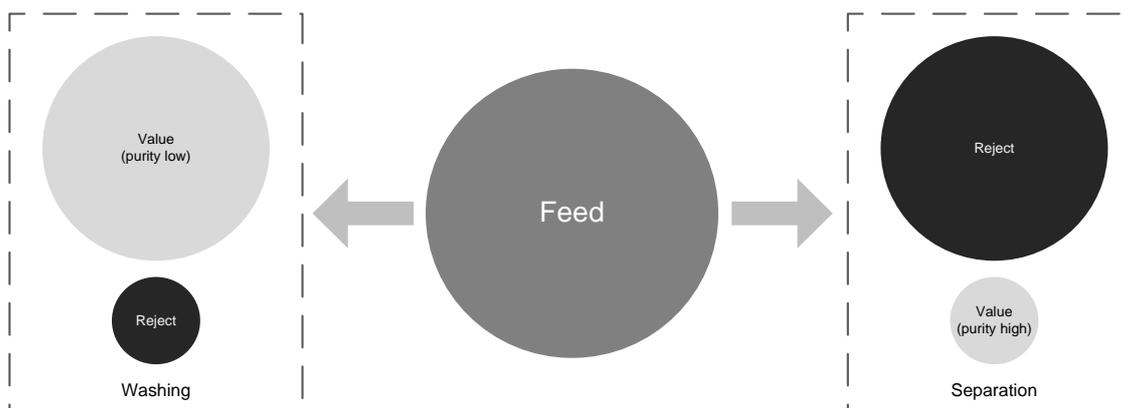


Figure 1. The relation between reject and valuable product in an washing and separation process.

Typical washing processes are scrubbing and wet sieving. In these processes impurities are removed from the feed based on the solubility of the impurities. For example in bottom ash



treatment soluble salts such as chlorides and sulphides can be removed by means of washing (Muchova, 2010).

Separation processes separate materials and particles based on their physical and physico-chemical properties. Therefore, the liberation degrees of desired particles are in essential position in order to create as high and pure separation property as possible. In Table 1 common separation processes with the desired properties of target particles has been presented.

Table 1. Separation processes

Physical and physico-chemical properties	Separation process
Shape and size	Screening and classification
Specific gravity	Wet or dry gravity separation
Electric charge	Electrostatic separation
Magnetic susceptibility	Wet or dry magnetic separation
Circulating eddy current	Eddy current separation
Surface properties	Flotation
Colour	Sorting (sensor)
Shape, size and hardness	Ballistic separation

Gravity separation

In gravity separation process particles with mixed sizes, shapes and specific gravities are separated from each other by the force of gravity or by centrifugal force (Gupta, 2003). In order for efficient separation, clear density difference between the target particles/material and the reject need to exist. For a preliminary estimate on gravity separation's applicability on feed material, a concentration criterion (C_r) can be calculated based on eq. 1.

$$C_r = \frac{\rho_{heavy} - \rho_{fluid}}{\rho_{light} - \rho_{fluid}} \quad (1)$$

In general terms if the C_r is greater than 2.5, whether positive or negative, the gravity separation is relative easy. (Gupta, 2003; Wills and Napier-Munn, 2006; Worrell and Reuter, 2014) Beside the specific gravity of particle, its size also effect on its motion in the fluid. Larger particles will be affected more than smaller ones. Therefore, the efficiency of gravity separation increases with particle size. (Wills and Napier-Munn, 2006)

Common gravity separation devices are jigs, spirals, shaking tables and dense medium separators. In Figure 2 a schematic description of a shaking table has been presented.

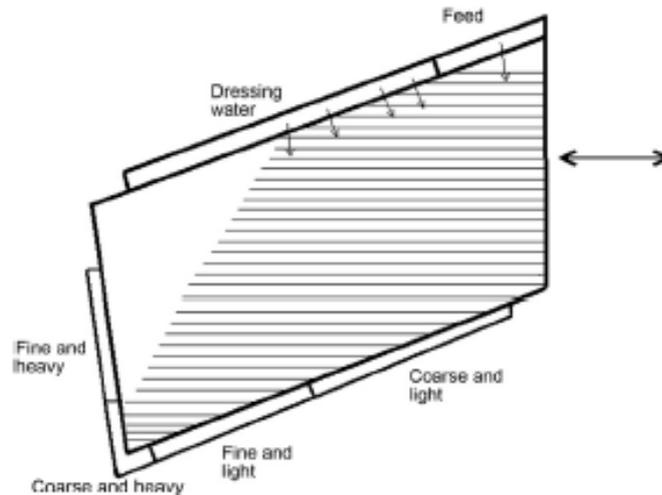


Figure 2. A shaking table. (Worrell and Reuter, 2014)

Magnetic separation

The magnetic separators exploit the differences in magnetic properties between the waste materials and are used to separate either valuable Fe metals from the feed such as in the end-of-life vehicle (ELV) recycling or to remove magnetic impurities such as in the glass recycling. All materials are affected in some way when placed in a magnetic field, although with most materials the effect is too slight to be detected. The separation is based on the difference on magnetic susceptibility. Diamagnetic materials such as plastics, rubber, glass, slags have a small negative susceptibility and are very weakly affected in the magnetic field. Therefore, these materials cannot be separated with magnetic separation. In turn, paramagnetic materials have a small positive susceptibility and can be separated from diamagnetic materials by high intensity field magnetic separation. Some metals such as Ti, V, Cr, Mn and PGM are paramagnetic. In addition, some Fe compounds exhibit paramagnetic properties. Finally, ferromagnetic materials such as Fe, Co and Ni have high susceptibility and may be even magnetized in a high intensity field magnetic separator. Therefore, low intensity separators should be utilized for the removal of ferromagnetic particles. (Wills and Napier-Munn, 2006; Worrell and Reuter, 2014)

Typical low intensity magnetic separators are drum separators, cross belt separators (Figure 3) and counter roll separators. High intensity (with a field of 2 T or more) separators are induced roll separators, ring type separators and Jones separators.

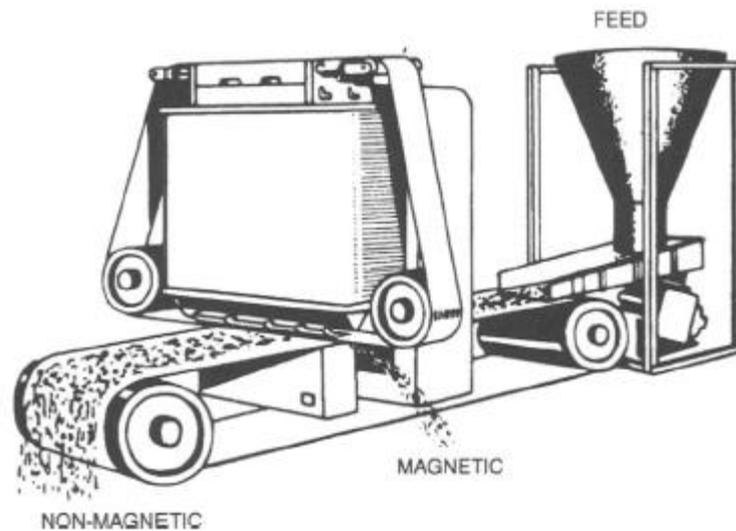


Figure 3. A low intensity cross belt magnetic separator. (Wills and Napier-Munn, 2006)

Eddy current separation

In eddy current separation an alternating magnetic field induces a circulating eddy current to conducting particles. This creates a force that is perpendicular to the magnetic flux and the direction of the eddy current. (Worrell and Reuter, 2014) This force shoots the particles from conveyer belt to separate containers. The force is generated in an eddy current separator by a rotating drum containing magnets placed in relays, positive magnet next to a negative one. This drum is placed in the end of the conveyer belt. Materials such as aluminium and magnesium can be separated easily with eddy current since the separation force is proportional to the ratio between particle's conductivity and density, which is high for aluminium and magnesium. Materials such as copper and silver have medium high ratio at which time relative high magnet speed is require. Beside conductivity and density, particle shape affect the separation force in the way that flat particles separate more easily than cylindrical. In Figure 4 the principle of eddy current has been presented.

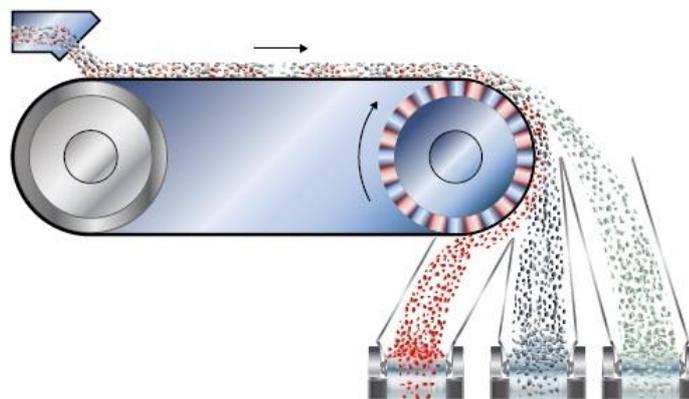


Figure 4. An eddy current separator where light grey particles are conductive.



Flotation

Froth flotation is a widely applied separation technique in mineral concentration and recovery processes. In the separation process, gas is introduced to the slurry where bubbles collide and attach on the surface of particles generating a bubble – particle aggregates that rise to the surface forming a froth layer. The froth can be separated manually or mechanically from the surface of the cell. (Yarar, 2000) In Figure 5 the principle of froth flotation has been presented.

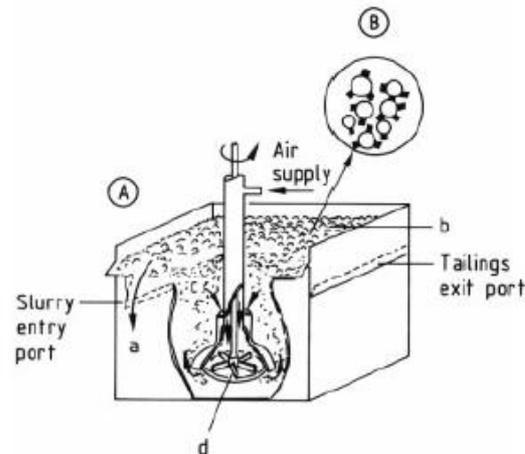


Figure 5. A schematic description of froth flotation process (mechanical), where A) flotation cell; a) froth overflow; b) froth layer; c) pulp; d) rotor for pulp agitation; B) bubble-particle aggregate within the cell. (Yarar, 2000)

The selectivity of froth flotation relies on the hydrophobicity of particles. For these particles the adhesion between the surface and the fluid is lower than the cohesion in the fluid, in which case the fluid tend not to wet the surface. As a result, gas bubbles will attach on the surface of the particles. (Worrel and Reuter, 2014) Consequently, for hydrophobic particles the surface energy and tension needs to be lower than for water (if used in flotation) whose surface energy and tension is 72 mJ/m² and 72 mN/m, respectively. For example, the apparent free surface energy of plastics is in the range of 30-45 mJ/m² making them hydrophobic, whereas for minerals the surface energy is in the range of 300-500 mJ/m² (Worrel and Reuter, 2014).

Since most of the materials are hydrophilic by nature, chemical reagents are used to manipulate target particles/materials surface energy generating hydrophobicity. These reagents are called collectors and by selecting the right collector significant selectivity can be achieved. Beside collectors other type of reagents such as frothers, depressants and activators are used to increase the efficiency of the flotation process. Other process parameters which affect the flotation process are particles size (10-300 µm) and shape, aeration rate, agitation speed and pulp density.

Flotation machines can be divided roughly to two groups: mechanical and pneumatic. In mechanical devise turbulent flotation conditions are generated by a rotor at which time heavier particles can be more easily separated from each other. Mechanical devises are used especially in mineral processing (organics separation, Cu and Zn enrichment) and slag



treatment. In pneumatic machines compressed air is introduced to the slurry in laminar conditions. This method is mainly used in water treatment to remove impurities.

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