ON THE DIRECT RECYCLING OF AUTOMOTIVE SHREDDER RESIDUE AND ELECTRONIC SCRAP IN METALLURGICAL INDUSTRY

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O PRIAMEJ RECYKLÁCII ZVYŠKOV AUTOMOBILOV A ELEKTRONICKÉHO ŠROTU PO DRVENÍ V HUTNÍCKOM PRIEMYSLE

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Abstrakt

Smernice týkajúce sa skládok odpadov na zvyšky po drvení zo starých motorových vozidiel a odpadových elektrických a elektronických zariadení sa v Európskej únii stávajú čoraz prísnejšími. Zároveň cena kovov a energie spôsobuje recykláciu tejto skupiny odpadových materiálov, čo má za následok zvyšovanie cien neželezných kovov a energie. Recyklácia menej hodnotných frakcií drviacich zvyškov, ako napr. zvyšky po drvení automobilov s nízkym obsahom medi a takmer bez ušľachtilých kovov vyžaduje jednoduchý a veľmi lacný postup bez spracovaní mechanickej separácie s úplnou spotrebou energie. Jednou z perspektívnych možností recyklácie je spoločné tavenie zvyškov po drvení ako také, alebo popolu z predchádzajúcich postupov rekuperácie energie (pyrolýza, splynovanie) v závodoch neželezných kovov. V článku sú diskutované perspektívy recyklácie zvyškov po drvení automobilov s dôrazom na pyrometalurgické alternatívy.

Abstract

Landfill regulations on shredder residue (SR) from End of Life Vehicles (ELV) and Waste Electric and Electronic Equipment (WEEE) are becoming increasingly rigorous in EU. At the same time the metal and energy value makes recycling of this waste material group more attractive at the moment due to increasing non-ferrous metals and energy prices. Recycling of the less valuable SR fractions like ASR (automotive shredder residue) with low copper content and practically without precious metals needs simple, low cost recycling route without complex energy consuming mechanical separation treatments. One perspective recycling alternative is co-smelting of SR as such or ash from preceding energy recovery treatments (pyrolysis/gasification) in nonferrous metals plants. Perspectives of (A)SR-recycling are discussed emphasising the pyrometallurgical alternatives.

Keywords: SR-recycling, mechanical separation, pyrometallurgical processing

Introduction

WEEE (Waste Electric and Electronic Equipment) and ELV (End of Life Vehicles) are increasingly important secondary source of ferrous and nonferrous metals. WEEE comprises a series of electrical equipment ranging from household appliances through electric and electronic tools to telecommunication equipment ELV all materials in cars. Two estimates estimations for annual WEEE and ELV disposal in EU are 9 to 10[1] Mton and 8 to 9 Mton [2], respectively. These two waste classes are composed of various metals and their solders mixed, connected and covered with various types of polymers, glasses and ceramics. Recycling of WEEE and ELV can comprise of a great number of physical/mechanical treatments: manual dismantling, disassembling, shredding, crushing, grinding, and separation (of different size fractions) by mechanical and physical properties. In the Figure 1. the main material fractions in WEE and ELV there are presented with rough estimation of limits for their relative amounts. To the main metal constituents belong usually iron, copper, aluminium, zinc and lead, medium constituents and chromium nickel, manganese and magnesium and to the minor components tin, antimony, titanium cadmium, mercury. The main precious metals are silver, gold and palladium. Besides the hazardous metals (cadmium and mercury) plastics fraction might contain bromine (in flame retardants) and chlorine.

The most problematic fractions of WEEE and ELV recycling treatments which have been mainly landfilled in the past are shredding residues (SR, ASR from ELV and ESR from WEEE) composed of organic (plastics, rubber and textiles), glass&ceramics and metal fractions. An estimate for the annual amount of ASR in EU is 20 to 25% from total ELV[2]. Due to the chemical and structural complexity of electric/electronic and automotive equipment as well as attendance of hazardous constituent’s selective fractioning of different materials, separation of various valuable and hazardous substances into easily recyclable fractions is very tough (highly expensive) task. This would be successful only by complete manual dismantling that is possible only if extremely cheap manpower is available. 80% of electronic waste collected in North America for recycling is reported [3] to be shipped in Asia for extraction and dumping operations. This solution for recycling is, however, humanly and environmentally hazardous and ethically questionably alternative. As the landfill directives concerning product recycling in EU are becoming increasingly strict, producer’s responsibility for recycling will increase and remarkable growth in landfill costs could be expected in the nearest future. Glass & ceramics and organics if not contaminated by toxic metals, bromine or chlorine can be used for landfill, but not for the metallic fraction. An important property of metals in opposite to plastics, glasses and ceramics that gives perspective for recycling is their practically indefinite recyclability.

On WEEE and ELV and their treatment and recycling

Although there seem to exist a great variety in WEEE and ELV recycling practices the first steps of WEEE and ELV recycling treatments seem to be (manual) *dismantling*, including separation of toxic, hazardous and most valuable constituents and *shredding* of equipments and vehicles. The most problematic fraction of both WEEE and ELV-recycling is the shredding residue consisting of fine fractions of organic materials, glass and ceramics as well metals. The amount of ASR i.e. the fine fraction that remains after recovery of valuable materials, mainly metals is varying but can be 20% or even more of the total. As the main idea of this presentation is co-recycling of those “hard to recycle fractions” of these two groups of wastes i.e. SR´s, they are treated together. Figure 1. shows very advisory estimate for relative amounts of the main fractions in mixed shredder residue and Table 1. the very advisory limits for contents of non-organic substances in mixed SR. Composition depends greatly on the origin of SR (WEEE / ELV relation) but relative amounts of the main fractions and metals in the metal fraction will alter within a wide range. In general amount of iron and G&C fraction in ASR is higher, lead, tin and precious metal lower (the latter being practically zero) than in ESR.

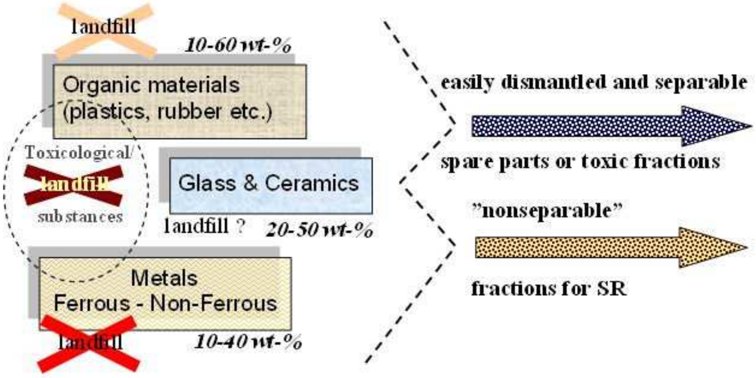

Fig.1 The main material groups in WEEE and EVL and rough estimates for relative amounts (sources mainly the same as given in Figure 1)

The energy content of SR and its utilisation is important for the economy of recycling. The calorific value of combustion depends on the relative amount of organic fraction and its composition. The calorific value of mixed plastics, main components in ASR fluff or printed circuit boards (PBCs) is slightly lower than that of fuel oils (40-43 MJ/kg). The usual processes/treatments of WEEE and ELV comprise a number stages in which the object is dismantled, the various material fractions are disintegrated (shredded, crushed, ground?) and finally mechanically separated.

Table 1 Suggestive limits for non-organic substances in mixed SR (information sources [4,5,6,7,8,9,10,11,12,13,14,15])

Major and medium SR (ASR-ESR)		**ASR**	**Minor**		**glass&ceramics**	
	wt-%	**wt-%**		**mg/kg**		**wt-%**
Fe	0.1-26	1 - 18	Au	0-3	SiO_2	14-20
Cu	0.04-30	0.4-3	Ag	0-1000	CaO	0.4-0.6
Al	0.7-5	0.7-3	Pt	0.1-200	Na_2O	0.06-3.3
Zn	0.3-6	0.5-3	Pd	0.1-1	K_2O	0.02-0.3
Pb	0.04-3	0.1-1.1	Cd	25-400	Al_2O3	4-6
Sn	0.01-4	0.01-0.04	Hg	0.1-15	Halogens	1-5
Mn	0.04-2.2	0.02-0.25				
Cr	0.02-1.1	0.1-1.1				
Ni	0.01-2	0.04-0.15				
Mg	0.05-0.8	0.05-0.8				
Ti	0.05-0.9	0.02-0.6				

SR treatments

The main fractions of SRs the organic fraction, glass & ceramics and metallic fraction have quite different physical properties (e.g. shape, size, density, brittleness, magnetic and electric properties) that makes their mechanical separation possible. Iron (carbon steels, cast iron) is ferromagnetic and easy to separate from the other fractions, non-ferrous metals and stainless steels (austenitic). Main mechanical separation methods are

- **Sieving:** separates different size fractions, not very selective
- **Vibrator**: separates fractions by density and particle size, not very selective

- **Air classification**: can be used for sieved fractions, separation by size and density
- **Sink and float**: separates fractions by density; questionable method for fine materials like bottom SR. An expensive method?
- **Magnetic separation**: weak and strong magnetic methods and eddy current separation

Pieces of individual metals even if covered by plastics or ceramics are relatively easily separated but metals thinly distributed in non-metallic materials or soldered with other metals are difficult to separate by physical methods.

The final collection of metal value can be carried out by ordinary or special hydro- or pyrometallurgical processing of various metal fraction or its subfractions.

If the share of organic fraction is high, SR can be incinerated as such or co-combusted with municipal waste or even used as secondary fuel in thermal power stations. High ash content limits substitution of fossil fuel by SR. Another possibility is pyrolysis or gasification on order to convert the organic fraction to solid, liquid or gaseous fuel with calorific value approaching that of coal or even oils. In combustion the metallic and glass&ceramic fractions will be sintered or even partially melted and metals oxidised, but in pyrolysis and gasification these fractions will not undergo any significant physical, chemical or morphological changes due to low temperature and reducing conditions. The inorganic fractions are obviously easy to separate even from organic products of pyrolysis. For separation of non-metallic from metallic fractions as well as and ferrous and non-ferrous metals in the coarse fractions of ashes from SR thermal treatments the above mentioned separation methods are available. For the final separation of non-ferrous metals, pyro- or hydrometallurgical processing is necessary.

Fig.2 shows very schematically the alternative routes to recycle SR.

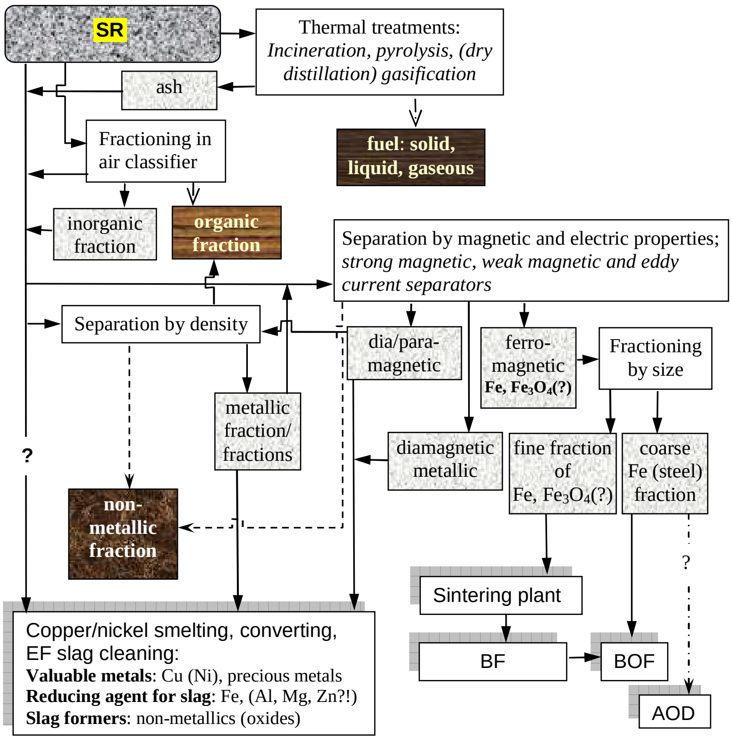

Fig.2 SR-recycling alternatives including thermal, mechanical and conventional ferrous and non-ferrous processes

High dismantling and fractioning degree means high complexity of mechanical treatments and high costs. The most cost effective way for recovery of metals of low value SR fractions would be their co-treatment as such or after minimum mechanical or thermal treatments in ordinary metallurgical processes.

On the perspectives of pyrometallurgical processing of ASR

Within EU there are at least three significant recyclers of electric&electronic scrap all using pyrometallurgical technique. New Boliden's Kaldo furnace in Skellefteå is treats at the moment +30 kton/y scrap of this category using plastics present in the scrap as fuel[16], Nordeutsche Affinerie treats +40 kton/y electronic scrap in their Lünen smelter[17] and Umicor is as well smelting remarkable annual amounts of electric&electronic scrap in their Isasmelt furnace[18] in Hoboken. For all these smelters precious metals and copper are the main value in the raw materials and processes utilise obviously the same principle: precious metals follow copper in smelting stages and are concentrated finally into the anode slime of copper tankhouse. Skellefteå, Lünen and Hoboken smelters treat (obviously) mainly electric&electronic scrap (ESR and related) with high copper and precious metal contents in their smelting-recycling operations.

ASR with less copper and practically without precious metals has been much less attractive and has been mainly landfilled. Low value ASR with low copper and precious metals content hardly interest electronic scrap smelters whose main interest is precious metals recycling. Tightening of waste management legislation in EU forces however to recycle in an increasing degree also low value wastes like ASR. The continuous price increase of copper and fossil fuel, especially oil products would affect to the same direction as ASR contains high calorific value organic constituents as one of the main fractions. Copper and valuable metal contents in ASR play an important role and by mixing WEEE-scrap (ESR) with ASR makes naturally its recycling economically more "sexy". Concentration of ASR with relation to copper by pyrolysis/gasification or by separation of organic, glass&ceramic and magnetic metallic fractions (same treatment is of course possible for ashes from thermal treatments) will also add its value as copper raw material, but each treatment increases the processing costs.

One possibility to recycle low value ASR is obviously by-smelting with primary ores in ordinary sulphide concentrate smelting processes for copper, nickel or lead sulphide ores. Magnetic fraction if separated from ASR or its thermal treatment ashes can be processed in iron and steelmaking (see figure 2). Ashes from thermal treatments are obviously suitable as such without any magnetic separation to be co-smelted copper smelting and converting units. As secondary raw material of some economic interest in copper making the copper content of SR or its thermal treatment ash should be something over 5 wt-%.

The main pyrometallurgical route for treating sulphide concentrates of copper comprises smelting, copper matte converting and fire refining of blister copper. From purely a metallurgical point of view ASR thermal treatment ashes can be treated both in matte smelting and matte converting processes. Copper content of high grade matte smelting slags amounts to 2 - 2.5 wt% being in slag blowing stage of copper matte converting three to four times higher. Major part of slagged copper is, however, recovered in slag cleaning processes. The other main components of shredder residues either oxidise and pass into slag (Fe, Al, Zn, Cr) or follow copper in matte (Pb, Sn). The first group of major components act, accordingly, as fuel or reductant for oxidised and slagged copper and other more noble metals (like Ni). As aluminium is highly reactive, the presence of its alloys in the charge can also cause problems especially in copper converter due to vigorous reactions resulting in slag splashing. Precious metals follow copper in a great degree.

Oxide constituents of ash (SiO_2, CaO, MgO, Al_2O_3, alkali oxides in glass, lime and sand) are slagged and act in fact as slag forming agents in smelting and converting processes and in some extent may substitute silica sand, used as flux. The typical impurity or hazardous metallic components present in ASR and ESR Zn, Pb, Sn (Cd, Hg) exist also in sulphide concentrates and do not require any special measures. If flue dusts from various processing stages and by-products from slag cleaning operations are recycled the only substantial route out of the process chain is slag, much more inactive environmentally than SR. Halogens, the main hazardous gaseous components in SR are neither unknown problem in sulphide smelters and can be removed in sulphuric acid production stages.

A material with typical fractional composition and size distribution of ASR cannot obviously be mixed with copper concentrate and fed through the dryer to the smelting furnace. SR pyrolysis or gasification ashes can be, however, directly fed to the (flash) smelting or converting furnace. Even the treatment of ASR without removing the organic fraction is not a metallurgical problem in copper smelting. Extra component with high calorific value in feed in sulphide smelting or converting may limit the amount of co-smelted ASR as the processes are highly exothermic. As enriched air with variable oxygen to air degree is as a rule practised in modern smelters, this problem might be easily controlled by varying the enrichment level. The technological problems of charging materials with morphological and thermal properties differing from conventional raw materials can always be overcame.

The possible recycling alternatives for SR (ASR, ESR and their mixtures) are summarised in Figure 2.

Concluding remarks

The environmental legislation in EU continuously tightens the regulations for the landfill of both organic and inorganic wastes. This leads to continuous extension the scope of recycling and forces to bring into it such waste classes that in the past have been mainly subjected to landfill. The share of shredder residue fractions of WEEE with high contents of copper and precious metals coming into the frames of recycling is rapidly increasing. Less optimistic view concerns ASR of low metal value.

From a metallurgical point of view recycling of SR including low metal value ASR and ESR as such or ashes of their thermal treatment is perspective even without mechanical separation. Also from environmental point of view co-smelting of SR with primary non-ferrous concentrates seems to be one of the most perspective alternatives for landfill.

In order to guarantee the maximum recycling degree of environmentally problematic wastes is the make the recycling economically more attractive by mixing low- and high-valued wastes. Concerning SR and related wastes the natural way would be mixing of low copper (A)SR with ESR higher valuable metal content. A less attractive alternative is to pay for SR recycling.

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