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Recovery of zinc from ashes of automobile tire wastes by pH controlled solutions of ammonium chloride

F.Baldassarre[1], P.Bruno[1], M.Caselli[1]*, P.Ielpo[1], G.Cornacchia[2], A.Canonico[2], G.Chita[3]

[1]Dipartimento di Chimica, Universita degli studi di Bari, Via Orabona 4, 70126 Bari, (ITALY)

[2]Enea ACS PROT-STP, CR Trisaia (Matera), SS106 Jonica Km 419+500, (ITALY)

[3]CNR , Istituto di cristallografia, Via G.Amendola 122, Bari, (ITALY)

Tel: 00390805442021; Fax 00390805442129

E-mail: caselli@chimica.uniba.it

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ABSTRACT

This paper concerns the recovery of zinc from fly ashes generated by incineration plant of automobile tire wastes. The recovery is obtained by two extraction steps with a pH-controlled ammonia chloride solution. The ashes contain about 51% wt of zinc, 1% wt of iron and aluminium and small quantities (less than 0.1% wt) of cobalt, copper and lead. Various factors affect the performance and efficiency of leaching: temperature, concentration, pH and time were studied using a factorial experimental design. After two steps with ammonium chloride 3mol/L, L/S=6 ml/g, pH 5.4±0.1 and T=72±3°C the leaching liquor has been purified in a simple step by cementation with metallic zinc powder without activation. Traces of Pb, As, Sb, Se, Mo, Ni have been cleared by cementation with zinc. The fly ash and residue composition was determined by X-ray and its elemental composition by ICP-OES and IC. The obtained results show that recovery efficiency amounts to 98% wt for zinc; the concentration of zinc in the leach liquors reaches more than 45 g/L while most of the iron is not leached. The purified solution containing zinc allows the direct recovery of high grade zinc by electro-deposition.

KEYWORDS

Fly ash;
Zinc oxide;
Zinc recovery;
Leaching;
Ammonium chloride.

INTRODUCTION

The absolute prohibition of disposing tires in any form, also grinded , in dumping sites has come in force in Italy beginning from July 2006 following the most recent European legislation. The accomplishing of this regulation will involve an increase of the activities concerning the tire disposal: retread activities, energy and material recovery, pyrolysis etc. According to ETRA (European Tyre Recycling Association) data, the percent of tires disposed in dumping decreased from 62% in 1992 down to 26.4% in 2003. The share destined to energy recovery, on the contrary, increased from 14% up to 24.4% in the same period[1]. The results obtained by incinerating the tires in the modern, high technological plants show that is possible to comply with both economical (energy and material recovery) and ecological (low emissions) requirements. It can be interesting to evaluate the possibility to recover useful materials from the by-products formed during the incineration process. In the tire production different metallic additives are employed, the main of which is the zinc oxide. Besides the tire contains smaller quantities of iron, aluminium, copper, and traces of manganese, lead, titanium[2]. All these metals are concentrated in the fly ashes captured by dry-bag filters present in the fume treatment of the plant[3]. The percent of zinc oxide that can be present in the fly ashes can reach 65%. Focussing the attention on Zinc, it is evident that the recovery of it from the fly ashes produced by tire incineration allows to obtain a material very utilized and therefore easily marketable and, at the same time, a reduction of the amount of fly ashes that one must get rid of. Various leaching solutions can be used for the dissolution of zinc[4,5,6,7,13,14,15,16]: in this paper the zinc was recovered by hydrometallurgical process using a solution of ammonium-chloride.

MATERIALS AND METHODS

Sample and analysis of fly ash

A representative sample of fly ashes, obtained from a dry-bag filter in fume-cleaning section in the incineration plant of automobile tire wastes has been utilized in this study. It was a 3 Kg homogeneous ash sample obtained from a tire sample of 20Kg. This ash sample contained a high percentage of zinc oxide (~65% wt) and consisted of a grey fine/hygroscopic powder; all sub samples were dried at 105°C for 24h before use. The metal content of the ashes and their residues were determined by dissolving 0.5g of the sample in a mixture of ultra pure acids formed by HNO_3 (8 ml), HCl (2 ml), HF (4 ml) by focussed microwave digestion (FKV mod. Ethos plus) and measuring the metal concentration (Zn, Fe, Al, Cu, Pb, Co, Sb, Sn, Mn, Cr, Cd, As, Ni, Be, Hg) by inductively coupled plasma atomic emission spectrometry (ICP-OES TJA Atomscan 25, Perkin Elmer mod. OPTIMA 2000 DV, AMA 254 A.A. for Hg), after dilution and acidification (HNO_3); the inorganic species (Ca, Mg, chloride and sulphate) of the ashes were dissolved with HNO_3 (8 ml) and their concentrations were measured by ionic chromatography (IC, DIONEX mod. DX-120), while C,N,H,S were measured by elemental analyzer(EA 1110 CE Instruments). The measurements were carried out in triplicate runs in all experiments. The leached was filtered using a membrane filter (glass-fibre Whatman GF/C); filtrates were analyzed by ICP-OES and IC. The ash samples and the residue were analysed by X-ray diffraction analysis (using XRD, Rigaku with Cu target -12 kW Power-Debye-Sherrer geometry).

Equipment

Serial batch tests were performed putting 5g of sample and 30ml of leaching solution (liquid/solid ratio L/S=6 ml/g) in a 150ml glass bottle. The solution was stirred (40r.p.m.) and heated; pH was measured with a portable apparatus (WTW) after calibration. The solution was filtered through a Whatman fibre glass filter and the filter cake was washed with small quantities of water (L/S~5) and dried at 105°C for 6h.

Purification of the leached solutions

Cementation is used for hydrometallurgy zinc solutions purification from easily reducible metals :

$$n/2\ Zn + Me^{n+} = Me + n/2\ Zn^{2+}\ (Me= Co, Pb, Cd, Cu, Ag....)$$

The rate and efficiency of this process depends on various factors; the use of surfactants and chemical activators increases the cementation process efficiency[8]. In this paper the effect of this factors was not studied; cementation was conducted in one step without activation agents or surfactants addition. It was performed using 24g/Kg fly ash of 100 mesh, 99.998% powder zinc at pH~5.5 and at a temperature 65°C for 20 minutes.

RESULTS AND DISCUSSION

The recovery of each element is expressed as wt % = weight of recovered element /weight of that element in fly ash *100.

Chemical composition of ashes

The fly ash chemical composition, determined as described in paragraph 2.1, is reported in TABLE 1 and TABLE 2 :

TABLE 1: Chemical composition of fly ash (metals)

Element	Zn	Fe	Al	Cu	Pb	Co	Sb	Sn	Mn	Cr,Cd,As	Ni,Be,Hg
[wt.%]	51.7	0.84	0.58	0.12	0.085	0.08	0.02	0.011	0.01	<<0.005	<<0.0008

TABLE 2: Chemical composition of fly ash (elements and inorganics)

Element	Ca	Mg	Si	Sulphate	Chloride	S	C	H
[wt.%]	2.1	0.3	10.5	10.7	0.4	4.1	0.71	0.14

Effects of different parameters investigates

The quantity of zinc extracted depends on temperature, pH and concentration.

Effect of temperature and NH_4Cl concentration

The effect of temperature and NH_4Cl concentration is shown in figure 1 at the pH 6.4 of minimum recovery (see later on)

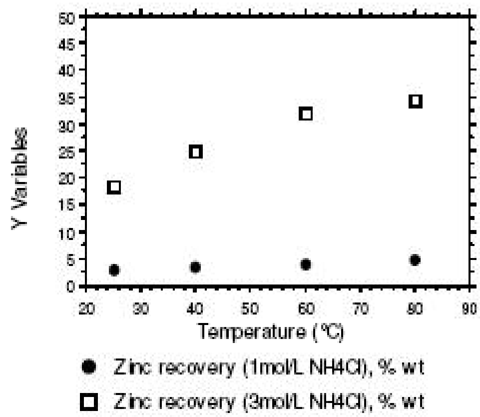

Figure 1: Effect of temperature and concentration (60min, L/S=6ml/g, pH 6.4)

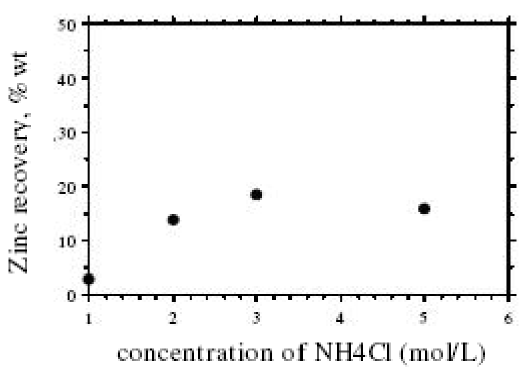

Figure 2: Effect of NH_4Cl concentration on the recovery of Zinc (T=25±2°C, 60min, L/S=6 ml/g, pH 6.4 no modified) The effect of pH was therefore studied at T=60°C and NH_4Cl 3M

Temperature influences appreciably the recovery only at higher NH_4Cl concentration. Optimum temperature is between 65 and 85°C. At T=25°C the recovery is maximum for NH_4Cl = 3 M as shown in figure 2 :

Effect of pH on the recovery of metals

The pH is the most important variable for metal solubilisation and recovery in the pH range 4.5-9. As it can be seen in figure 3, recovery is higher at low and high pH values for all metals except lead, and has a minimum at pH 6.5 for the others three metals. Metals are present in fly-ashes under different chemical species with different tendency to form ammoniacal and chloroammoniacal complexes. Leaching with ammonium chloride the oxides of Zn, Pb, Cu, Co pass into solution while zinc ferrite and silicates remain insoluble.

Purification by cementation

Compositions of the original and purified leach liquors is reported in TABLE 3.

Leaching with acid and alkaline solution of ammonium chloride

In TABLES 4 and 5 the results of Zn, Cu Pb and Co recovery in acid and alkaline solution of NH_4Cl are

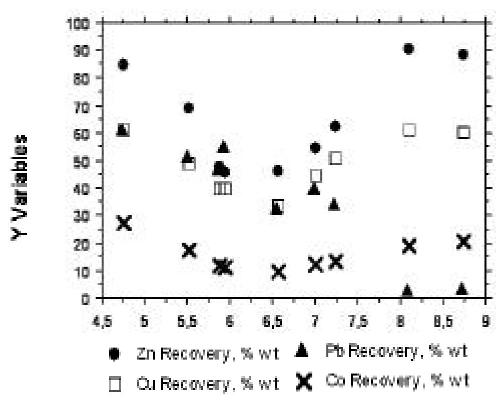

Figure 3: Effect of pH on the recovery of metals; Y variables = Metal Recovery, %wt (T=77±5°C, 60min, L/S=6 ml/g, NH_4Cl_3 mol/L)

TABLE 3: Composition of liquors

Leach liquor	Concentration of elements (mg/L)												
	Zn	Fe	Co	Mn	Pb	Cu	As, Sb,Se,Mo,Ni	Si	Al	Ca	Mg	Br	SO_4^{2-}
Original	43800	0.5	38	3.3	15	64	-	89	-	-	-	-	-
Purified	44900	0.2	24	2	<0.1*	3.3	< 0.1*	30	45	1010	27	495	7730

***= LoD (Limit of detection of element)**

TABLE 4: Recovery of metals in NH_4Cl acid solution

Samp. no.	T (±2°C)	pH (±0.2)	Recovery of Zn (% wt)	Recovery of Cu (% wt)	Recovery of Pb (% wt)	Recovery of Co (% wt)
1	58	5,98	43,0	39,6	47,4	11,5
2	62	5.55	65.0	47.0	46.0	15,0
3	63	6,66	39,0	38,3	43,6	10,5
4	63	5,60	67,3	48,4	48,3	16,3
5	63	6,66	39,0	38,3	43,6	10,5
6	71	5,88	48,0	40,3	46,5	12,0
7	72	4,75	84,8	61,7	60,9	27,5
7	73	7,00	54,5	44,9	39,6	12,3
8	73	7,00	54,5	44,9	39,6	12,3
9	85	6,56	46,2	33,9	32,2	9,9
10	91	5,93	45,7	40,3	54,5	11,5

TABLE 5: Recovery of metals in NH_4Cl alkaline solution

Samp. no.	T (±2 °C)	pH (±0.2)	Recovery of Zn (% wt)	Recovery of Cu (% wt)	Recovery of Pb (% wt)	Recovery of Co (% wt)
1	40	9,10	86,8	62,5	2,7	19,8
2	42	7,84	58,0	48,1	14,2	12,9
3	45	7,23	44,5	40,5	34,9	10,4
4	62	6,22	29,0	56,5	13,8	16,6
5	63	7,91	77,9	56,5	13,9	16,6
6	63	7,99	81,6	57,9	13,5	16,7
7	64	7,90	77,4	58,4	14,1	17,4
8	64	7,96	82,9	58,8	12,8	17,4
9	64	9,38	90,4	63,3	3,0	21,3
10	82	7,24	62,4	50,8	34,1	13,8
11	82	8,74	88,7	60,5	2,9	20,9
12	83	8,10	90,7	61,5	2,5	19,3

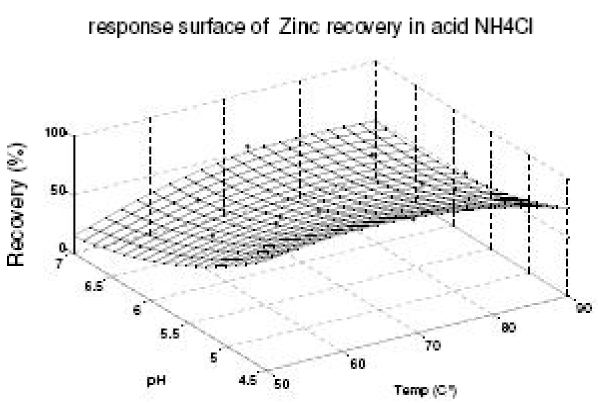

Figure 4: Effect of pH and temperature in acid solution

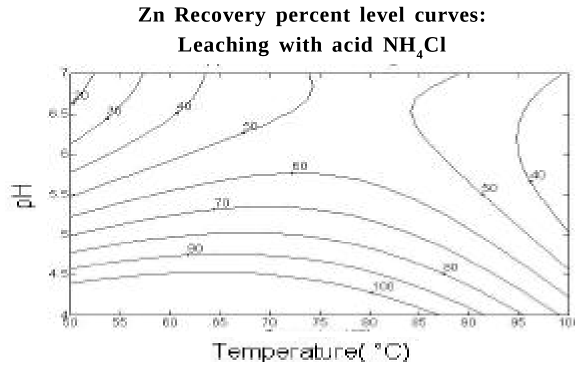

Figure 5: Level curves

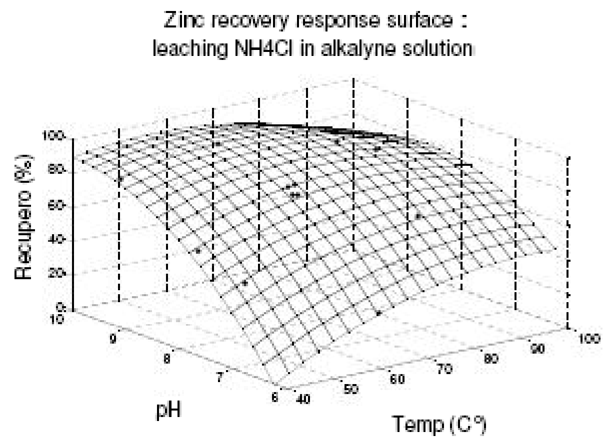

Figure 6: Effect of pH and temperature in alkaline solution

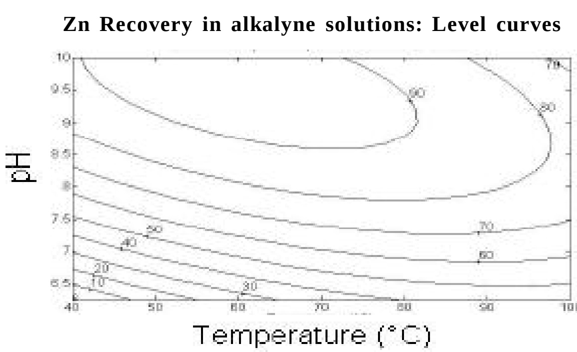

Figure 7: Level curves

reported.

The temperature and pH values form a two factor central composite design on the base of which response curves can be obtained. The model consider the variables, their squares and the interaction between them. Recovery surface and isorecovery lines for Zn in acid and alkaline solution are reported in figures 4-7. Zn recovery is practically total for temperature 80-90°C at pH 4.5-5 or for temperature 60-70°C at pH 9.5-10. In both cases the recovery of Copper is 70-80% while lead and cobalt recovery is no more than 20-25%. Lead can be extracted in acid solution (pH<4 at temperature 80-90°C).

Experimental flow chart

A flow chart of Zn recovery process in acid NH_4Cl solution is proposed in figure 8 :

Leaching solution and residue composition

The residue composition after two leaching steps is reported in TABLE 6:

X-ray diffraction of fly ash and residue

The X-Ray spectrum of the original ash and of the leaching are reported in figures 9 and 10 respectively. In the initial ash Zn is present as Zincite. Other present compounds are quartz, silica and anidride. In the residue

TABLE 6 : Chemical composition of residue

Element	Si	Zn	Fe	Al	Co	Pb	Cu	Ca	Mg	C	S	H	N
[wt.%]	75	8.4	4.2	4	0.44	0.2	0.17	14.6	3.5	1.3	0.44	0.14	0.14

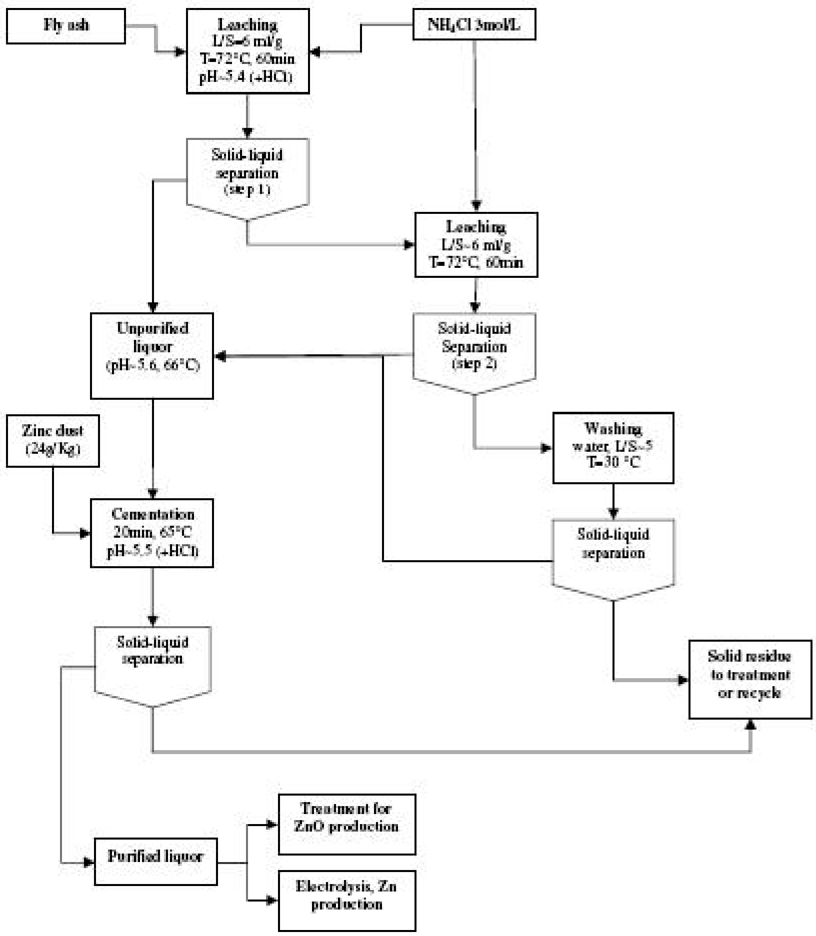

Figure 8: Flow sheet for zinc recovery

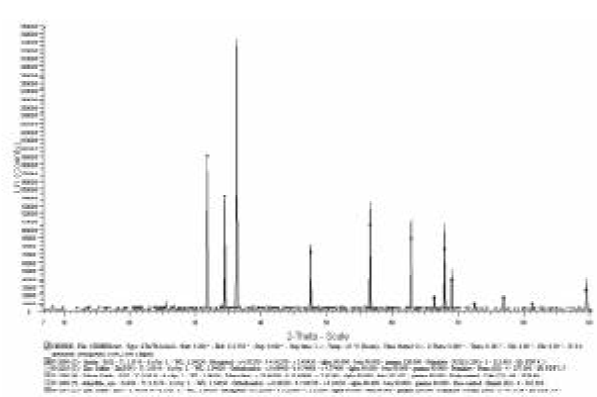

Figure 9: X-ray pattern of fly ash before treatment (■ = zinc oxide, ▼ = silicon oxide)

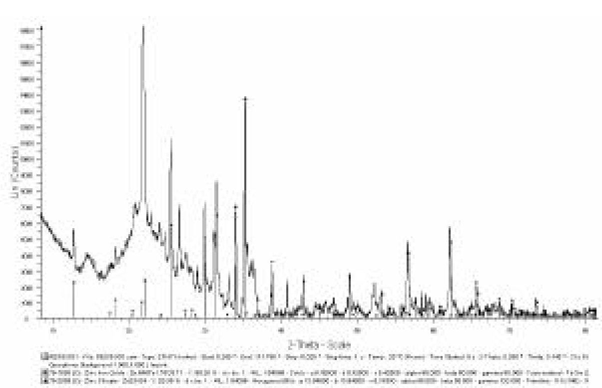

Figure 10: X-ray pattern of residue, after treatment (■ = ZnFe2O4, ♦ = Zn_2SiO_4)

Zn is present as Zinc ferrite. A remarkable quantity of Silica is also present.

CONCLUSIONS

The initial composition of the tire combustion ashes is characterized by high Zn quantity and very low percent of other toxic metals. From the ashes was possible to recover 98% of Zn reducing the ash to 15% of the original weight. After two leaching steps at acid controlled pH the solution contains ~45g/l of Zn , few tenth of ppm of some metals and traces of Mn, Fe, Pb, Cu, As, Sb, Se, Mo, Ni. From this solution Zn can be separated using electrolysis in cells without chlorine [9-11] production or alternatively precipitating it as Zn hydroxide. According to the chemical composition of the residual (TABLE 6) detoxification and solid waste disposal is possible; the zinc-ferrite in the residue is difficult to remove by further leaching. Alternatively it is possible to inactive and reduce the volume of the residuals by chemical stabilization using the WES-PHix®, ISWA 2003 process[12]. According to the results described in this paper the implement of a hydro metallurgic process aimed to Zn recovery from tire incineration ashes represents a suitable solution both from the economical and environmental point of view.

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