



Energy, Resources and Environmental Technology

Extraction of metals from automotive shredder residue: Preliminary results of different leaching systems



Francesco Ferella*, Ida De Michelis, Agostino Scocchera, Mario Pelino, Francesco Vegliò

DIIIIE — Dipartimento di Ingegneria Industriale, dell' Informazione ed Economia, Università degli Studi di L'Aquila, Via G. Gronchi 18, 67100 L'Aquila, Italy

ARTICLE INFO

Article history:

Received 13 March 2014

Received in revised form 11 June 2014

Accepted 23 September 2014

Available online 14 November 2014

Keywords:

ASR

Vehicles

Automotive

Metals

Leaching

ANOVA

ABSTRACT

The study is focused on the extraction of valuable metals from automotive shredder residue (ASR) by different leaching solutions. First, ASR samples were roasted at 600 °C to simulate a thermal treatment processing. Distilled water, citric and sulphuric acid were preliminarily investigated, thus two further full factorial systems entailing $\text{H}_2\text{SO}_4\text{--H}_2\text{O}_2$ and $\text{H}_2\text{SO}_4\text{--H}_2\text{O}_2\text{--Fe}^{3+}$ were tested. The preliminary experimental results showed that $0.1 \text{ mol}\cdot\text{L}^{-1}$ H_2SO_4 solution extracted 100% of Cu, Fe and Zn, whereas citric acid leached 100% of Zn and Pb, 59% of Fe and 62% of Cu; whereas, $\text{H}_2\text{SO}_4\text{--H}_2\text{O}_2$ and $\text{H}_2\text{SO}_4\text{--H}_2\text{O}_2\text{--Fe}^{3+}$ (Fenton's) leaching media showed that Cu, Fe and Zn can be extracted simultaneously and completely from the ASR ashes before final disposal.

© 2014 The Chemical Industry and Engineering Society of China, and Chemical Industry Press. All rights reserved.

1. Introduction

The European Union placed technologies for environment at the core of sustainable development strategy; it fostered innovation in order to shift from laboratory to industrial applications and market; it encouraged to promote recycling technologies for the valorisation of secondary raw materials and improved processes in eco-factories and eco-products. In particular, recent EU Directives set specific targets for the recovery and recycling of end of life vehicles (ELV), fostering the development of new and more efficient recycling technologies as well as opening a new field of scientific investigation and process development.

In car shredding process, steel is recovered by magnetic separation, whereas non-ferrous metals by eddy current. Some plastic fractions are also reclaimed. Automobile shredder residue (ASR) is the residual fraction made up of plastics, rubber and fabrics (globally 70%), metals (20%), glass and other debris (10%). Currently, about 75% of the total mass of ELV is recycled, while the remaining 25% of ASR, also called “car fluff”, is landfilled [1]. The average composition of ASR resulted to be 60% (by mass) plastics (PE, PVC, PP, PS, PU, PA, polychloroprene, elastomers, epoxy resins), 10% textiles, leather and wood, 10% paint, dust and rust, 15% minerals (glass and sand) and 5% metals [1]. The quantities of ASR is likely to increase in the coming years due to the growing number of ELV and larger use of plastics in car production. Every year

between 8 and 9 millions of vehicles in the European Union arrive to their end of life [2]. Car waste can have a very high metal content, falling into hazardous waste classification.

Depending on the presence and quantity of hazardous substances, such as heavy metals, PCB and organic compounds, ASR can be classified as “special waste” or as “hazardous waste” (Decisions 2000/532/EC, 2001/18/EC, 2001/119/EC and 2001/573/EC of Council). Another typical characteristic of ASR is the high heterogeneity and variable composition, even in samples arising from the same source, but sampled at different times. Guideline 2000/53/EC established that after January 2015 recovery and recycling of all ELV will be increased to a minimum of 95% and 85%, respectively [3,4].

In order to remove heavy metals from ASR, two different methodological approaches were investigated in the scientific literature:

1. chemical treatments to remove metals from the original ASR (as delivered from processing plant), followed by decontamination;
2. thermal treatment of ASR by combustion or fluidised bed gasification, followed by a quantitative recovery of valuable metals from the ashes by hydrolysis in different media.

Lanoir *et al.* [5], Morselli *et al.* [6] and Passarini *et al.* [7] carried out several studies on characterization of ASR and determination of main metals. In the work by Fiore *et al.* [8] ASR materials underwent an extended characterization and some post-shredding processes, consisting of dimensional, magnetic, electrostatic and densimetric separation phases, tested on laboratory scale, with the main purpose of the enhancement of ASR recovery/recycling and the minimization of the landfilled fraction. Granata *et al.* [4] investigated the Zn extraction by

* Corresponding author.

E-mail address: ferellafrancesco@virgilio.it (F. Ferella).

leaching the original ASR in a $0.4 \text{ mol} \cdot \text{L}^{-1}$ sulphuric acid solution at a solid to liquid ratio (S/L) 1:5. The other valuable metals contained in the ASR, mainly Fe, Al and Cu, required a stronger acid concentration to be removed. Kurose *et al.* [9] extracted the metals from the original ASR using a hydrochloric acid solution. By this procedure, they showed that the concentration of heavy metals was effectively lowered after the leaching process.

The second methodological approach, *i.e.* thermal treatment, is justified by the fact that the low heating value (LHV) of the ASR is about $18 \text{ MJ} \cdot \text{kg}^{-1}$; on the other end, the EC Directive 1999/31 does not allow landfilling of waste with calorific value exceeding $13 \text{ MJ} \cdot \text{kg}^{-1}$. It is well known that ASR pre-treatments before gasification increase the LHV and, moreover, increase the recovery of metals. The latter operation is needed both to reduce the release of pollutants during gasification and to recover valuable metals [4].

Almost all of the recycling methods carry out a thermal treatment because of ASR's heating value; some of these processes use pyrolysis [10–12] whereas others perform gasification [13–15]. After thermal treatments, metals are concentrated in the bottom and fly ashes for their different boiling points. H.Y. Lee [16] characterised the metal composition in the different fractions of bottom and fly ashes arising from a traditional combustion plant. They found a remarkable high Cu concentration in the bottom ashes, coming from the remaining copper wires in the ASR, while most of the Pb was vaporised and concentrated in the bag filters. Leaching of the different fractions was carried out by the toxicity characteristic leaching procedure (TCLP). The final purpose of this study was to evaluate the possibility of recycling the ASR ashes into construction or lightweight aggregate materials. As regards lead, it was found that it is more concentrated in the finer fractions than in the coarser ones [17]. Cossu and Lai [18] tested a washing treatment with water to study the release of hazardous compounds before landfilling. Results showed that around 60% of dissolved organic carbon (DOC), chemical oxygen demand (COD), total Kjeldahl nitrogen (TKN), metal chlorides, sulphates and fluorides were removed; moreover, grain size did not affect such removal efficiency. Yoshida *et al.* [19] investigated the direct Cu recycling, while Shibayama *et al.* [20] were able to recover Zn and Cu from fly ash by distillation, precipitation and cementation. Nieminen *et al.* [21] studied an air-blown fluidised-bed gasification as a potential technology for a more efficient utilisation of ASR in energy production as well as to improve the metal recovery yield. The study was focused on the assessment of the technical feasibility of air-blown fluidised-bed gasification for thermal treatment of ASR with the development of a fluidised-bed gasifier and a gas cleaning section.

Mancini *et al.* [22] characterised the ASR thermal residue coming from a full scale plant: on the basis of the analytical results, the slag and bottom ash from the combustion process were classified as non-hazardous wastes. Rossetti *et al.* [23] studied the recycling of ASR as granules suitable to be used as aggregates in cement or asphalt mixtures; granules were obtained by granulating the non-metallic fraction of ASR. Pèra *et al.* [24] investigated two processes for recycling a 700°C calcined ASR by transformation into aggregates after chemical treatment. Ciacci *et al.* [25] performed a life cycle assessment (LCA) of five different processes for the treatment of ASR. De Stefanis *et al.* [26] made a survey on ASR management in Italy and a resume of the European legislations on the topic. Different ways of treatment and disposal were examined and a comparison among seven industrial technologies was made. The review written by Srogi [27] compared the thermo-chemical processes and was mainly focused on pyrolysis and gasification treatments. Other studies concerned kinetics models of ASR pyrolysis and gasification [28–30]. Evaluation of leachability of ASR ashes, in accordance with EA NEN 7371, showed that the amount of metals released over a long period of time could be much higher than the value estimated with the EN or TCLP methods [20]. In the study of Hyks and Astrup [31] different results achieved in metal leaching were associated with difference in ageing; in particular,

leaching of metals, *i.e.* Sb and Cr, from aged bottom ashes was generally lower than from fresh ashes.

Most of the aforementioned processes do not provide recovery of the metallic fraction after thermal treatment by further leaching of the bottom ashes. It is important to recover metals from ashes, also from those produced by other thermal treatments like incineration of municipal solid waste (MSW) [32,33]: this leads to avoid any leaks of heavy metals in the ground and groundwater table when ashes are landfilled. However, when using temperatures higher than 1000°C , sintering of the bottom ashes may take place, reducing the yield of extraction of the metals. High temperature processes can be performed to obtain a vitrification so that ashes can be landfilled as inert or reused as secondary raw material. However, during vitrification, a consistent fraction of the volatile metals is vaporised [34,35]. An economic assessment of ASR treatment was carried out by Ruffino *et al.* [36]: according to their physico-mechanical process that includes size, density, magnetic and electrostatic separations, the treatment cost was estimated in the range 20–25 euro per tonne of ASR. Nevertheless, considering the market price of iron and non-ferrous metals scraps, the proposed process is economically sustainable.

The aim of this work is to study the recovery of the most concentrated and valuable metals contained in ASR. All published studies concentrated their efforts in recovery of energy from ASR, leaving out the metal content of such material. This study has investigated the extraction of Fe, Cu, Zn and Pb from non-vitrified ASR ashes to recover them from the pregnant solution. Moreover, the extraction of metals from ASR after energy recovery is very useful before final disposal of decontaminated ASR ashes.

2. Materials and Methods

After the quartering procedure, two different samples of 10 kg each were considered in the present study, selected in two different Italian ELV dismantling plants. They were indicated as FLUFF FIORI (FF) and GREEN FLUFF (GF) and the main difference consisted in the fact that FF was more homogeneous with a finer grain size. Fig. 1 shows FF and GF, respectively, as received from the processing plants.

Particle size distribution was carried out on the FF sample only. In performing this test, 1 kg of FF was placed in an electric vibrating screen (Set.El, Erimaki) equipped with 5.6, 4.0, 2.8, 1.7, 1.0 and 0.5 mm standard sieves. Fig. 2 shows the grain size distribution of the FF sample, where the largest fraction, about 50% of the total, is included in the range 1.0–2.8 mm. Different tests, carried out on the GF sample did not provide comparable results and therefore were not considered in the present study.

2.1. Characterization of ASR

The samples were dried at 105°C for 2 h to constant mass in an oven (Mod.780, Galli) and successively calcined at 600°C for 12 h in a muffle furnace (Humboldt, H-30204F). The mass loss before and after the thermal treatments was measured by an analytical balance (PE600, Mettler). The residues after drying at 105°C were 98.7% and 96.3% of the original mass, while after the thermal treatment at 600°C they resulted to be 46.3% and 40.1% for FF and GF, respectively. After drying at 105°C and grinding, the FF showed a density of $1.80 \text{ g} \cdot \text{cm}^{-3}$, while the density of GF sample was $1.63 \text{ g} \cdot \text{cm}^{-3}$.

In order to obtain a fine granulometry, the original FF sample was milled at liquid nitrogen temperature by a Fritsch Pulverisette Mod. 06 102/2045 in a stainless steel jar. Due to the high degree of non-homogeneity, the GF sample was not milled. After the cryogenic milling, the FF sample showed a high degree of homogeneity and a particle size below $80 \mu\text{m}$.

The average bulk density was evaluated by a helium intrusion Micromeritics mod. AccuPyc 1330 pycnometer. The FF sample after grinding was also characterized by a thermogravimetric analysis (TGA)

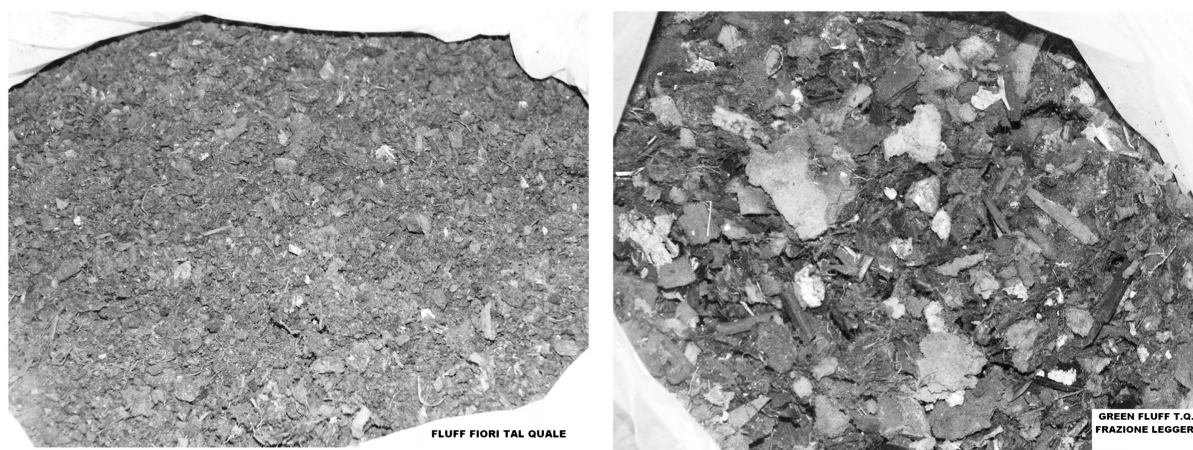


Fig. 1. Original ASR “FIORI” (FF) on the left and original ASR light fraction “GREEN FLUFF” (GFL) on the right.

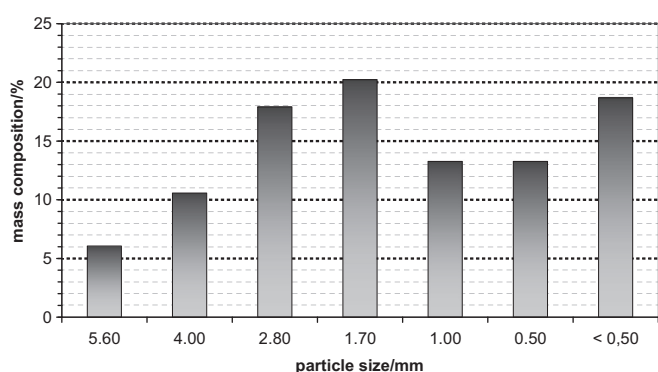


Fig. 2. Grain size classification of dried and milled FF sample.

and a differential thermal analysis (DTA) performed in air by a Netzsch STA 409 apparatus with a heating rate of $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ from 50 to $1000\text{ }^{\circ}\text{C}$.

2.2. X-ray diffraction and fluorescence

After the preliminary characterization, subsequent analyses were carried out on FF only, due to the high degree of non-homogeneity observed in the GF samples. The X-ray diffraction analysis (XRD) was carried out by a Philips PW 1830 diffractometer in order to establish the crystalline phases present in the original sample and in the same sample roasted at $600\text{ }^{\circ}\text{C}$. The X-ray fluorescence analysis (XRF) was performed using a Spectro Xepos diffractometer on the dried and the cryogenically milled original sample as well as on the calcined one. The analysis was repeated on several samples and the average values for the most abundant metals in the samples were considered.

2.3. Leaching tests

The leaching tests were carried out in different solutions aimed at obtaining the highest yield of metal extraction. Preliminary tests were performed by distilled water, sulphuric acid and citric acid solutions as leaching media; other tests were carried out by Fenton's process and $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ mixture. Leaching tests were performed in 250 ml closed flasks submerged in a thermostatically controlled water bath equipped with a mechanical stirrer (Dubnoff, ISCO). For each test, the solution mixture was freshly prepared by dissolving the required amount of sample in 100 ml solution, according to the experimental plan. During each test, 1 ml of leach liquor was withdrawn at different times to measure the concentration of Cu, Fe, Zn and Pb by AAS. Each sample was

diluted 1:10 by a solution of nitric acid to avoid precipitation of metals and stored for analysis. At the end of every test, when the reaction was stopped, pH was measured by a digital pH-metre (Mettler Toledo MP220). The leaching solutions at different times were analysed by a Varian AA 240 FS Fast Sequential Absorption Spectrometer, whereas the extraction yields of Cu, Fe, Zn and Pb were calculated as follows:

$$\text{EY} = \left[\frac{(C \cdot V / 1000 \cdot p)}{X / 100} \right] \cdot 100\% \quad (1)$$

where EY is the extraction yield, %; C is the concentration of metal in solution, $\text{mg}\cdot\text{L}^{-1}$; V is the final volume of solution, ml; p is the mass of solid sample, g; X is the mass concentration of metal, % [37]. Concentration of the main metals contained in each sample (X) was determined by leaching in aqua regia ($\text{HCl}:\text{HNO}_3 = 3:1$) and HF (1 g of catalyst in 20 ml of mixture) using a microwave digestion bomb (Mod.4781, Parr Instruments); metal concentration was measured by AAS.

3. Results and Discussion

3.1. Physico-chemical characterization of samples

The TGA and DTA curves in air of the dried FF sample are shown in Fig. 3. In the TGA, the mass loss starts after $250\text{ }^{\circ}\text{C}$ with a maximum mass loss at around $320\text{ }^{\circ}\text{C}$. This behaviour is due to combustion of organic materials such as rubber, plastics and leather. From $400\text{ }^{\circ}\text{C}$ to $750\text{ }^{\circ}\text{C}$ the sample shows a 20% mass loss at constant rate for the combustion of fire resistant materials containing flame retardants. The total mass loss of the FF sample resulted to be about 47%, in line with

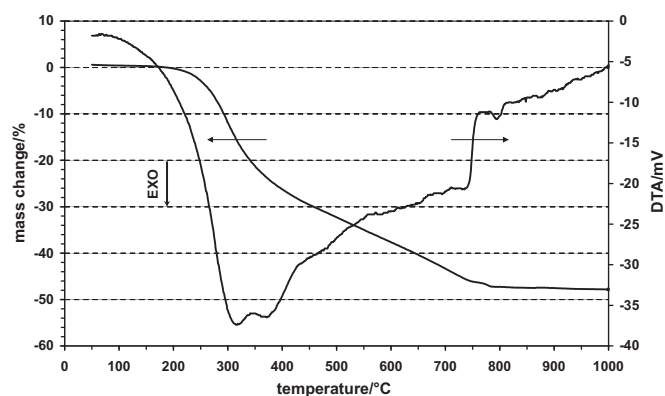


Fig. 3. TGA and DTA of the dried FF sample.

the value obtained by 12 h calcination at 600 °C (46.3%). This value is not so far from 62% which was obtained by Lanoir *et al.* [5] even though the latter was carried out at 650 °C and after different physico-mechanical stages. The DTA trace shows the maximum exothermic effect at 320 °C indicating that most of the ASR materials have a low ignition temperature.

3.1.1. XRF and XRD analyses

The FF sample was analysed by XRF and XRD in order to determine the chemical and structural compositions of metals (mainly Cu, Zn, Fe and Pb) contained in the ASR. Table 1 reports the results of the XRF of FF carried out on the original 105 °C dried sample and on five samples calcined at 600 °C. Notwithstanding a certain degree of non homogeneity of the FF sample, the results show a good consistency between the values obtained. In particular, the average concentration (mass fraction) of metals in the calcined samples resulted to be Fe ($7.80 \pm 1.00\%$), Cu ($9.50 \pm 1.30\%$), Zn ($1.63 \pm 0.12\%$), and Pb ($0.26 \pm 0.02\%$). Standard deviation values were quite low considering the typology of waste studied in the present work.

Table 1

Composition (% by mass) of FF by XRF analysis after drying (105 °C, 24 h) and roasting (600 °C, 2 h)

Element	105 °C	600 °C ^①
Magnesium	<0.50	2.60
Aluminium	0.54	1.76
Silicon	4.43	7.89
Phosphorus	<0.05	0.10
Sulphur	0.30	1.50
Chlorine	0.78	10.40
Potassium	0.16	0.30
Calcium	3.47	11.99
Titanium	0.74	0.78
Iron	4.10	7.76
Copper	4.08	9.44
Zinc	0.78	1.63
Tin	0.016	0.07
Antimony	0.022	0.08
Barium	0.529	2.02
Lead	0.126	0.26

^① Mean values of five tests.

The aforementioned values correspond to the concentrations in “original” and calcined ASR found by other authors [2–4,10,11,14,16, 22]. The XRD spectrum of the original FF shows a large amorphous halo and some main peaks corresponding to CaSiO_3 – ZnCl_2 – AlCl_3 and $\text{Al}_8\text{Fe}_2\text{Si}$. After thermal treatment at 600 °C for 24 h, the amorphous halo is consistently reduced and the most probable phases are CuO – CaSO_4 – $\text{Ca}_3\text{Fe}_{1.5}\text{Al}_5(\text{SiO}_4)_{2.75}(\text{OH})$ – $\text{Mg}_{1.55}\text{Fe}_{1.6}\text{O}_4$ – $\text{Ca}_{1.97}\text{Al}_{3.8}\text{Si}_{8.2}\text{O}_{24}(\text{CO})_{1.83}$ and BaO_2 . The results are shown in Figs. 4 and 5.

3.2. Preliminary leaching tests

The preliminary leaching tests were carried out with the aim of evaluating the more appropriate leaching medium and experimental conditions.

The tests were carried out on the original and 600 °C treated FF samples in 0.1 mol·L^{−1} sulphuric acid (solution A), distilled water (solution B), 0.1 mol·L^{−1} citric acid (solution C), at 25 °C in 100 ml of leaching solution, with a solid to liquid (S/L) ratio of 1:10. For the sake of comparison, the leaching tests on the 600 °C GF sample were also carried out in the same experimental conditions. The original GF samples were not considered because of its non-homogeneity both in composition and morphology. Tables 2 and 3 show the results of the leaching tests expressed as concentration and extraction yield of Cu, Fe, Pb and Zn, respectively.

These extractions are in agreement with those obtained by Granata *et al.* [4] by using a 0.4 mol·L^{−1} H₂SO₄ solution: Zn 95%, Fe 5.8%, Cu 5.3 and Pb around 7% after 10 h of reaction. The 24 h leaching in distilled water shows that only a very little amount of Zn and Pb were leached out on both the FF 600 and GF 600 samples. The leaching effect of the citric acid solution is mild on Cu and Fe and relatively strong on Zn and Pb on both 600 °C FF and GF samples. The leaching effect of 0.1 mol·L^{−1} sulphuric acid is stronger on all elements with the exception of Pb due to the low solubility of PbSO₄. From these preliminary tests it can be inferred that sulphuric acid is the most effective leaching medium; citric acid can be considered a promising medium due to the good yields and the low environmental impact.

3.3. Full factorial design with H₂SO₄–H₂O₂

After the preliminary tests, the H₂SO₄–H₂O₂ leaching procedure was tested on the FF600 sample. The addition of H₂O₂ is justified by its oxidising capability which improves, in synergy with sulphuric acid, the dissolution of the metal components in the ASR. The experimental tests were carried out according to a full 2³ factorial design where factors (low and high level in parentheses) were: H₂SO₄ concentration (0.5 mol·L^{−1}; 1 mol·L^{−1}), H₂O₂ [0%; 5% (by volume)], and temperature (30 °C; 70 °C). Pulp density was kept constant at 10% (by mass). Samples were withdrawn after 1 h to check the dissolution rate. After 2 h each final sample was filtered, diluted and stored for AAS analysis. Tests were numbered in conformity with the Yates' algorithm. Three central point experiments were carried out to have a good evaluation of the experimental error and to test the adequacy of the models. The experimental results of the full factorial design at different leaching times are shown in Table 4, where the results are expressed in terms of concentration of metals and their extraction yields. Pb data was not reported because all extraction yields were lower than 1%.

From the analysis of the data it is possible to highlight that:

- the yield of extraction of Fe and Zn is good in sulphuric acid and is a direct function of his concentration. On the other hand, the increase of H₂O₂ concentration has a negative effect on the yield of dissolution of those elements;
- the yield of dissolution of Cu is relatively low in the investigated leaching conditions; the increasing concentration of H₂O₂ has a positive effect on the dissolution of that metal;
- the increase of reaction time from 1 to 2 h has no significant effect on extraction yields.

The concentration data in Table 4 regarding Cu, Zn and Fe after 2 h were analysed by applying the Yates' algorithm in order to establish the influence of the investigated factors on the behaviour of the system, *i.e.* which process parameter generates a positive variation of the system. The ANOVA results, not reported here, shows that none of the factors has, in the investigated range, a positive influence on the extraction yield of Cu, Zn and Fe. In conclusion, the ANOVA approach highlighted that the investigated factors in the considered ranges have a low effect on the extraction of the valuable elements contained in the ASR. Nevertheless, from the data of Table 4 it is possible to note that the temperature lowers the extraction yield of copper only: this effect is probably due to the degradation of H₂O₂ into water and oxygen at higher temperature [38]. Accordingly, less H₂O₂ is available to oxidize metallic copper that was previously not oxidized by the thermal treatment.

3.4. Preliminary leaching tests with Fenton's reagent

On the basis of the preliminary results, Fe³⁺ ions were added to the H₂SO₄/H₂O₂ leaching system. The experimental conditions were: S/L

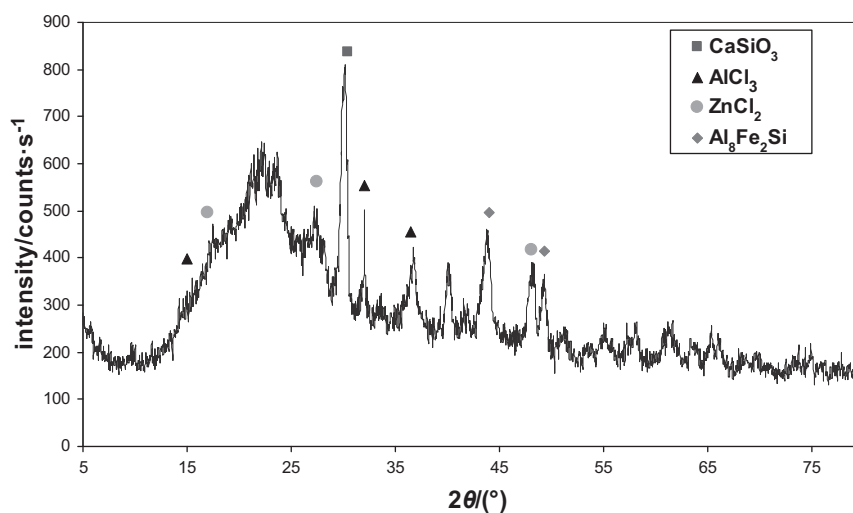


Fig. 4. XRD spectrum of the original FF sample.

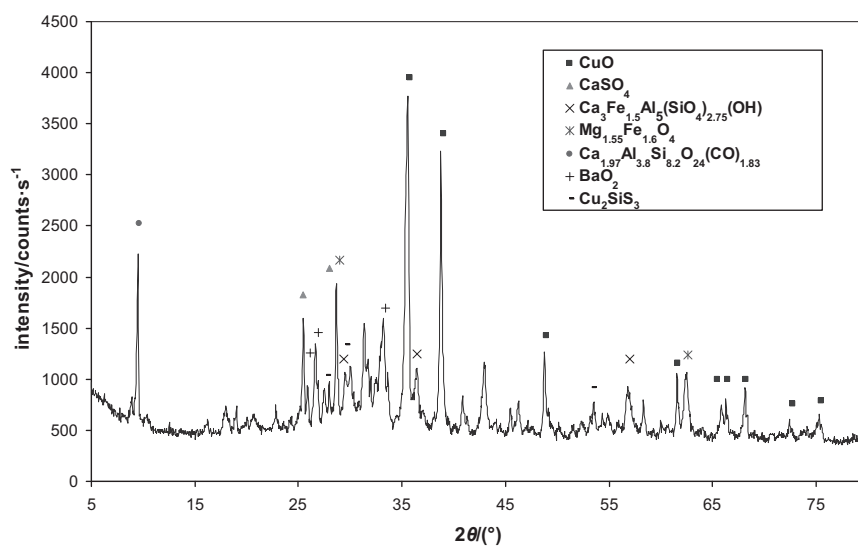


Fig. 5. XRD spectrum of FF sample roasted at 600 °C.

Table 2

Results of the preliminary leaching tests after a reaction time of 24 h at 25 °C (FF = Fluff Fiori; FF600 = Fluff Fiori roasted at 600 °C; GFL600 = Green Fluff light fraction roasted at 600 °C; GFH600 = Green Fluff heavy fraction roasted at 600 °C)

Element sample	[Cu]/mg·L ⁻¹				[Zn]/mg·L ⁻¹			
	FF	FF600	GFL600	GFH600	FF	FF600	GFL600	GFH600
H ₂ SO ₄ 0.1 mol·L ⁻¹	114.0	109.0	1033.0	541.5	114.1	201.1	301.0	525.0
H ₂ O	0.2	<0.1	<0.1	<0.1	0.1	0.6	0.1	0.2
Citric acid 0.1 mol·L ⁻¹	45.7	202.0	585.1	167.2	46.2	111.1	294.4	416.2

Element sample	[Fe]/mg·L ⁻¹				[Pb]/mg·L ⁻¹			
	FF	FF600	GFL600	GFH600	FF	FF600	GFL600	GFH600
H ₂ SO ₄ 0.1 mol·L ⁻¹	201	2.43	71.8	67.5	4.1	0.0	2.0	1.9
H ₂ O	1.04	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Citric acid 0.1 mol·L ⁻¹	157	1.43	56.2	66.3	1.2	120.9	36.9	

ratio 10%, H₂SO₄ 2 mol·L⁻¹, H₂O₂ 10% (by volume), temperature 80 °C, Fe³⁺ concentration 0, 10, 20 g·L⁻¹. Fig. 6 shows the concentration of the metals as a function of time and Fe³⁺ concentration for the FF600 sample.

It can be noted that, compared to the previous results with H₂SO₄ and H₂SO₄/H₂O₂, the addition of ferric ions improves copper extraction, while it has a slight effect on dissolution of the other metals. From those results it can be inferred that the maximum extraction yields are already

Table 3

Extraction yields (%) of the most important metals after a reaction time of 24 h at 25 °C; (FF = Fluff Fiori; FF600 = Fluff Fiori roasted at 600 °C; GFL600 = Green Fluff light fraction roasted at 600 °C; GFH600 = Green Fluff heavy fraction roasted at 600 °C)

Element sample	EY (Cu)/%				EY (Zn)/%			
	FF	FF600	GFL600	GFH600	FF	FF600	GFL600	GFH600
H ₂ SO ₄ 0.1 mol·L ⁻¹	12.11	11.50	100	57.28	70.08	100	100	100
H ₂ O	0.02	0	0	0	0.10	0.30	0.04	0.03
Citric acid 0.1 mol·L ⁻¹	4.83	21.34	61.94	17.65	27.93	54.94	97.61	79.27

Element sample	EY (Fe)/%				EY (Pb)/%			
	FF	FF600	GFL600	GFH600	FF	FF600	GFL600	GFH600
H ₂ SO ₄ 0.1 mol·L ⁻¹	25.96	100	9.26	8.70	14.01	0.00	1.57	5.15
H ₂ O	0.13	0	0	0	0.04	0.04	0.01	0.03
Citric acid 0.1 mol·L ⁻¹	20.24	58.72	7.19	8.51	75.34	4.54	100	100

EY: extraction yield.

Table 4

Results of leaching tests of 600 °C FF sample by H₂SO₄-H₂O₂

Test	[H ₂ SO ₄] /mol·L ⁻¹	[H ₂ O ₂]/% (by volume)	T/°C	Cu				Fe				Zn			
				1 h		2 h		1 h		2 h		1 h		2 h	
				Conc./g·L ⁻¹	EY/%	Conc./g·L ⁻¹	EY/%	Conc./g·L ⁻¹	EY/%	Conc./g·L ⁻¹	EY/%	Conc./g·L ⁻¹	EY/%	Conc./g·L ⁻¹	EY/%
(1)	0.50	0	30	0.5860	5.10	0.7580	6.59	6.79	31.29	6.21	30.63	1.3083	52.73	1.2135	47.00
a	1.00	0	30	0.1300	1.13	1.6980	14.77	9.23	46.55	11.17	50.36	1.3065	52.66	1.3653	52.88
b	0.50	5	30	2.4180	21.03	2.8560	24.83	3.14	15.81	5.06	22.80	0.4779	19.26	0.4830	20.71
ab	1.00	5	30	5.6160	48.83	5.8860	51.18	4.27	21.53	6.44	29.03	1.3026	52.50	1.3836	53.59
c	0.50	0	70	0.7200	6.26	0.8640	7.51	10.31	51.99	10.33	52.19	1.2429	50.10	1.1127	43.09
ac	1.00	0	70	0.0312	0.27	0.0300	0.26	14.67	73.98	15.29	74.97	2.2556	90.91	1.9768	76.56
bc	0.50	5	70	0.8500	7.39	0.9540	8.30	11.12	56.08	13.46	60.71	0.8355	33.68	0.8520	34.00
abc	1.00	5	70	0.9020	7.84	1.1560	10.05	19.83	97.35	22.17	100.00	1.5345	61.85	1.6140	62.81
0	0.75	2.5	50	1.1110	9.66	1.1900	10.35	16.28	81.27	18.23	88.02	2.2230	89.60	2.2030	85.32
0	0.75	2.5	50	0.6930	6.03	0.8430	7.33	18.18	88.75	19.68	91.65	2.4810	99.13	2.5820	100.00
0	0.75	2.5	50	0.9460	8.23	0.8760	7.62	16.65	81.96	17.40	84.07	1.7190	69.29	1.7040	67.05

EY: extraction yield.

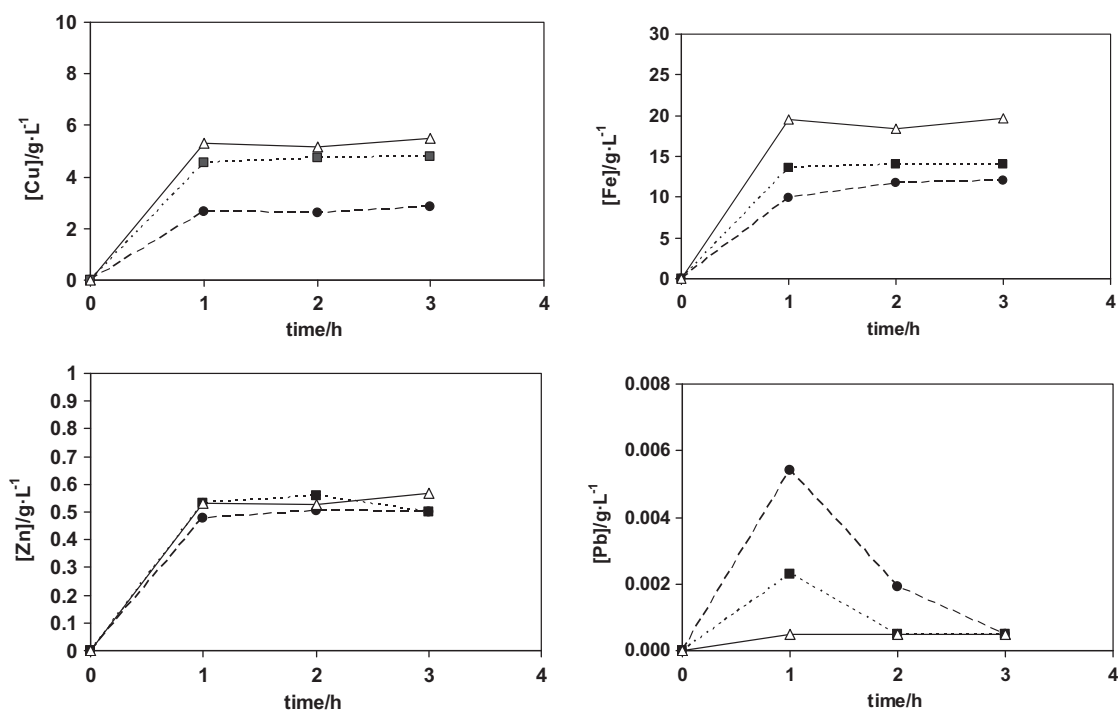


Fig. 6. Concentration of Cu, Fe, Zn, Pb at different reaction times and Fe³⁺ amount. —●— [Fe³⁺] = 0 g·L⁻¹ ---■--- [Fe³⁺] = 10 g·L⁻¹ —△— [Fe³⁺] = 20 g·L⁻¹.

achieved after 1 h. The behaviour of lead extraction is rather different to the other three: as a matter of fact, in the first phase lead is leached with its own kinetics but after 1 h PbSO_4 starts precipitation because of the great amount of SO_4^{2-} ions contained in the solution.

3.5. Full factorial design with H_2SO_4 – H_2O_2 – Fe^{3+}

On the basis of the preliminary tests, leaching of the FF 600 sample was carried out by the combined effect of sulphuric acid–hydrogen peroxide–ferric ions. A 2^4 full factorial design with replicated central point test was chosen for conducting the leaching process where factors were A, sulphuric acid concentration, B, hydrogen peroxide concentration, C, ferric ion concentration, D, temperature. Pulp density was kept constant for all tests and equal to 10% (by mass). Experimental conditions for each treatment are given in Table 5. Even in this experimental plan, tests were numbered in conformity with the Yates' algorithm. Four replicated central point tests were carried out to have a good evaluation of the experimental error. Moreover, further eight axial tests (17–24, see Table 5) were also carried out to better understand the shape of the response surface.

Table 5 also lists the extraction yields of Cu and Zn at different reaction times. In this series of tests, Fe concentration was not measured because of the addition of the Fenton's reagent (Fe^{3+} ions).

By examining the data shown in Table 5, it seems that the extraction of Cu ends after 30 min in most of the tests, whereas the kinetics of Zn extraction is slower, since the higher extraction yield is achieved after 1.5 h.

The highest yield of Cu was 83%, obtained in test 15, i.e. with $1 \text{ mol} \cdot \text{L}^{-1}$ of H_2SO_4 , 9% (by volume), H_2O_2 , $15 \text{ g} \cdot \text{L}^{-1}$ of Fe^{3+} at 70°C ; in the same test the Zn yield resulted to be nearly 87%. As far as Zn extraction is concerned, the maximum yield for this element was achieved in several tests, i.e. ab, ac, acd and abcd. According to the nomenclature of the Yates' algorithm, it can be noted that in the four aforementioned

tests those factors whose letters are missing are at the lower levels. From the data reported it can be inferred that the optimal experimental conditions to obtain the highest simultaneous extraction yield of Cu and Zn are H_2SO_4 $1 \text{ mol} \cdot \text{L}^{-1}$, H_2O_2 9% (by volume), Fe^{3+} $5 \text{ g} \cdot \text{L}^{-1}$, temperature 70°C and 1.5 h as reaction time. Nevertheless, the effect of temperature on Cu extraction is negligible compared to that obtained in the H_2SO_4 – H_2O_2 full factorial design.

3.5.1. ANOVA

The experimental results expressed as extraction yield of Zn and Cu at 1.5 h obtained in the Fenton's full factorial design were analyzed by ANOVA. Their significance was determined by *F*-test method at 97% confidence level [39]. Only the main effects and interactions affecting Cu and Zn extractions are shown in Fig. 7. Effects with a statistical significance lower than 97% were not reported.

As regards Cu extraction, the most significant factors and interactions are B, C, AD, ABCD. Factor B, i.e. hydrogen peroxide concentration, has a positive effect on Cu extraction, so that increasing its concentration from 3% to 9% (by volume), the extraction yield is greater. Fe^{3+} concentration has a positive effect as well, whereas interactions AD has a negative effect; this means that increasing simultaneously sulphuric acid concentration from 1 to $1.5 \text{ mol} \cdot \text{L}^{-1}$ and temperature from 40 to 70°C the extraction yield of Cu decreases. Interaction of highest order ABCD, on the contrary, influences positively the yield of Cu. As regards Zn, hydrogen peroxide concentration has a positive leaching effect, as well as ACD. Increasing H_2SO_4 , H_2O_2 and Fe^{3+} concentrations, the Zn extraction is reduced.

ANOVA of Cu and Zn extraction yields at 1.5 h was used to derive simple empirical equations to predict Cu and Zn extraction yields in a wide range of operating conditions included in the experimental ranges given in Table 5. Nevertheless, the second order model does not fit adequately the experimental data of Cu and Zn.

Table 5

Experimental conditions of the full factorial design (pulp density 10%) and extraction yields of Cu and Zn at 0.5, 1.0, 1.5 h

Test	Treatment	A	B	C	D	pH	Cu yield/%			Zn yield/%		
		$[\text{H}_2\text{SO}_4]/\text{mol} \cdot \text{L}^{-1}$	$[\text{H}_2\text{O}_2]/\%$	$[\text{Fe}^{3+}]/\text{g} \cdot \text{L}^{-1}$	$T/^\circ\text{C}$	1.5 h	0.5 h	1 h	1.5 h	0.5 h	1 h	1.5 h
1	(1)	1	3	5	40	1.74	7.60	5.43	5.13	78.11	87.06	82.09
2	a	1.5	3	5	40	1.66	5.70	4.78	4.27	60.45	70.90	74.00
3	b	1	9	5	40	1.72	10.07	6.73	5.83	84.95	88.06	89.68
4	ab	1.5	9	5	40	1.53	48.96	52.17	56.26	100	100	100
5	c	1	3	15	40	1.70	18.37	5.23	5.23	71.02	80.72	93.78
6	ac	1.5	3	15	40	1.53	41.65	32.87	36.09	100	100	100
7	bc	1	9	15	40	1.64	64.00	64.70	65.30	48.88	54.60	100
8	abc	1.5	9	15	40	1.51	35.43	40.87	47.61	51.12	75.50	69.78
9	d	1	3	5	70	1.47	13.08	9.57	9.91	66.17	76.24	85.32
10	ad	1.5	3	5	70	1.41	13.17	15.15	21.82	66.79	90.80	86.69
11	bd	1	9	5	70	1.58	21.18	23.77	20.10	61.07	82.34	87.19
12	abd	1.5	9	5	70	1.46	14.32	14.52	15.22	70.40	81.97	88.68
13	cd	1	3	15	70	1.55	44.78	58.43	62.35	40.05	57.34	66.04
14	acd	1.5	3	15	70	1.44	8.35	6.93	7.67	91.92	96.74	100
15	bcd	1	9	15	70	1.60	64.91	78.04	83.43	58.46	83.58	86.82
16	abcd	1.5	9	15	70	1.42	54.61	62.91	67.96	100	100	100
17	–	0.75	6	10	55	1.47	47.00	48.61	47.22	35.88	46.83	63.31
18	–	1.75	6	10	55	1.31	14.43	6.31	6.09	100	100	100
19	–	1.25	0	10	55	1.40	34.78	36.09	18.78	46.58	69.09	80.91
20	–	1.25	12	10	55	1.36	28.00	9.13	12.43	83.71	105.16	77.74
21	–	1.25	6	0	55	1.26	24.78	15.57	12.57	54.60	72.76	84.14
22	–	1.25	6	20	55	1.29	51.17	51.26	48.43	37.94	53.36	65.11
23	–	1.25	6	10	25	1.57	34.78	30.26	29.78	59.08	76.87	77.55
24	–	1.25	6	10	85	1.41	28.52	26.30	34.22	83.02	82.52	81.22
25	0	1.25	6	10	55	1.36	45.61	55.78	52.48	46.46	67.72	78.92
26	0	1.25	6	10	55	1.38	34.17	32.26	38.00	40.55	64.99	71.27
27	0	1.25	6	10	55	1.39	39.48	33.74	34.61	30.41	44.96	66.54
28	0	1.25	6	10	55	1.16	77.39	40.43	44.00	40.34	53.78	69.37

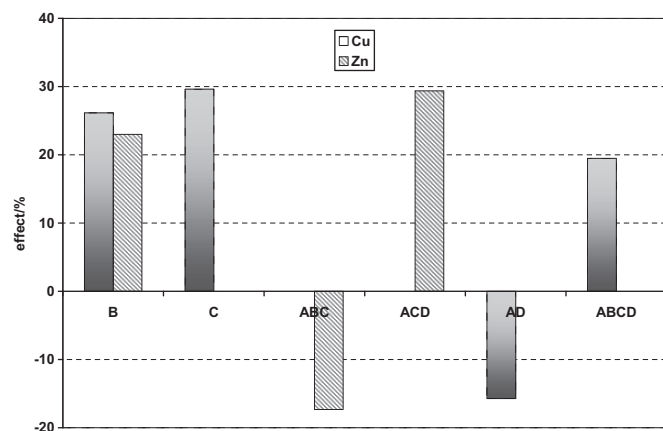


Fig. 7. Effects of the most significant factors and interactions on Cu and Zn extraction yields after 1.5 h.

4. Conclusions

In this study several leaching media were tested in order to extract valuable metals, in particular Cu, Zn, Fe and Pb, from ashes resulting from energy recovery of ASR.

The following conclusions can be drawn:

- ASR samples used in the present study showed a great variability of composition and dimension, making very difficult to standardise the characteristic even for samples arising from the same treatment plant; therefore, in order to obtain a reliable compositional value, several samples at different times were analysed;
- leaching tests carried out by using three different media: they showed that distilled water has not a significant effect on both original and 600 °C calcined ASR; citric acid quantitatively leached Zn and Pb, but Cu and Fe extraction was very low; after ASR calcination at 600 °C, 0.1 mol·L⁻¹ H₂SO₄ solution can extract 100% of Cu, Fe and Zn;
- H₂SO₄–H₂O₂ leaching medium showed a quantitative extraction of Fe and Zn but 50% Cu as maximum extraction only;
- Cu and Zn can be completely extracted in H₂SO₄–H₂O₂–Fe³⁺ leaching solution, although by different reaction times. The best experimental conditions for Cu were H₂SO₄ 1 mol·L⁻¹, H₂O₂ 9% (by volume), Fe³⁺ 15 g·L⁻¹, at 70 °C and 1.5 h reaction time. In the same conditions, Zn is completely leached in 30 min.

The present experimental work represents a preliminary study for the recovery of metals from ASR. Afterwards, an economical and effective process has to be tested to recover metals from leach liquor. Moreover, a feasibility study should be carried out considering the overall recovery process and the concentration of the metals in the ASR ashes.

References

- [1] ANPA, La caratterizzazione del fluff di frantumazione dei veicoli – Quadro normativo di riferimento e metodi di analisi, On line at: http://www.apat.gov.it/site/_contentfiles/00023700/23774_Rapporti_02_15.pdf 2002.
- [2] O. Gonzalez-Fernandez, M. Hidalgo, E. Margui, M.L. Carvalho, I. Queralt, Heavy metals' content of automotive shredder residues (ASR): Evaluation of environmental risk, *Environ. Pollut.* 153 (2008) 476–482.
- [3] M. Nourreddine, Recycling of auto shredder residue, *J. Hazard. Mater.* 139 (2006) 481–490.
- [4] G. Granata, E. Moscardini, G. Furlani, F. Pagnanelli, L. Toro, Automobile shredded residue valorisation by hydrometallurgical metal recovery, *J. Hazard. Mater.* 185 (2011) 44–48.
- [5] D. Lanoir, G. Trouvè, L. Delfosse, D. Froelich, A. Kassamaly, Physical and chemical characterization of automotive shredder residues, *Waste Manag. Res.* 15 (1997) 267–276.

- [6] L. Morselli, A. Santini, F. Passarini, I. Bassura, Automotive shredder residue (ASR) characterization for a valuable management, *Waste Manag.* 30 (2010) 2228–2234.
- [7] F. Passarini, L. Ciacci, A. Santini, I. Vassura, L. Morselli, Auto shredder residue LCA: Implications of ASR composition evolution, *J. Clean. Prod.* 23 (2012) 28–36.
- [8] S. Fiore, B. Ruffino, M.C. Zanetti, Automobile shredder residues in Italy: Characterization and valorization opportunities, *Waste Manag.* 32 (2012) 1548–1559.
- [9] K. Kurose, T. Okuda, W. Nishijima, M. Okada, Heavy metals removal from automobile shredder residues (ASR), *J. Hazard. Mater.* 137 (2006) 1618–1623.
- [10] O.T. Forton, L. Mc Grady, M.M. Singh, E.M.R. Taylor, N.R. Moles, M.K. Harder, Characterisation of rotary kiln residues from the pyrolysis of shredder residues: Issues with lead, *J. Anal. Appl. Pyrol.* 79 (2007) 395–402.
- [11] M.K. Harder, O.T. Forton, A critical review of developments in the pyrolysis of automotive shredder residue, *J. Anal. Appl. Pyrol.* 79 (2007) 387–394.
- [12] P. Donaj, W. Blasiaka, W. Yanga, C. Forsgren, Conversion of microwave pyrolysed ASR's char using high temperature agents, *J. Hazard. Mater.* 185 (2011) 472–481.
- [13] P. De Filippi, F. Pochetti, C. Borgianni, M. Paolucci, Automobile shredder residue gasification, *Waste Manag. Res.* 21 (2003) 459–466.
- [14] M.H. Lopes, M. Freire, M. Galhetas, I. Gulyurthu, I. Cabrita, Leachability of automotive shredder residues burned in a fluidized bed system, *Waste Manag.* 29 (2009) 1760–1765.
- [15] K.S. Lin, S. Chowdhury, Z.P. Wang, Catalytic gasification of automotive shredder residues with hydrogen generation, *J. Power Sources* 195 (2010) 6016–6023.
- [16] H.Y. Lee, Characteristics and heavy metal leaching of ash generated from incineration of automobile shredder residue, *J. Hazard. Mater.* 147 (2007) 570–575.
- [17] O. Gonzalez-Fernandez, S. Pessanha, I. Queralt, M.L. Carvalho, Analysis of lead content in automotive shredder residue (ASR), *Waste Manag.* 29 (2009) 2549–2552.
- [18] R. Cossu, T. Lai, Washing treatment of automotive shredder residue (ASR), *Waste Manag.* 33 (2013) 1770–1775.
- [19] T. Yoshida, H. Tateiwa, F. Tanno, M. Kahata, H. Seto, Cu recycling from low Cu containing waste, *Proceedings of REWAS 99 – Global Symposium on Recycling Waste Treatment and Clean Technology*, 2006.
- [20] A. Shibayama, T. Otomo, Y. Takasaki, Y. Cao, T. Murakami, K. Watanabe, H. Inoue, Separation and recovery of valuable metals from automobile shredder residue, *Int. J. Soc. Mater. Eng. Resour.* 13 (2006) 54–59.
- [21] M. Nieminen, M. Suomalainen, T. Mäkinen, Gasification of shredder residue, VTT Research Notes 2344/2006. (ISBN 951.38.6800.1. On line at: <http://www.vtt.fi/publications/index.jsp>).
- [22] G. Mancini, P. Viotti, A. Luciano, D. Fino, On the ASR and ASR thermal residues characterization of full scale treatment plant, *Waste Manag.* 34 (2014) 448–457.
- [23] V.A. Rossetti, F. Di Palma, F. Medici, Production of aggregate from non-metallic automotive shredder residues, *J. Hazard. Mater.* 137 (2006) 1089–1095.
- [24] J. Pèra, J. Ambroise, M. Chabannet, Valorization of automotive shredder residue in building materials, *Cem. Concr. Res.* 34 (2004) 557–562.
- [25] L. Ciacci, L. Morselli, F. Passarini, A. Santini, I. Vassura, A comparison among different automotive shredder residue treatment processes, *Int. J. Life Cycle Assess.* 15 (2010) 896–906.
- [26] P. De Stefanis, V. Iaboni, V. Valent, Il recupero energetico dei residui da autodemolizione, Rapporto ENEA, ISBN: 978-88-8286-243-5, 2011.
- [27] K. Srogi, An overview of current processes for the thermochemical treatment of automotive shredder residue, *Clean Technol. Environ.* 10 (2008) 235–244.
- [28] A. Chiarioni, A.P. Reverberi, A.H. El-Shaarawi, V.G. Dovì, Modelling of an ASR countercurrent pyrolysis reactor with nonlinear kinetics, *Appl. Therm. Eng.* 23 (2003) 1847–1855.
- [29] A. Chiarioni, A.P. Reverberi, B. Fabiano, V.G. Dovì, An improved model of an ASR pyrolysis reactor for energy recovery, *Energy* 31 (2006) 2460–2468.
- [30] J.L. Hau, R. Ray, R.B. Thorpe, A. Azapagic, A thermodynamic model of the outputs of gasification of solid waste, *Int. J. Chem. React. Eng.* 6 (2008) 1–20.
- [31] J. Hyks, T. Astrup, Influence of operational conditions, waste input and ageing on contaminant leaching from waste incinerator bottom ash: A full-scale study, *Chemosphere* 79 (2009) 1178–1184.
- [32] J. Li, E. Chen, H. Su, T. Tan, Biosorption of Pb²⁺ with modified soybean hulls as absorbent, *Chin. J. Chem. Eng.* 19 (2011) 334–339.
- [33] A. Meng, Q. Li, J. Jia, Y. Zhang, Effect of moisture on partitioning of heavy metals in incineration of municipal solid waste, *Chin. J. Chem. Eng.* 20 (2012) 1008–1015.
- [34] M. Pelino, A. Karamanov, P. Piscicella, D. Zannetti, S. Crisucci, Vitrification of electric arc furnace dusts, *Waste Manag.* 22 (2002) 945–949.
- [35] A. Karamanov, M. Pelino, A. Hreglich, Sintered glass-ceramics from MSW-incinerator fly ashes Part I: The influence of the heating rate on the sinter-crystallization, *J. Eur. Ceram. Soc.* 23 (2003) 827–832.
- [36] B. Ruffino, S. Fiore, M.C. Zanetti, Strategies for the enhancement of automobile shredder residues (ASRs) recycling: Results and cost assessment, *Waste Manag.* 34 (2014) 148–155.
- [37] F. Ferella, A. Ognyanova, I. De Michelis, G. Taglieri, F. Vegliò, Extraction of metals from spent hydrotreating catalysts: Physico-mechanical pre-treatments and leaching stage, *J. Hazard. Mater.* 192 (2011) 176–185.
- [38] I. Birloaga, I. De Michelis, F. Ferella, M. Buzatu, F. Vegliò, Study on the influence of various factors in the hydrometallurgical processing of waste printed circuit boards for copper and gold recovery, *Waste Manag.* 33 (2013) 935–941.
- [39] D.C. Montgomery, Design and Analysis of Experiments, third ed. Wiley, New York, 1991.