Zinc Recovery from Spent Chemical Sorbent by Dry Chlorination and Electrodeposition from Chloride Solutions

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Authors' contributions

This work was carried out in collaboration between all authors. Authors FJP and JMG performed the measurements. Authors GDM and JMG managed the literature searches and wrote the first draft of the manuscript. All authors revised the manuscript and participated in group discussions. All authors read and approved the final manuscript.

Original Research Article

ABSTRACT

Spent catalysts, chemical traps and sorbents are types of solid wastes generated worldwide, which contain potentially valuable or environmentally hazardous materials that need to be recovered before final deposition. Chlorination and electrolysis are unit processes applied in extractive metallurgy for metal extraction from poly-metallic or low-grade ores. The primary aim of this study was to assess the possibility of applying pyrometallurgy (chlorination) and electrometallurgy to spent chemical sorbents used as sulfur traps and to recover zinc. The spent sorbents may include zinc in different phases: ZnO, ZnS and $Zn_{0.65}Al_{0.35}(OH)_2(CO_3)_{0.167}(H2O)_{0.5}$. It was found that 96.8% of the zinc can be separated by dry chlorination at 475ºC with pure chlorine. Before chlorination, addition of $CaCO_3$ (17 wt.%) is necessary to prevent formation of $ZnSO_4$. The zinc chloride obtained is

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dissolved in water and electrolyzed to generate chlorine which can be recycled to the chlorination reactor, and metallic zinc as a non-adherent layer on the cathode. The electrolyte composition is 65 g.L^{-1} ZnCl$_2$ with 20 g.L^{-1} H$_3$BO$_3$ and 200 g.L^{-1} KCl. It is possible to recover pure zinc (99.9 wt.%) from chemical sorbents with the methodology proposed. These results are important for the development of new and more efficient recovery strategies to prevent environmental damage and obtain valuable elements from wastes.

1. INTRODUCTION

Accelerated population growth concentration in urban areas and the increase in industrial activity and consumption patterns all contribute to the serious problem of solid waste generation. Mishandling of this waste has direct impact on environmental degradation and deterioration of public health.

After usage, catalysts, chemical traps and sorbents from the petrochemical industry may contain absorbed hydrocarbons, coke, sulphur and metals such as V, Ni, Zn and Hg, among others. It is essential to recover valuable elements from these materials in order not only to lower catalyst costs but also to reduce solid waste and prevent environmental pollution.

Steam reforming of fossil resources such as natural gas (NG) is a common industrial practice to produce SYNGAS. NG must be pre-treated prior to its processing because sulphur (H$_2$S) is seriously poisonous to the reforming catalysts. A common treatment for sweetening NG is the use of reactive adsorption of sulphur in ZnO traps. After completion of the ZnO + H$_2$S → ZnS + H$_2$O conversion, the adsorbent can either be discarded or regenerated. The high content of S and Zn in the spent sorbent makes it a dangerous residue, so its S and Zn content must be reduced before final disposal. The zinc may be recycled for coatings, making use of its capacity to protect ferrous substrates against corrosion.

Several papers have been published on the recovery of zinc from different sources, including copper slag, flotation tailings, zinc oxide minerals and mine sludge, among others. Most of them used hydrometallurgical processes such as leaching and solvent extraction to recover zinc [1-8]. Selective reduction roasting and facilitated transport through bulk liquid membrane processes for zinc extraction have also been reported [9,10]. The extent of zinc recycling is about 6% of the primary metal, which indicates that there is still great scope for growth of the zinc recycling industry [11].

Few papers are available on zinc recovery from spent catalysts [12-14], and none of them apply dry chlorination for zinc separation. Alane et al. [13] propose an acid leaching methodology to recover zinc oxide and alumina from the catalysts, achieving a zinc recovery efficiency of 72.2%. Mohapatra et al. [14] studied a process of leaching in alkaline solutions in which over 92% of the Zn can be extracted from the spent catalyst. Hsu et al. [12] use carbon in presence of calcium carbonate at high temperatures (900 to 1100ºC) to extract zinc from spent catalysts. They analyzed the effect of different experimental parameters, such as temperature, sample height, apparent initial density, argon flow, Zn/C and Zn/CaCO$_3$ molar ratios and grain size of the coal, in the initial rate of zinc recovery and ultimate recovery of zinc. Maximum recovery was achieved at the highest temperature (1100ºC) and was about 90% after 2 hours' reaction.

Zinc coatings are of major industrial interest because they protect ferrous substrates against corrosion [15-17]. The most widely used coating process is the methodology known as hot dip galvanizing. Another approach is electrodeposition. Mendoza-Huzar et al. [18] conducted an interesting study of zinc electrodeposition from chloride solutions onto glassy carbon electrodes. Several factors such as zinc concentration [19], complexing agents [20], anions [21], acidity [22] and additives [23] play fundamental roles in zinc electrodeposition from chloride solutions. These factors may modify the texture and morphology of the electrodeposited zinc [24,25]. Although the literature includes several studies, the relation between the morphology of the deposits and their electrochemical parameters is still not clear [26]. There are many studies that have attempted to gain insight into nucleation and crystal growth processes [26-30] on which we have based this proposal.

The aim of this paper is to develop a process for recovering zinc from spent sorbents in order to convert a dangerous residue into a source of zinc. For this purpose, zinc recovery by dry chlorination and subsequent electrolysis of zinc chloride solutions was analyzed. The operational parameters were obtained for separating zinc as $ZnCl_2$ from the sorbents, and metallic zinc and chlorine by electro-deposition from $ZnCl_2$ solutions.

Our objective is to find the optimum Zn chlorination and electrolysis recovery conditions in order to recycle it to hot galvanizing processes at minimum cost and to recover chlorine from the zinc extraction process. Our interest is to achieve a non-adherent zinc deposit by electrolysis that will allow an ingot of recovered metal to be obtained.

2. EXPERIMENTAL DETAILS

The solids studied were: spent chemical sorbents of which the nominal composition according to the manufacturer (Sud-Chemie Company, Germany) was zinc oxide 85-95 wt.% and calcium aluminate 5 - 15 wt. % obtained from an industrial reactor for natural gas pre-treatment.

2.1 Zinc Separation by Dry Chlorination

To perform this study, the sorbent was mechanically ground to 400 mesh (ASTM, square aperture of 37 microns) in a grinding mill (Herzog Mill HSM100H).

The gases used were Ar 99.99% purity (Linde), N_2 99.99% purity (Linde) and Cl_2 99.8% purity (PRAXAIR), and the solid reactive was $CaCO_3$ from Sigma-Aldrich (99% ACS). The initial characterization of the sorbent was performed in a themogravimetric analyzer (TGA, TherMax400, Thermoscientifc) in an argon-oxygen atmosphere (3.2 L h^{-1} of Ar and 0.8 L h^{-1} of O_2), using 50 mg of sample mass and a heating rate of 5 C min^{-1}. For isothermal treatments, a muffle furnace was used, and 0.5 gr samples were placed in quartz crucibles and heated in still air.

The chlorination reactions [31] were carried out in a quartz reactor, which consists of a horizontally mounted tube of 30 mm diameter located inside an electric furnace, into which the sample was placed using a silica glass crucible. A flow of 2 L h^{-1} of pure chlorine and total reaction times of 3 and 5 hours were used. The total reaction times needed to complete the reactions at each temperature were estimated according to preliminary experiments. To end the reactions, the gas flow was switched to N_2 and the flow rate was increased. Before chlorination reactions, initial treatments were performed to some of the samples. In these treatments the sorbents were maintained at constant temperature (200, 500 and 850ºC, respectively) in air during 4 hours.

The gaseous chlorination products condensed in the cold zone of the reactor. For analysis, the products were collected from the reactor inside a glove box to prevent decomposition. To verify the reproducibility of the results, the experiments at one temperature were repeated and it was found that the variations obtained were in the order of the experimental scattering.

2.2 Zinc and Chlorine Recovery by Electrolysis

Condensed $ZnCl_2$ from dry chlorination reactions was recovered and dissolved in demineralised water (conductivity 0.055 mS cm^{-1}). In a first series of experiments, solutions were prepared at concentrations of 32.5; 65 and 130 g.L^{-1} $ZnCl_2$ to which 20 g.L^{-1} H_3BO_3 were added, following Mouanga et al. [32]. After determining the most suitable $ZnCl_2$ concentration for recovering the Zn, 200 g.L^{-1} KCl were added to improve chlorine yield and increase the zinc deposition rate. All solutions were electrolyzed at room temperature (25ºC). The electrochemical laboratory cell (Fig. 1) was a 500 cm^3 cylindrical glass vessel with a flat cup. A funnel and an inverted burette were used to collect and measure the chlorine gas generated at the anode. For the anode, a platinum wire 1 mm in diameter and 10 cm long was wound into a conical spiral and placed below the funnel. For the cathode, a rectangular 316 stainless steel plate 2 cm wide, 3.19 cm long and 0.13 cm thick was used.

The exposed surface area was polished to a mirror finish with alumina of different grades down to 0.05 µm and cleaned ultrasonically before the experiments. Each experiment was performed at a constant cell voltage of 4.5 V for 30 or 60 min. After the experiments, the volume of chlorine generated, and the weight and characteristics of the cathodic deposition were evaluated. The mean errors in the experimental measurement of the mass of Zn and volume of chlorine recovered in two experiments performed under the same conditions were less than 3% and 5%, respectively.
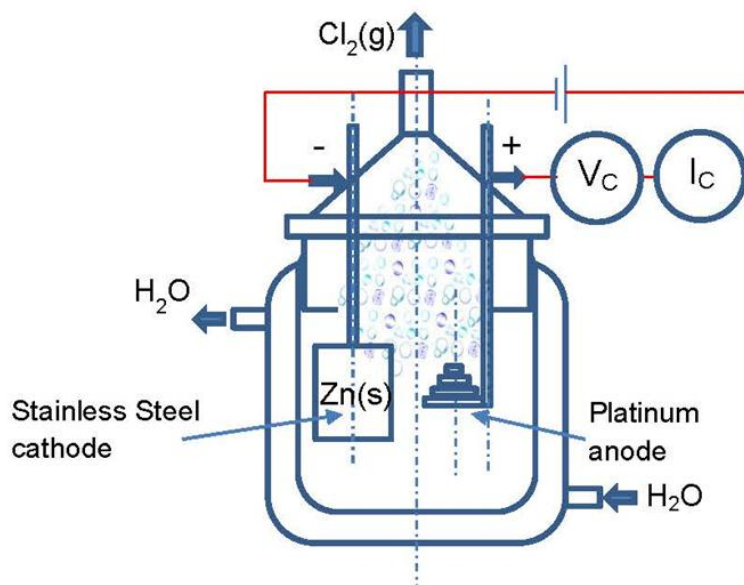
Fig. 1. Electrochemical laboratory cell

With these data, zinc and chlorine recovery performance was calculated according to the weight of the deposit obtained and the theoretical mass predicted by Faraday's Law, as:

$$W_{Zn,T} = \frac{I * t}{F} * \frac{M_{Zn}}{z_e} \qquad (1)$$

where $W_{Zn,T}$: theoretical value of Zn recovery in grams, g; I: constant current applied in Amperes, A; t: total time during which the constant current was applied in seconds, s; F: Faraday constant: 96485 A.s mol^{-1}; M_{Zn}: molar mass of Zn in grams per mole; z_e: valence number of Zn ions (electrons transferred per ion).

With the theoretical value of Zn recovery and the stoichiometric data, it is possible to calculate the theoretical amount of chlorine produced from decomposition of ZnCl$_2$.

$$ZnCl_2(aq) \rightarrow Zn(s) + Cl_2(g) \qquad (2)$$
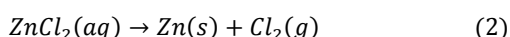
$$W_{Cl_2,T} = 1.0845 * W_{Zn,T} \qquad (3)$$

With both theoretical values and the real measured values, $W_{Zn;R}$ and $W_{Cl2;R}$, it is possible to obtain the yield of zinc and chlorine in the electrolysis. The $W_{Zn;R}$ is obtained directly by weighing the deposit. The $W_{Cl2;R}$ is calculated with the ideal Gas Law and measuring the volume of gas produced at known temperature and pressure.

$$W_{Cl_2,R} = n_{CL_2} * M_{CL_2} = \frac{P * V_{Cl_2} * M_{Cl_2}}{R * T}$$
$$= 2.9017 * 10^{-3} * V_{Cl_2} \qquad (4)$$

$$\eta_{Zn} = 100 * \frac{W_{Zn,R}}{W_{Zn,T}} \qquad (5)$$

$$\eta_{Cl_2} = 100 * \frac{W_{Cl_2,R}}{W_{Cl_2,T}} \qquad (6)$$

2.3 Product Characterization

The condensed products of the chlorination reactions and the recovered zinc deposits were characterized by scanning electron microscopy (SEM 515; Philips XL30 Electronics Instruments and SEM NanoNova 230, FEI) and X-ray powder diffraction with Bragg-Bretano geometry Ni-filtered and Cu K$_\alpha$ radiation (Bruker D8 Advance). The patterns were analyzed by Rietveld refinement of the powder XRD data using the Diffract Plus Topas 4.2 software. For the XRD measurements the following conditions were used: step size 0:02 and scan speed 1.5 seconds step^{-1}. The quality of the Rietveld fits was checked visually and against the values of the following parameters: weighed profile R-factor (R$_{wp}$), expected R factor (R$_{exp}$), Bragg's factor (R$_{Bragg}$) and Goodness of Fit indicator (GOF). It was considered a good fit when the GOF<2 and the R$_{parameters}$<5.

To determine the elemental composition of the condensed phases, they were dissolved in water

and analyzed by ion chromatography (Metrohm IC 850 Professional) and Atomic Absorption Spectrometry (Perkin Elmer Analysts 200).
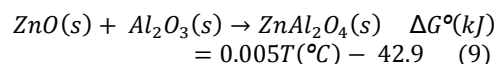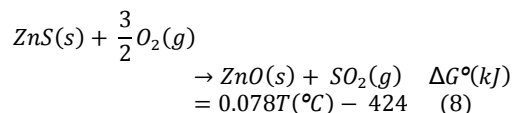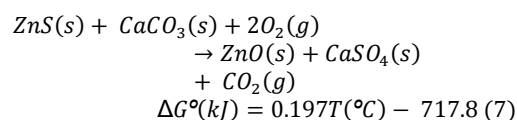
3. RESULTS AND DISCUSSION

3.1 Initial Characterization of the Sorbent

After use, the sorbent may contain other elements and substances such as sulphur, carbon and water, and the initial phases may change due to operational temperatures (about 500ºC), therefore an initial characterization was performed. Fig. 2 shows SEM images of the sorbent particles, with several particles of different sizes ranging from a few microns to about 50 microns in diameter. Fig. 2b shows in detail the surface of one particle, which consists of clusters of particles with irregular surfaces, and provides sample composition measured by EDS. The following phases where identified by XRD: ZnO, ZnS, SiO_2, Al_2O_3, $CaCO_3$ and $Zn_{0.65}Al_{0.35}(OH)_2(CO_3)_{0.167}(H_2O)_{0.5}$.

Thermal treatment in Ar/O_2: 80/20 was performed in a thermogravimetric analyzer. The sorbent was heated from room temperature to 900ºC at a heating rate of 5ºC s^{-1}, and mass change was registered every 1 second, as shown in Fig. 3. The curve shows a decrease in mass as temperature increases, providing evidence of formation of gaseous species. Isothermal treatments were performed in air for 4 hours at 200, 500, 600 and 850ºC, to identify the phases present at each temperature and understand the changes taking place in the catalyst during heating. The phase composition at the beginning (with no thermal treatment) and at each temperature was determined by Rietveld

refinement, also shown in Fig. 3. The initial mass loss corresponds to water released from the $Zn_{0.65}Al_{0.35}(OH)_2(CO_3)_{0.167}(H_2O)_{0.5}$ phase. At 200°C and 500ºC the residue contains zinc and aluminium oxides, zinc sulphide and calcium carbonate. At 650ºC disappearance of zinc sulphide and calcium carbonate, and formation of calcium sulphate and zinc aluminates is observed.

This can be understood considering the following reactions, which are thermodynamically feasible over the whole temperature range:

$$ZnS(s) + CaCO_3(s) + 2O_2(g)$$
$$\rightarrow ZnO(s) + CaSO_4(s)$$
$$+ CO_2(g)$$
$$\Delta G°(kJ) = 0.197T(°C) - 717.8 \quad (7)$$

$$ZnS(s) + \frac{3}{2}O_2(g)$$
$$\rightarrow ZnO(s) + SO_2(g) \quad \Delta G°(kJ)$$
$$= 0.078T(°C) - 424 \quad (8)$$

$$ZnO(s) + Al_2O_3(s) \rightarrow ZnAl_2O_4(s) \quad \Delta G°(kJ)$$
$$= 0.005T(°C) - 42.9 \quad (9)$$

The $CaCO_3$:ZnS ratio at 200°C and 500 ºC is 1:3 according to Rietvield refinement, so the reaction shown in equation 1 is expected to proceed until $CaCO_3$ has disappeared completely. Excess ZnS can subsequently react according to equation 2, leading to a mass loss which is in accordance with the TG measurement for temperatures above 500°C. Finally, at 650°C and 850ºC, the same phases were detected but at the higher temperature there is an increase in the amount of zinc aluminates with the corresponding decrease in zinc and aluminium oxides content, according to reaction shown in equation 3.
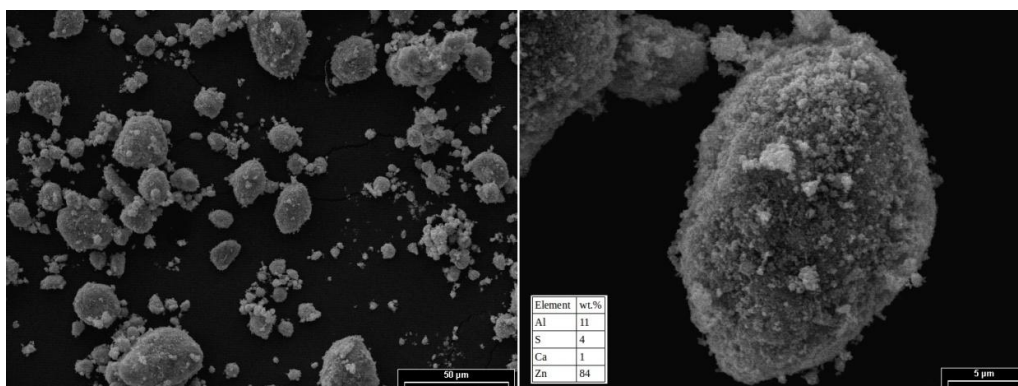

Element	wt.%
Al	11
S	4
Ca	1
Zn	84

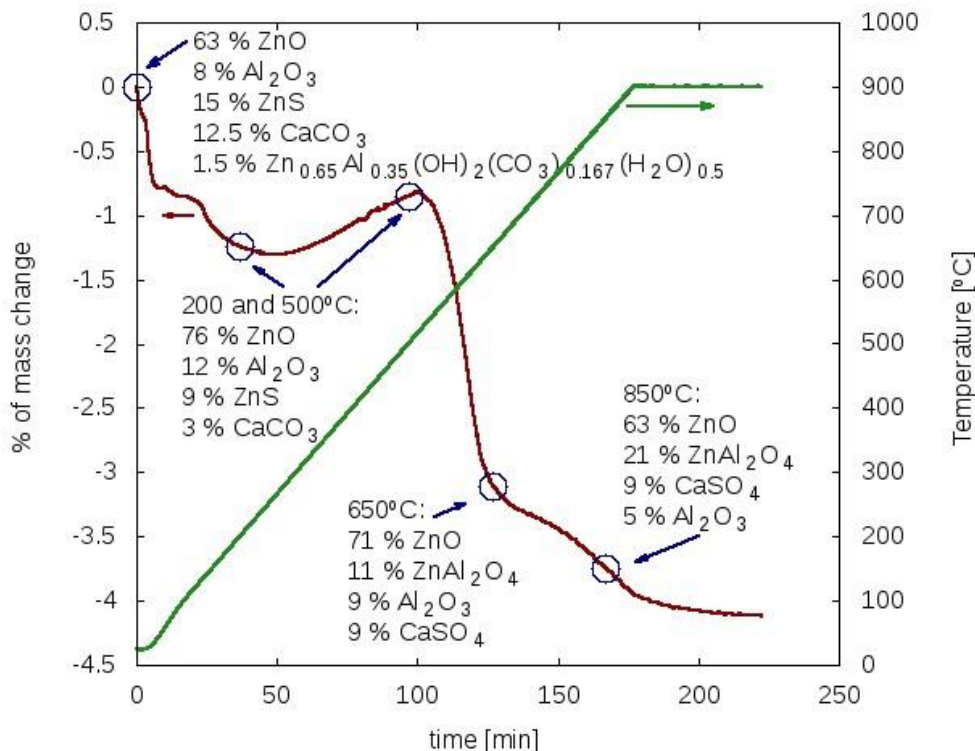**Fig. 2. Initial characterization of the sorbent**

Fig. 3. Non-isothermal treatment in air

3.2 Chlorination Reactions

Chlorination reactions of the sorbent with different thermal treatments were performed at 550ºC for 5 hours for the untreated sorbent and 3 hours for all the others. During the chlorination reactions, zinc separation takes place because it reacts with chlorine forming gaseous $ZnCl_2$, leaving the crucible and condensates in the cool region of the reactor. Table 1 shows the results of the different reactions.

These experiments show that $ZnAl_2O_4$ is formed during the chlorination reaction, because during the thermal treatment of the sorbent in air, it is formed only above 650ºC. The percentage of $ZnAl_2O_4$ formed is higher for the untreated sorbent because the chlorination was longer (5 hours) than for the sorbent treated at 200°C and 500ºC (3 hours). Its formation is not desired because the zinc contained in $ZnAl_2O_4$ does not react with chlorine and consequently cannot be separated and recovered. In subsequent experiments, the sorbent was treated at 200ºC where all the initial zinc was in the form of oxide or sulphide that reacts with chlorine. Zinc sulphates were also formed during the

chlorination reactions. Since zinc sulphate does not react with chlorine, it is also not desired. To prevent its appearance, $CaCO_3$ was added to the sorbent before chlorination to promote the reaction shown in equation 7. The results of the chlorination of mixtures of the sorbent treated at 200ºC and $CaCO_3$ are presented in Table 2. Two mixtures of sorbent + $CaCO_3$ were prepared with 8.5% and 17% wt. $CaCO_3$. The first row in Table 2 corresponds to the chlorination of the mixture containing 8.5% wt. showing that formation of $ZnSO_4$ still takes place; consequently in subsequent reactions (rows two to four) the mixture which has a higher amount of $CaCO_3$ was used. $ZnSO_4$ is absent from all these reactions, and the zinc that remains unreacted is that contained in $ZnAl_2O_4$ and in a small amount of ZnO. The amounts of $ZnAl_2O_4$ decrease slightly with decreasing temperature, even though formation rate is slow at lower temperatures, longer reaction times are required to achieve almost complete chlorination of zinc oxide, consequently the amount of $ZnAl_2O_4$ formed is almost constant. In all cases the condensed product was $ZnCl_2$, as determined by XRD. No calcium or aluminium content was detected by atomic absorption measurements.

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Table 1. Chlorination of catalysts with different thermal treatments at 550ºC for 3 and 5 hours

Chlorination	Initial treatment	Products and residues that remain in the crucible XRD - Quantitative analysis - Rietveld	Gaseous product
500ºC 5 hrs	No treat.	32.8% $ZnAl_2O_4$, 22% Al_2O_3, 19.5% $ZnSO_4$, 18.5% $CaSO_4$, 4.7% $Zn_3O(SO_4)_2$, 1.8% $ZnSO_4.H_2O$, 0.7% ZnO	$ZnCl_2$
550ºC 3 hrs	200 ºC	26% $ZnAl_2O_4$, 19% Al_2O_3, 18% $CaSO_4$, 15% $ZnSO_4$,	$ZnCl_2$[1]
	500 ºC	12% $ZnSO_4.H_2O$, 8% $Zn_3O(SO_4)_2$, 2% ZnO	$ZnCl_2$
	850 ºC	59% $ZnAl_2O_4$, 27% $CaSO_4$, 14% Al_2O_3	$ZnCl_2$[2]

[1] *Ca < 0.03 wt.%, Al < 0.1 wt.%*
[2] *Ca < 0.03 wt.%, Al < 0.02 wt.%*

Table 2. Chlorination of mixtures of sorbent treated at 200ºC and $CaCO_3$ at different temperatures

Temp ºC	time hs	wt. % $CaCO_3$	Products and residues that remain in the crucible XRD - Quantitative analysis - Rietveld
550	3	8.5	56% $CaSO_4$, 21% $ZnAl_2O_4$, 15% Al_2O_3, 8% $ZnSO_4$
500	5	17	76.4% $CaSO_4$, 13% $ZnAl_2O_4$, 10% Al_2O_3, 0.6% ZnO
475	7	17	78% $CaSO_4$, 11% Al_2O_3, 10.5% $ZnAl_2O_4$, 0.5% ZnO
450	8	17	80% $CaSO_4$, 10% $ZnAl_2O_4$, 9.4% Al_2O_3, 0.6% ZnO

In the reaction at 450ºC the presence of a hygroscopic phase in the reaction crucible and lower mass loss was observed. This can be understood considering that evaporation of $ZnCl_2$ is not complete at that temperature. Consequently, a temperature of 450ºC is not high enough to achieve the separation.

Finally, Table 3 compares the efficiency of different conditions as percentage of zinc recovered from the sorbent. It can be concluded that a reaction temperature of 475ºC and $CaCO_3$ content of 17 wt. % are the best conditions for zinc recovery.

**Table 3. Efficiency of different chlorination conditions**

Reaction temp. ºC	wt. % $CaCO_3$	% of Zinc recovered
475	17	96.8
550	8.5	94.6
550	-	89.1

## 3.3 Recovery of Zn and Cl_2 by Electrolysis

Electrolysis of the solutions of condensed $ZnCl_2$ after separation by dry chlorination allows recovery of Cl_2 at the Pt anode and Zn on the stainless steel cathode. Under the conditions set out in the experiments, the principal reactions that occur at each electrode are:

$$anode: 2Cl^- \rightarrow Cl_2(g) + 2e^- \qquad (10)$$

$$cathode: Zn^{2+} + 2e^- \rightarrow Zn(s) \qquad (11)$$
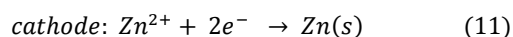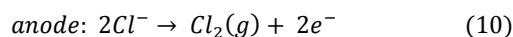
In addition to the main reactions which occur during the electrolysis of $ZnCl_2$, depending on the cell potential applied, secondary reactions may occur at the electrodes. At the cathode, the parallel reaction that competes with zinc deposition is the formation of H_2. The secondary reactions that can occur at each electrode are:

$$anode: 2OH^- \rightarrow O_2(g) + 2H^+ + 4e^- \qquad (12)$$

$$cathode: 2H^+ + 2e^- \rightarrow H_2(g) \qquad (13)$$
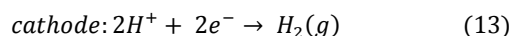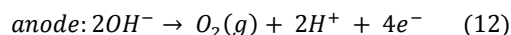
At the anode, oxygen formation competes with chlorine formation. In addition, when the concentration of Cl^- ions is low, the gaseous chlorine formed on the anodic surface can be disproportionate, according to the following reaction:

$$Cl_2(g) + H_2O(l) \rightarrow HClO(s) + Cl^- + H^+$$
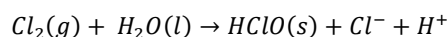
The evolution of this reaction can be verified by the yellowish green colour of the solution and the drop in pH to lower values. The disproportionate reaction can be controlled by increasing Cl^- ion concentration. However, care must be taken since the Zn^{2+} ions can interact with Cl^- ions forming metal-ion complexes, $ZnCl_4^{2-}$, whose stability constants are 100.96 at 25ºC. Therefore, strong interaction of Zn^{2+} ions with anions results

in larger overpotentials [33]. A high overpotential implies greater energy consumption.

Taking into account the above analysis, the first series of experiments were performed without addition of KCl and we were therefore able to determine the optimal $ZnCl_2$ concentration in the electrolyte solution. To increase the yield of chlorine formation, other experiments were performed with the addition of KCl. Table 4 shows the results of these experiments.

Maximum yield in zinc deposition with low chlorine recovery rate is obtained at an intermediate $ZnCl_2$ concentration of 65 g.L^{-1}. With the addition of KCl, the metal deposition rate increases significantly, producing a rough, powdery dendritic deposit and improving the recovery of chlorine. This would thus be the most adequate working condition evaluated. Table 4 further shows that by increasing the $ZnCl_2$ concentration in the electrolyte, the circulating current increases for the same cell voltage applied. This generates Zn layers that form and grow at different speeds.

The images of Table 4 show the deposits obtained under different electrolysis conditions. It is observed that as the concentration of Zn increases, the dendritic and disordered characteristics of the deposit increases, being more abundant in the edges for low concentrations of Zn, corresponding to zones of higher current density, and spreading throughout the surface when the concentration of Zn increases. In the particular case of electrolysis with KCl aggregate, a completely irregular and porous deposit of low adhesion is observed, which can easily be detached from the support cathode. This confirms a high deposition rate of the Zn, maintaining high electrical performance.

To further analyze these deposits, their morphology and microscopic structure were observed by Scanning Electron Microscopy (SEM). Fig. 4 shows the morphology of the deposit obtained with the electrolyte with the lowest $ZnCl_2$ concentration, 32 g.L^{-1}. As the reaction of Zn deposition is controlled by mass transfer, when the concentration is low, the rate of deposition is also low. The coatings obtained consisted of thin stacked platelets of hexagonal crystals. Fig. 5 shows the deposit obtained with the electrolyte of medium concentration, 65 g.L^{-1} − a perpendicular growth of the hexagonal crystals and the formation of corns or arrangements in the form of fine grouped fibres,

as well as small dendrites on the deposit. Fig. 6 shows the clear dendritic growth detected in the deposits obtained by electrolysis of the most concentrated solution, 130 g.L^{-1}, with thinner, more plentiful fibres,

If we look at the images of the Zn deposits as the scale decreases and we compare the three Figures we can see the increase in layer density and roughness as the concentration of the cation in solution increases. When the cathodic reduction is carried out at a low speed, a less rugged deposit is obtained and more adhered to the surface, which then makes it difficult to remove the recovered metal. For the 2 nm scale, Fig. 4 shows the growth of plated plates at low deposition speeds of average thickness of 250 Å. Fig. 5 already shows the formation of branched structures with a mean diameter of 150 Å. for an intermediate deposition rate and significant porosity growth, with a more spongy deposit. Fig. 6 shows very branched fibres with a mean diameter of 50 Å and greater abundance of voids, for the deposit obtained with the highest current density.

The two-step methodology proposed can be successfully applied to recover zinc from spent chemical sorbents. A flow sheet of the zinc recovery methodology is presented in Fig. 7.

The preliminary chlorination and electrolysis experiments confirm that the recovery of Zn and the recycling of chlorine are viable operations to carry out on an industrial scale. One possibility would be to use a high alumina refractory-lined reactor in order to withstand the chlorination conditions of 475°C and chlorine atmosphere, and a rotating cylinder electrochemical reactor, as in Grau et al. [33], which works continuously at constant $ZnCl_2$ concentration with continuous recovery of solid zinc and chlorine gas. The addition of KCl increases the zinc deposition rate and chlorine yield, improving the process. In the scaled-up chlorination process a caustic scrubber system should also be considered to scrub unreacted chlorine gas and uncondensed $ZnCl_2$ gas.

The process studied herein may have a direct application for zinc coating production using the method of zinc electrodeposition from chloride solutions proposed by Mendoza-Huzar et al. [18]. It would be useful to develop an economic cost-benefit balance in order to make further progress in the development of the proposed methodology.

Table 4. Electrolysis of ZnCl₂ solutions of different concentrations

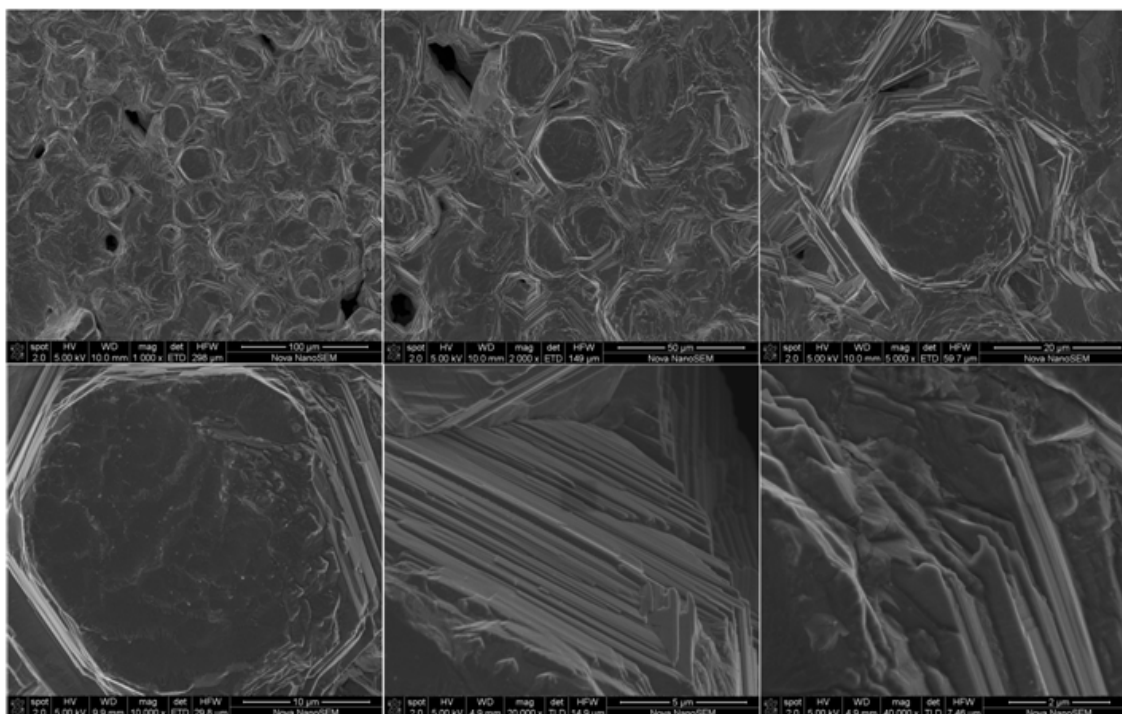| Experiment	1	2	3	4
$ZnCl_2$, g.L^{-1}	32.5	65	130	65
H_3BO_3, g.L^{-1}	20	20	20	20
KCl, g.L^{-1}	-	-	-	200
pH at t=0	4.27	4.35	4.42	5.57
pH at t=TOS	1.92	2.13	2.08	3.72
V_{Cell}, V	4.5	4.5	4.5	4.5
I, A	0.368	0.519	0.689	2.240
j, mA.cm^{-2}	28.9	40.7	54.0	175.5
TOS, min	60	60	60	30
V_{Cl2}, cm 3	16.5±0.8	24.0±1.2	28.2±1.4	124.5±6.2
W_{Zn}, g	0.355±0.007	0.594±0.012	0.710±0.014	1.295±0.026
η_{Zn}, %	79.1	93.8	84.5	94.8
η_{Cl2}, %	10.7	11.1	9.8	24.4
View of the cathode after electrolysis				

Fig. 4. Images of Zn electrodeposited under potentiostatic conditions V_C=4.5 V with an electrolyte with 32.5 g.L⁻¹ ZnCl₂ and 20 g.L⁻¹ H₃BO₃ (pH 4.5) system
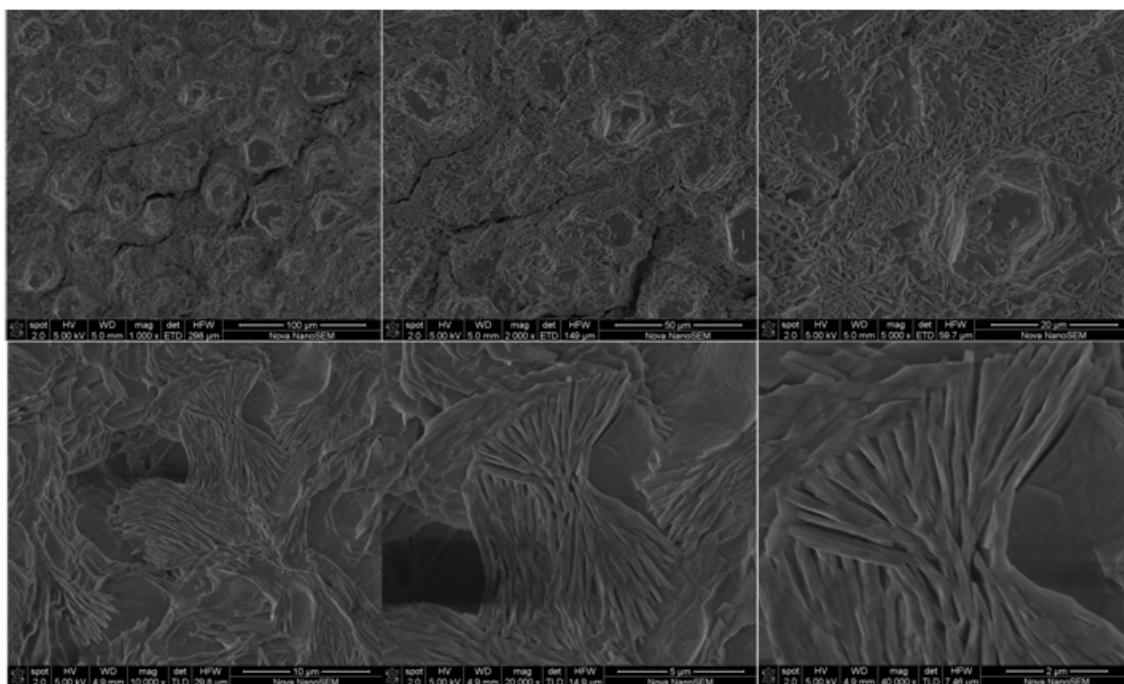
Fig. 5. SEM images of Zn electrodeposited under potentiostatic conditions V_C =4.5 V with an electrolyte with 65 g.L^{-1} ZnCl$_2$ and 20 g.L^{-1} H$_3$BO$_3$ (pH 4.5) system
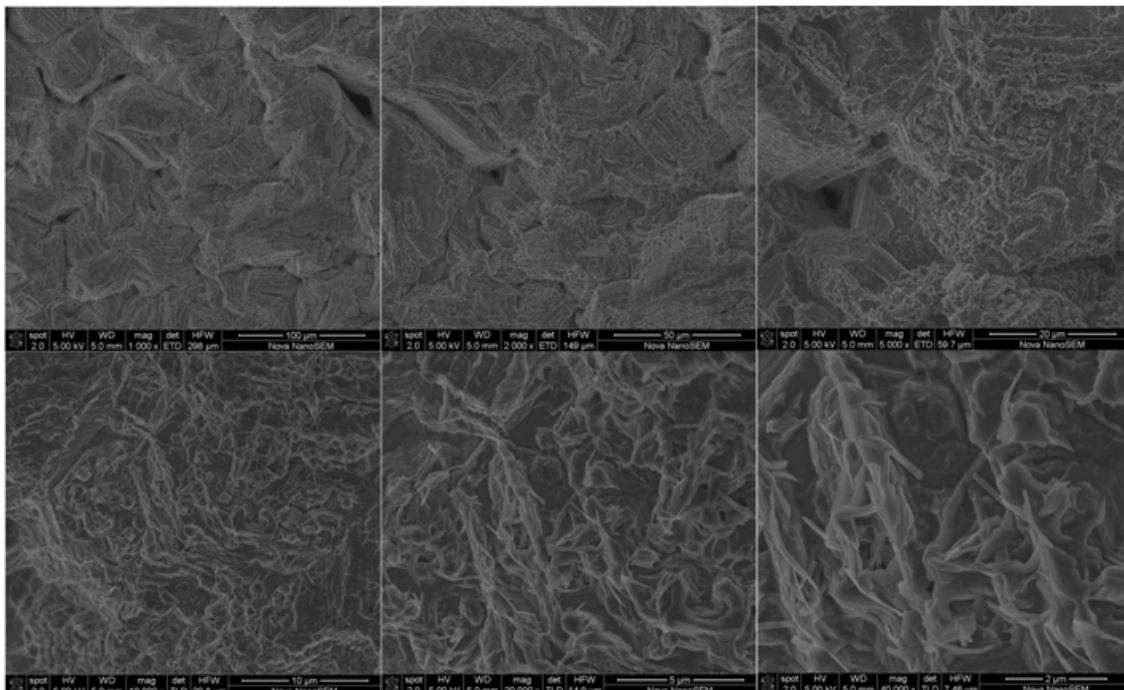

Fig. 6. SEM images of Zn electrodeposited under potentiostatic conditions V_C=4.5 V with an electrolyte with 130 g.L^{-1} ZnCl$_2$ and 20 g.L^{-1} H$_3$BO$_3$ (pH 4.5) system
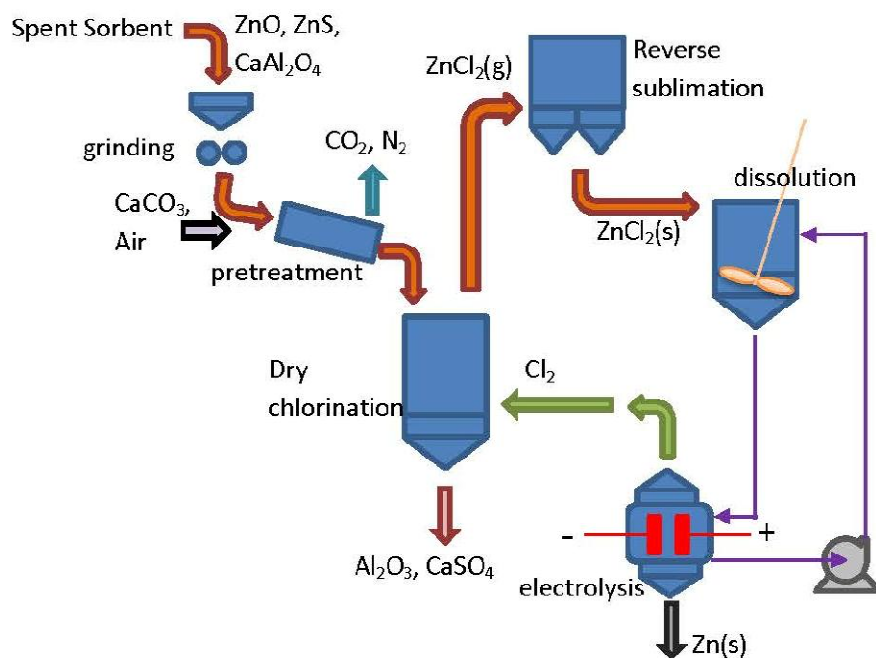
Fig. 7. Flow sheet of the zinc recovery methodology

4. CONCLUSION

It is possible to recycle zinc from spent chemical sorbents applying a two-step methodology of dry chlorination and electrochemical recovery. For the chlorination step a temperature of 475°C in a pure chlorine atmosphere, and a $CaCO_3$ content of 17 wt.% are the best conditions for zinc recovery as $ZnCl_2$. Addition of $CaCO_3$ promotes formation of $CaSO_4$ with the sulphur contained in the residue and prevents $ZnSO_4$ occurrence.

For the electrolysis step the best electrolyte composition analyzed was 65 g.L^{-1} $ZnCl_2$ with 20 g.L^{-1} H_3BO_3 and 200 g.L^{-1} KCl. Operating in a single batch electrochemical reactor the most suitable electrolysis conditions found were: cell voltage 4.5 V, current density 175.5 mA.cm^{-2} on a stainless steel cathodic surface with a platinum anodic surface. Under the conditions proposed, Zn recovery yield was 96.8%, the purity of the zinc obtained was 99.9 wt.% and Cl_2 recovery yield was 24.4%. The Zn is deposited in a non-adherent form and can be easily removed from the cathodic surface.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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