



Automobile shredded residue valorisation by hydrometallurgical metal recovery

Giuseppe Granata, Emanuela Moscardini, Giuliana Furlani, Francesca Pagnanelli*, Luigi Toro

Department of Chemistry, Sapienza University of Rome, P.le Aldo Moro 5, 00185 Rome, Italy

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ABSTRACT

The aim of this work was developing a hydrometallurgical process to recover metals from automobile shredded residue (or car fluff). Automobile shredded residue (ASR) was characterised by particle size distribution, total metal content and metal speciation in order to guide the choice of target metals and the operating conditions of leaching. Characterisation results showed that Fe is the most abundant metal in the waste, while Zn was the second abundant metal in the fraction with diameter lower than 500 μm . Sequential extractions denoted that Zn was easily extractable by weak acid attack, while Fe and Al required a strong acid attack to be removed. In order to recover zinc from <500 μm fraction leaching tests were operated using acetic acid, sulphuric acid and sodium hydroxide at different concentrations. Sulphuric acid determined the highest zinc extraction yield, while acetic acid determined the highest zinc extractive selectivity. Sodium hydroxide promoted an intermediate situation between sulphuric and acetic acid. Zn recovery by electro winning using acetic leach liquor determined 95% of Zn electro deposition yield in 1 h, while using sulphuric leach liquor 40% yield in 1 h and 50% yield in 2 h were obtained. Simulation results showed that the sulphuric leaching process was more attractive than acetic leaching process.

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1. Introduction

Growing concern towards environmental impact of end of life vehicle (ELV) along with the lack of primary raw materials focused the attention towards the development of new recycling strategies for the valorisation of secondary raw materials.

Currently, about 75% of ELV (expressed as total weights) is recycled in EU countries, while the remaining 25% is called auto shredder residues (ASRs) or car fluff.

Presently about 3 Mt of ASRs are annually generated in North America and 2 Mt of ASRs per year are generated in EU countries (Italian ASR production is about 400,000 t/y). The quantities of shredder fluff are likely to increase in the coming years due to the growing number of cars being scrapped and to the increase in the amount of plastics used in car production [1].

In the course of car shredding process, iron and steel are generally recovered by magnetic separation, and non ferrous metals by eddy current separation. Some plastic fractions are reclaimed too. ASR is the residual fraction made up of plastic, rubber and tissue (globally 70%), metals (20%), glass and other rubbles (10%).

Due to its high heterogeneity and variable composition ASR can be classified as “special waste” or as “hazardous waste” depending

on the presence of hazardous substances (Decisions 2000/532/EC, 2001/18/EC2, 2001/119/EC3 e 20001/573/EC4 of Council).

Guideline 2000/53/EC established that after January 2015:

1. reuse and recovery of all ELV shall be increased to a minimum of 95%;
2. recovery and recycling of all ELV shall be increased to a minimum of 85%.

In this scenario several researches showed that the best final destination for this waste is thermal treatment such as gasification or pyrolysis because ASR's heat of combustion is about 18 MJ/t. However ASR pre-treatment could be required before gasification to increase the heat of combustion and to remove metals. The aim of metal removal is both to reduce pollutant release during gasification and to recover valuable metals. Different kinds of processes could be used to recover metals from industrial wastes, but hydrometallurgical processes showed several advantages such as cost effectiveness and flexibility [2,3]. Concerning metal recovery from wastes, Yoshida et al. [4] investigated direct copper recycling, while Shibayama et al. [5] recovered zinc and copper from fly ash after combustion by distillation, precipitation and cementation.

Several techniques have been investigated to handle ASR: landfill, material recycling, thermal valorisation. In the scientific literature many works can be found regarding the treatment of fluff, focusing mainly on materials recovery or on thermal treatments. The research about ASR material recycling focuses on its use as a filler in concrete, binder in asphalts or similar.

* Corresponding author. Tel.: +39 06 49913333; fax: +39 06 490631.
E-mail address: francesca.pagnanelli@uniroma1.it (F. Pagnanelli).

So far car fluff valorisation by a process oriented to metals recovery was not investigated.

The aim of this work was the preliminary assessment of the technical and economical feasibility of an innovative and simple hydrometallurgical process for the treatment of ASR and the recovery of valuable metals before final destination of this waste for energy production.

The characterisation of ASR was then performed in terms of total metal content and speciation into the different size fractions in order to guide both the identification of target metals and leaching strategies. Preliminary experimental results of leaching, leach liquor purification and product recovery were used as input data for process simulation.

2. Materials and methods

2.1. Particle size distribution

A sample of 16 kg of ASR supplied by “Italferrero s.r.l.” was quartered by the ring and cone method and a quarter was grounded by an industrial knife mill. The grounded fluff was then quartered to obtain 1 kg of grounded sample quartered itself to a sample shredded by a laboratory knife mill (RESTCH SM2000) in order to obtain particle dimensions lower than 4 mm [6].

Particle size distribution was determined using four sieves to separate bulk ASR into four particle size fractions $d < 500 \mu\text{m}$, $500 < d < 1000 \mu\text{m}$, $1000 < d < 2000 \mu\text{m}$ and $4000 > d > 2000 \mu\text{m}$.

2.2. Acid digestion

Total metal content (Al, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn) was determined by extraction with aqua regia: 10 g of dried ASR sample (5 replicates) were leached using a mixture 3:1 of HCl–HNO₃ for 16 h at room temperature and then for 2 h at 130 °C in the presence of H₂O₂ [7]. Metal concentrations were determined by an inductively coupled plasma-optical emission spectrometer (ICP/OES).

2.3. Batch sequential extraction

Metal speciation was determined by batch sequential extraction using three different extracting agents with increasing extractive strength: CH₃COOH 0.11 M, NH₂OH–HCl 0.5 M and H₂O₂–CH₃COONH₄ 1 M [8]. They were used in sequence at solid–liquid ratio 1:40 for 16 h in the Dubnoff stirrer. After each extractive step the solid was separated from liquid by filtration and then dried, weighted and used in the subsequent step. Liquid samples were further filtered and analysed by ICP/OES.

2.4. Leaching

Leaching tests were performed on <500 μm size fractionated samples. 2 g of <500 μm dried ASR samples were leached using two kinds of acids, H₂SO₄ (0.05, 0.1 and 0.2 g_{H₂SO₄}/g_{powder} by H₂SO₄ 0.1, 0.2 and 0.4 M) and CH₃COOH (0.06, 0.12 and 0.24 g_{CH₃COOH}/g_{powder} by 0.2, 0.4 and 0.8 M) and one alkaline agent as NaOH (0.2, 0.5 and 1.5 g_{NaOH}/g_{powder} by NaOH 0.5, 1.25 and 2.5 M) in solid–liquid ratio

1:5. Solid suspensions were stirred by Dubnoff thermostatic bath at 25 °C and liquid samples were sampled every 2, 5 and 10 h, filtered and analysed by ICP/OES. Zn extractive yield was calculated as ratio between mg/g of extracted Zn and mg/g of total Zn, while Zn extractive selectivity was calculated as:

$$S = \frac{\text{zinc extractive yield}}{\sum \text{all metal extractive yield}} \quad (1)$$

2.5. Precipitation

Optimum pH value for impurity removal was investigated adding different amounts of 2 M KOH to leach liquor samples which needed purification. These tests were carried out at room temperature adding KOH under stirring in 100 mL leach liquor samples. After KOH addition, leach liquor was filtered and analysed by ICP/OES.

2.6. Electro winning

Electro winning was performed using a synthetic solution resembling sulphuric leach liquor (Zn 3.2 g/l) and a real acetic leach liquor (Zn 1.3 g/l) at pH 4–5, fixed-cathodic potential of 1.7 V [9], using an aluminium foil as cathode and graphite as anode. Potentials were controlled using an AMEL 7060 potentiostat connected to a computer with JUNIOR ASSIST V60 software.

The degree of purity of obtained solids was evaluated by dissolving weighted samples of deposited metallic zinc by HCl and by analysing the zinc in solution by ICP/OES.

3. Results and discussion

3.1. Particle size distribution

Particle size distribution results showed that about 60 wt.% of shredded ASR had a diameter (d) lower than 500 μm. Fractions with $4000 > d > 2000 \mu\text{m}$, $1000 < d < 2000 \mu\text{m}$ and $500 < d < 1000 \mu\text{m}$ were 20%, 7% and 13% of total weight, respectively.

3.2. Total metal content

Results of metal content listed in Table 1 clearly showed that Fe was the most abundant metal (65%) in each size fractionate sample. Zn was the second most abundant metal especially in the fraction lower than 500 μm, whereas Cu was the second most abundant metal only in the fractions 500–1000 μm and 1000–2000 μm. Metal content and particle size distribution results showed also that all metals, with the exception of copper, were mainly contained in the smallest fraction.

3.3. Metal speciation

Sequential extractions showed that Zn, Cd, Fe and Al presented the same behaviour independently of particle size. In particular Zn and Cd were weakly bounded to the matrix and they were easily removable by weak acid attack (first step of sequential extraction).

Table 1
Metal content in the different granulometric fractions.

Diameter	Al (mg/g)	Cd (mg/g)	Cr (mg/g)	Cu (mg/g)	Fe (mg/g)	Mn (mg/g)	Ni (mg/g)	Pb (mg/g)	Zn (mg/g)
<500 μm	12.4 ± 0.5	0.12 ± 0.001	0.3 ± 0.1	6 ± 2	119 ± 8	1.2 ± 0.5	0.3 ± 0.1	5.1 ± 0.3	16 ± 1
>500, <1000 μm	12 ± 2	0.030 ± 0.001	0.18 ± 0.05	35 ± 10	116 ± 10	1.0 ± 0.3	0.19 ± 0.05	2.0 ± 0.3	9 ± 1
>1000, <2000 μm	20 ± 7	0.032 ± 0.001	0.18 ± 0.02	22 ± 10	141 ± 50	1.2 ± 0.5	0.14 ± 0.02	1.03 ± 0.07	9 ± 1
>2000 μm	7 ± 3	0.020 ± 0.001	0.088 ± 0.005	5 ± 2	57 ± 10	0.40 ± 0.05	0.08 ± 0.01	1.2 ± 0.2	5 ± 1
Real waste	15 ± 2	0.03 ± 0.01	0.31 ± 0.08	15 ± 4	93 ± 7	0.9 ± 0.2	0.4 ± 0.1	3.1 ± 0.9	11 ± 2

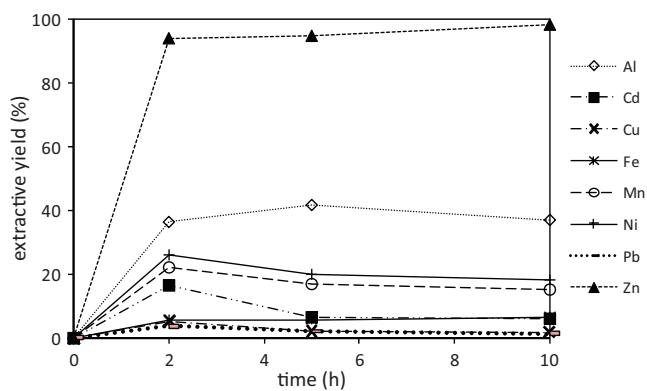


Fig. 1. Metal extractive yields using 0.25 of H_2SO_4 for g of car fluff.

On the other hand Fe and Al were mainly extracted in the second extractive step by strong acid-reducing attack. Data also showed that Zn was extracted from the $<500 \mu m$ fraction for about the 80% by a weak acid (CH_3COOH), while using a strong acid Zn extraction yield increased to 95%.

3.4. Leaching tests

On the base of characterisation results the study of metal recovery was focused on zinc because of its high content and economic value, while other valuable metals as Al and Cu could be better recovered by physical methods improving the pre-treatment step before leaching.

The zinc recovery was tested by using two different acids and an alkaline agent (Table 2) to exploit zinc amphoteric behaviour [10]. Leaching tests were performed on the fraction lower than 0.5 mm because of its higher metal content.

3.4.1. Sulphuric acid

The advantage of employing H_2SO_4 was to promote Zn extraction yield proportional with the amount of used leachant (Table 2). In fact using 0.2 g H_2SO_4 for g of ASR (corresponding to H_2SO_4 0.4 M in S/L ratio 1:5), Zn extractive yield was 95% after 2 h and it became 99% after 10 h (Fig. 1). Using 1:5 as solid-liquid ratio final zinc concentration in solution was 3.2 g/l.

Nevertheless sulphuric acid leaching was characterised by low zinc extractive selectivity (<1) mainly because of the extractive yield of other metals as Al (36%), Ni (26.1%) and so on. Since this waste contains high amount of iron, even if iron extractive yield is quite low (5.8%), its concentration in solution is high enough to interfere with subsequent zinc recovery.

3.4.2. Acetic acid

Even if all metals were soluble as acetates, acetic acid presented a low extractive strength with zinc extractive yields included between 35 and 75% (Table 2). However, using this acid higher Zn extraction selectivity was obtained than with sulphuric one. In par-

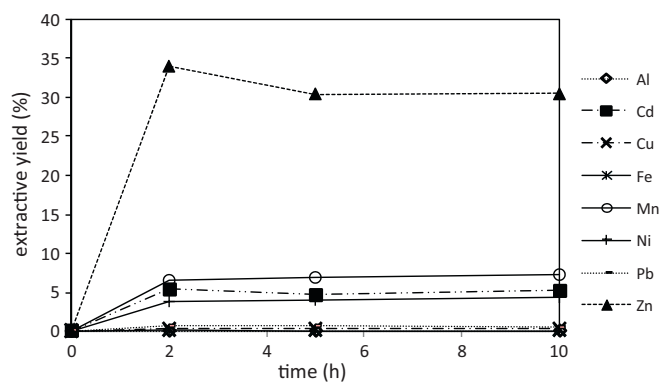


Fig. 2. Metal extractive yields using 0.05 g of CH_3COOH for g of car fluff.

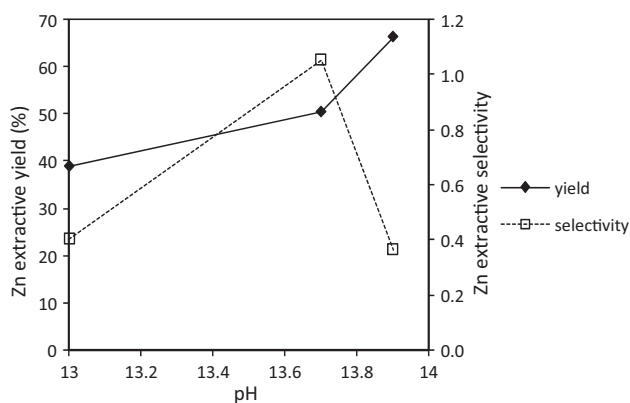


Fig. 3. Zinc extractive yield and selectivity at different pH values.

ticular using 0.06 g of CH_3COOH per g of ASR (by CH_3COOH 0.2 M in S/L ratio 1:5) selectivity index was about 2 while using 0.25 g of CH_3COOH for g of ASR sample (CH_3COOH 0.8 M in S/L ratio 1:5) Zn extractive selectivity was 1.5.

0.05 g of CH_3COOH for g of ASR could be used in order to promote the most selective leaching. In fact even if zinc extractive yield was only 35% (Fig. 2) the concentration of the other metals was lower enough to limit the need of subsequent purification treatment.

3.4.3. Sodium hydroxide

Sodium hydroxide was used in order to exploit the zinc amphoteric behaviour extracting it as sodium zincate (Na_2ZnO_2). Maximum zinc extractive yield (67%) was obtained using 1.5 g of this leachant for each g of ASR powder ($NaOH$ 2.5 M). Yield values (Table 2) were included between 40 and 70% and present a linear dependence with equilibrium pH values (Fig. 3).

Zinc extractive selectivity was higher for a pH value included between 13 and 14 (Fig. 3) because if pH increased too much other amphoteric metals, such as lead and cadmium, were extracted too.

Table 2
Metals extractive yield during leaching test.

Leachant	g_{acid}/g_{powd}	Al (%)	Cd (%)	Cu (%)	Fe (%)	Mn (%)	Ni (%)	Pb (%)	Zn (%)	S_{Zn}
H_2SO_4	0.05	<0.1	5 ± 1	0.15 ± 0.01	<0.1	11.2 ± 0.2	7.0 ± 0.1	0.11 ± 0.02	21.8 ± 0.1	0.9
	0.10	40.1 ± 0.1	10 ± 1	6.3 ± 0.1	7.8 ± 0.3	30 ± 1	28.5 ± 0.5	1.11 ± 0.01	79.9 ± 0.5	0.6
	0.20	36.5 ± 0.1	16.4 ± 0.5	5.3 ± 0.2	5.8 ± 0.2	22.3 ± 0.1	26.1 ± 0.1	3.88 ± 0.05	94.2 ± 0.2	0.8
CH_3COOH	0.06	<0.1	5.3 ± 0.1	0.2	<0.1	6.5 ± 0.2	3.7 ± 0.1	0.65 ± 0.01	34 ± 2	2.1
	0.12	0.12 ± 0.05	4.5 ± 0.6	0.4 ± 0.1	0.12 ± 0.02	12 ± 2	8.5 ± 0.6	1.1 ± 0.2	37.1 ± 0.4	1.4
	0.24	0.8 ± 0.1	7.7 ± 0.2	1.6 ± 0.5	0.9 ± 0.1	15 ± 2	8.7 ± 0.5	10.4 ± 0.6	60 ± 1	1.3
	0.60	44 ± 2	0.2 ± 0.1	3.4 ± 0.5	<0.1	0.3 ± 0.1	0.7 ± 0.1	8.5 ± 0.5	45 ± 2	0.8
NaOH	0.80	37 ± 1	<0.10	1.8 ± 0.5	<0.1	0.2 ± 0.1	0.4 ± 0.1	2.2 ± 0.5	33 ± 1	0.8
	2.40	47 ± 3	98 ± 5	2.5 ± 0.5	<0.1	0.2 ± 0.1	0.5 ± 0.1	11 ± 1	48 ± 2	0.3

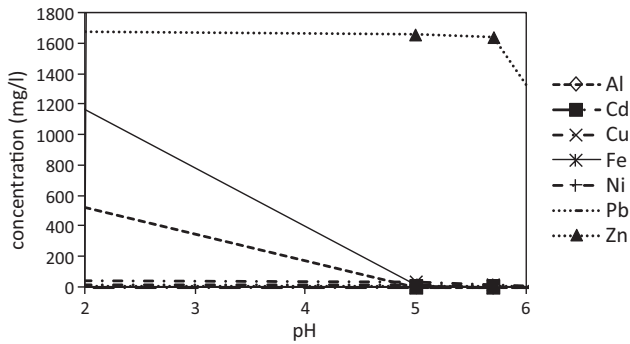


Fig. 4. Metal concentrations at different pH values.

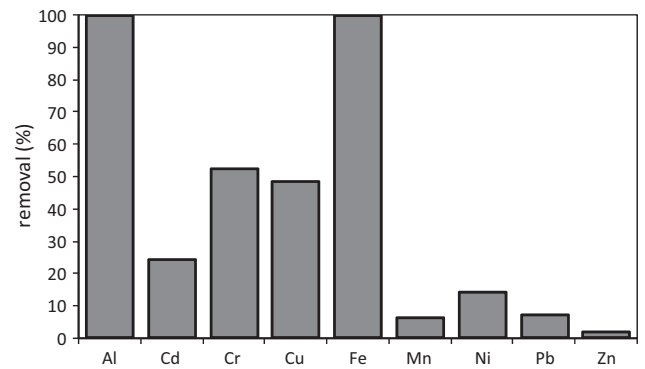


Fig. 5. Precipitation on sulphuric leach-liquor (0.2 g/g).

3.5. Precipitation

Since acetic acid ensured high selectivity for Zn extraction, purification was performed only on sulphuric leach-liquor in order to eliminate impurities such as Fe and Al as hydroxide ($k_{psFe(OH)_3} = 3 \times 10^{-38}$, $k_{psAl(OH)_3} = 6 \times 10^{-12}$).

Precipitation was operated adding KOH until pH 5–5.5 (Fig. 4). In this pH range Fe and Al were totally removed, Cu and Cd were partially removed, while Zn remained in solution (Fig. 5).

3.6. Electro winning

Electro winning process on the purified sulphuric electrolyte showed an electro deposition yield of zinc 50% in 2 h. Using this

purified electrolyte zinc purity was about 99% and energy consumption for electrolysis in laboratory scale was 2.9 kWh/kg_{Zn}.

Zinc electro deposition from real acetic leach liquor was operated with a yield of 90% in the same time but the obtained metallic zinc had a purity of 90%. Energy consumption for electrolysis in laboratory scale was 2.1 kWh/kg_{Zn}.

3.7. Preliminary technical–economical feasibility

On the base of these experimental results two different hydrometallurgical processes were proposed and two simulations were operated using 40 kt/y as ASR input flow rate. This input flow rate (10% of national production) was based on the assumption

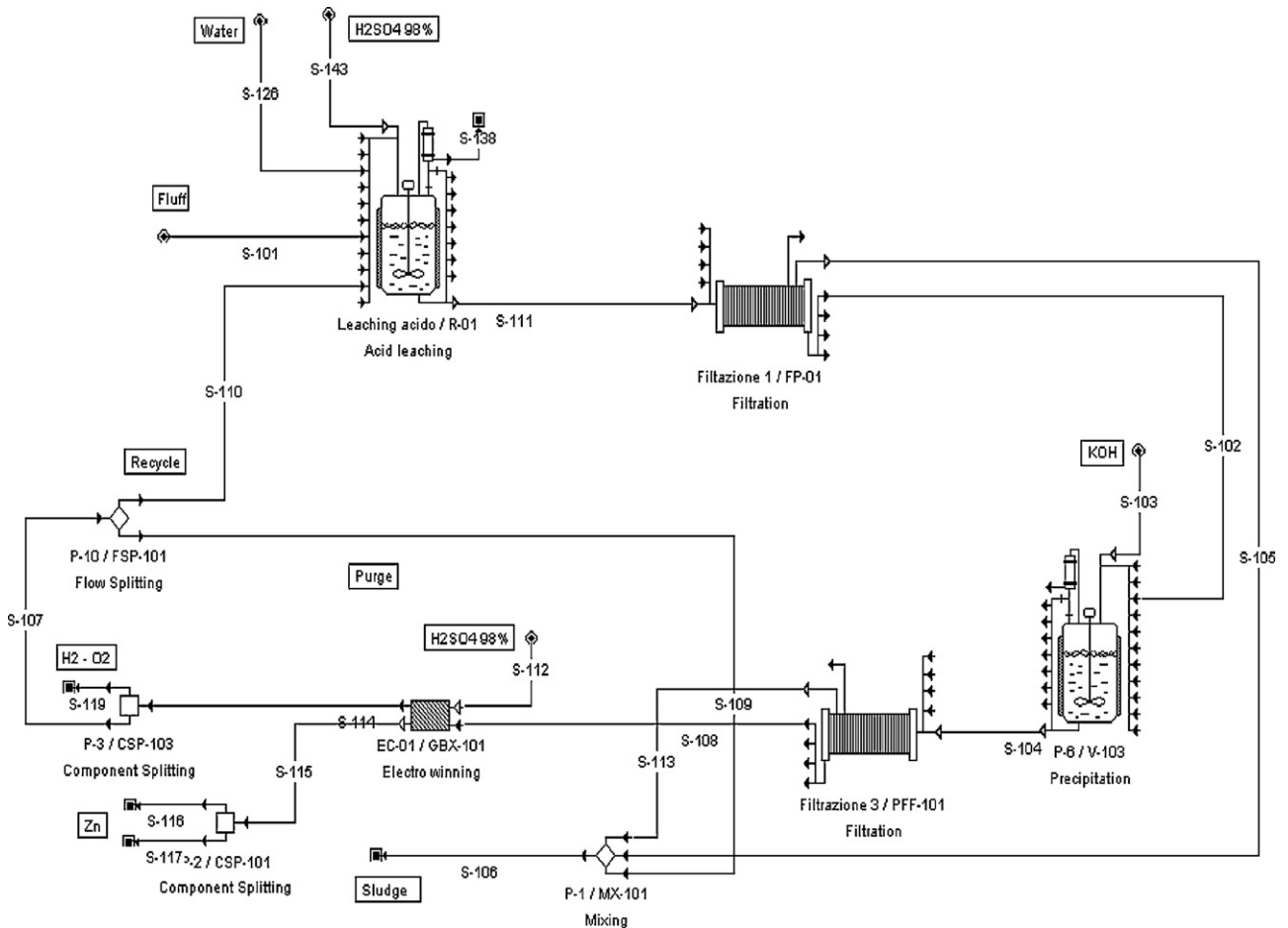


Fig. 6. Sulphuric process flow sheet.

Table 3
Main simulation results.

	Sulphuric	Acetic
Processing rate (t/y)	40,000	40,000
Total capital investment (\$)	7,662,000	4,062,000
Operating cost (\$/y)	8,451,000	9,838,000
Total revenues (\$/y)	11,827,000	11,310,000
Payback time (y)	2.83	3.50
Gross margin (%)	28.55	13.02

Table 4
Main operating cost for both sulphuric and acetic process.

	Sulphuric		Acetic	
	\$/y	% op. cost	\$/y	% op. cost
Waste treatment/disposal	5,490,000	65	7,815,000	79
Raw materials	1,281,000	14	1,281,000	11
Labour-facility	1,251,000	15	1,251,000	7
Utilities	412,000	5	220,000	2
Other operating cost	17,000	1	17,000	1

that more than one plant should treat car fluff in order to avoid logistic problems and decrease the costs of transport. Simulations were performed in order to have preliminary matter balance and economical evaluations of a small treatment plant. This operation was performed by “Super Pro Intelligen” software assuming a price surcharge equal to 0.2 \$/kg of car fluff treated (price surcharge is a common price paid by waste producers to the waste disposer). Other hypotheses were: disposing cost of sludge 0.1 \$/kg, cost of labour dependent 250,000 \$/y, cost of facility-dependent 1,000,000 \$/y, project lifetime 10 years, depreciation period 9 years, inflation rate 3%, income taxes 40% [11]. Grinding and its cost were not included in the simulation because of the assumption that it would be directly performed by car fluff producers.

First flow sheet (Fig. 6) contains a leaching operation by H_2SO_4 , precipitation by KOH and electro winning operation. Second flow sheet (not reported here) does not contain any purification step between leaching and electro winning operations.

Simulation results (Table 3) showed that both sulphuric and acetic processes were economically feasible feeding the plant at least with 400,000 t/y. Using this input flow rate revenues were higher than operating costs, especially for sulphuric process and payback time (PBT) was lower than 3 years for sulphuric process.

In particular operating costs were mainly (65%) composed by waste (sludge) disposal/treatment but this cost could be reduced including this process in a integrate cycle in which the final destination is thermal treatment (as transposition of European guidelines land filling is forbidden). For acetic process operating cost was higher than that of sulphuric process because of the higher amount

of waste to treat/dispose. Even if acetic acid has a purchase price higher than sulphuric acid, raw material costs were lower for acetic process because it did not contain any purification step, and potassium hydroxide was not included. All operating costs are listed in Table 4.

4. Conclusions

The aim of this work was evaluating how ASR could be valorised before final thermal treatment.

Preliminary characterisation results showed that ASR contains different metals and principally Fe, Al, Cu and Zn. In particular Zn was the second most abundant metal in the waste in particular in the fraction which has diameter <500 μm and it was easily extracted by weak acid attack. Leaching tests showed that acetic acid had the highest Zn extractive selectivity and acetic leach liquor did not require purification before electro winning.

Sulphuric acid leaching was characterised by the highest Zn extractive yield but its leach liquor required purification by precipitation before electro winning.

Simulation results showed that sulphuric process was more economically attractive than acetic process.

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