

FROM C.Z.O. TO ZINC CATHODE WITHOUT ANY PRE-TREATMENT. THE EZINEX PROCESS

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Abstract

The zinc recycling is assuming more and more importance. A lot of zinc secondaries and wastes are ready to be collected and converted to zinc metal. The impurities present in these materials and the technical and economical problems that some traditional ways of treating these materials are facing, call for new technologies.

The EZINEX Process, a fully hydrometallurgical process industrially proven to convert oxidised zinc bearing materials directly to zinc cathodes, is an innovative process that can deal with any kind of zinc waste/secondaries in a very powerful way.

In this paper the highlights of this process will be shown and discussed to demonstrate the robustness of the process and its economic viability.

1. Introduction

Zinc is a very important metal widely diffused in the manufactured products used every day. The zinc market, and in particular the zinc galvanising market, has grown significantly in the last years and the trend for the next years seems to confirm this growing. For these reasons, zinc has to be considered a very attractive commodity with a good potential market.

Zinc is contained in numerous wastes and secondary raw materials that can be considered high zinc concentration mines easily exploitable. However only a part of these materials are processed while most of them are landfilled with or without previous stabilisation processes. In the last years some processes, mainly pyrometallurgical, were developed to convert zinc in crude zinc oxide (C.Z.O.). The zinc bearing materials are usually submitted to a thermal treatment [1] in which the zinc is vaporised and re-oxidised producing crude zinc oxide (C.Z.O.) containing also quite high concentrations of heavy metals and halides. The C.Z.O. has to be then transformed in zinc metal and, until now, it is used in two main processes: the sulphate system leaching and electrowinning and the ISP. ISP is facing a crisis because of technical and economical reasons that led to the shutting down of most of the existing plants. In any case, before being fed to these processes, the C.Z.O. has to be treated to eliminate or reduce the content of impurities, in particular halides, which are noxious to these processes.

Many potential crude zinc oxides sources, such as electric arc furnace (EAF) dust, galvanising ashes, brass foundry and converters fumes, usually contain chlorides, fluorides and alkali metals that will be found in the produced crude zinc oxide including the Waelz oxide [2]. Two of the possible uses of the crude zinc oxides are the zinc

sulphate E.W. and the ISP (Imperial Smelting Process). The chlorides fed in the zinc sulphate E.W. lead to anodic chlorine evolution causing labour health problems and increase the anode corrosion rate, compromising the zinc quality. The fluorides, even at very low concentration (some hundreds of ppb), heavily compromise the cathode stripping. The halides content causes problems to the ISP too because of the problems induced to the condenser.

In the last years some treatment for C.Z.O. were studied and installed. The proposed processes are based on a water (or Na_2CO_3 solution) wash that are showing some problems. For these reasons, a zinc recovery based on a chloride system, to produce metallic Zn, would therefore be appreciated [3,4,5].

A couple of Zn chloride E.W. had been operated at the beginning of this century in U.K. and Germany [6], but, the technical problems related to chlorine evolution, anode corrosion, diaphragm materials and the emerging of the sulphuric E.W. led to the shut-down of these two plants.

The Zn chloride E.W. was intensively studied because of the high conductivity of the electrolyte and the lower anodic voltage (Cl_2 instead of O_2) resulting in an energy saving if compared to the sulphuric E.W [7].

The major drawback in the zinc chloride E.W. is the Cl_2 anodic evolution instead of O_2 [8,9]. This problem has been overcome introducing a cationic permselective membrane using H_2SO_4 in the anodic compartment obtaining O_2 evolution at the anode. This conceptually elegant solution allows to work with the chloride solution coming out of a leaching of the above mentioned materials even if some technical problems have not yet been overcome.

At the beginning of nineties, Engitec developed first the EZINEX and then the INDUTEC Processes [10] to treat zinc bearing materials, mainly EAF dust. In 1993 an pilot plant producing 500 t/y zinc from EAF dust was erected and operated. After one year operation, an industrial plant producing 2000 t/y of zinc cathodes was designed and then it was erected and operated. During the plant operation, a thermal pilot plant for the conversion of zinc bearing materials to C.Z.O. was built and operated as well.

INDUTEC is the thermal process, based on an induction furnace, capable of producing C.Z.O. from zinc bearing materials and EZINEX [11] is the hydrometallurgical process, based on an NH_4Cl electrolyte, producing metallic zinc directly from C.Z.O. The first industrial scale EZINEX plant [12] was designed to produce zinc directly from EAF dust. In this plant some C.Z.O. was also tested as a feed, instead of EAFD, with very good results. These tests oriented Engitec to a new approach: the EZINEX Process was considered the perfect terminal for the direct treatment of C.Z.O., because it is insensitive to the impurities that are critical for the other processes. Besides, feeding C.Z.O., the most problematic operations of the EZINEX Process were simplified.

The life cycle for zinc is schematised in the block diagram shown in Figure 1. The introduction of the EZINEX Process will simplify this cycle.

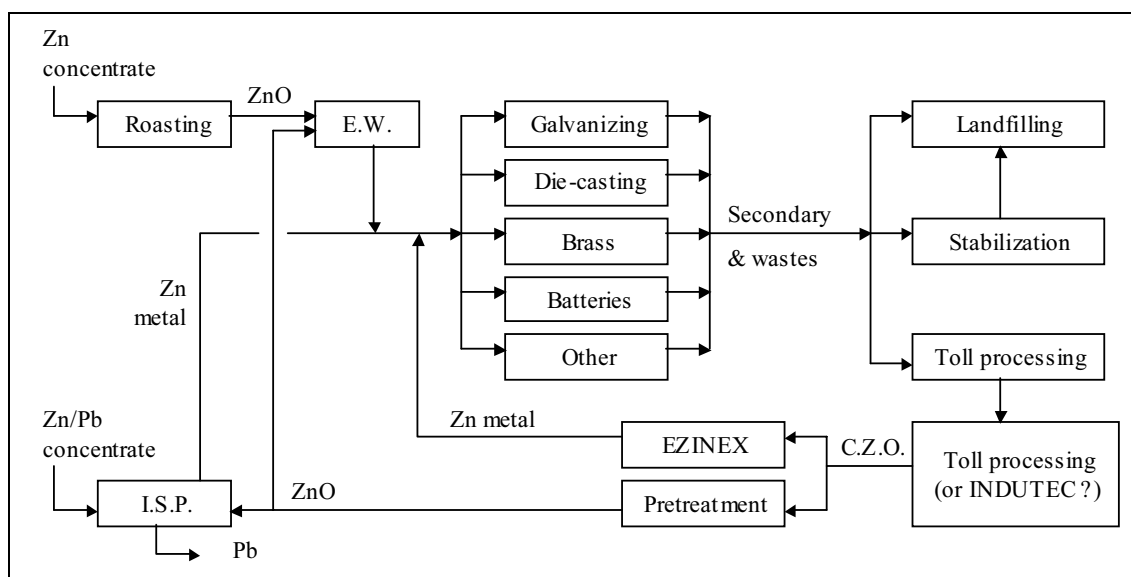


Figure 1: Zn life cycling – Block flow diagram

In this paper we would like to describe in details the EZINEX Process features to outline its big potential in the treatment of secondary bearing zinc materials

2. The EZINEX Process

The EZINEX Process, schematised in Figure 2, is a chloride based leaching and electrowinning system which can deal with materials based on oxidised zinc and consists of five main operations:

- Leaching of Zn bearing materials
- Solution purification
- Zinc electrowinning
- Evaporation/crystallisation unit
- Control of the build up of elements less noble than zinc (Carbonation)

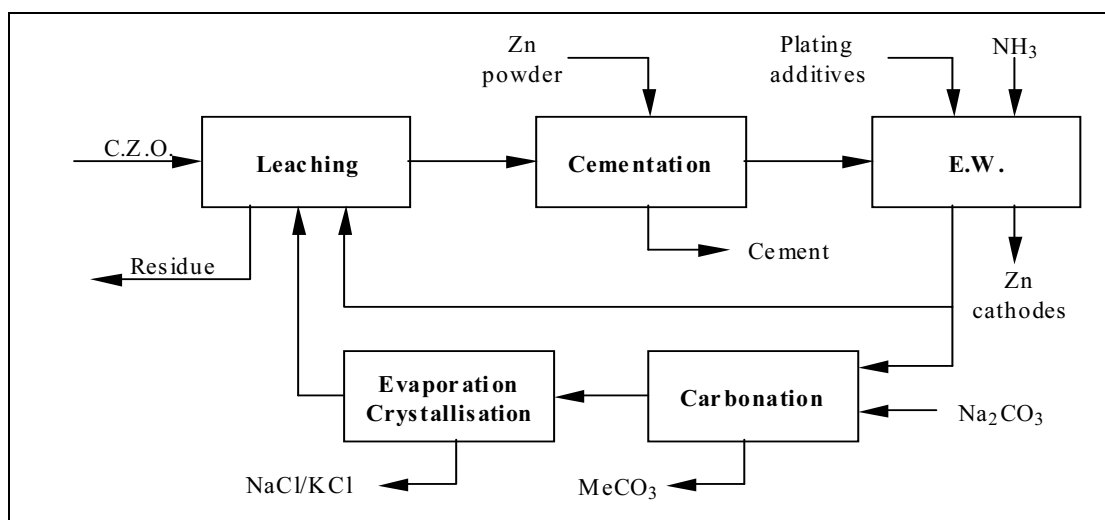
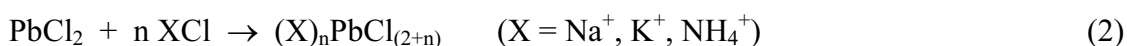
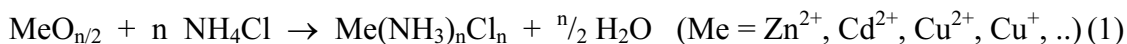


Figure 2: The EZINEX Process – Block diagram

The technical aspects relevant as well as a fast description of each one of these operations is going to be given here below.

2.1 Leaching

The leaching system is a neutral pH solution of alkali and alkaline-earth chlorides containing quite high concentrations of ammonium chloride. In the leaching reactor Zn and the other heavy metals contained are dissolved together with alkaline chlorides and part of alkaline earth salts according to the following reactions:



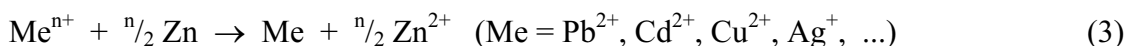
Practically all the contained zinc is leached. Only the zinc ferrite, coming from gas carryover, is not leached.

The leaching is run at a relatively high temperature (75 °C) because of the relatively low solubility of zinc amino chloride and it is a very fast operation. The big advantage of this neutral leaching is that iron is practically not extracted.

The leaching residue is recycled back to the thermal system generating the C.Z.O.

2.2 Solution purification

The most problematic impurities for the E.W. are the metals more noble than Zn that could be co-deposited together with Zn into the cathode. This operation is run adding some zinc powder or granules that causes the removal of such impurities because of the following cementation or displacement reaction:



The chemical Zn dissolution is kinetically very slow at the operative pH and so it is not a serious competitive reaction for the cementation. To achieve complete removal of all the impurities optimising the zinc powder consumption, particular care has to be taken in designing this unit. This operation, of course, will influence the final quality of the deposited zinc. We saw that that the higher is the required Zn cathode purity, the higher is number of cementation stages. A multistage can also be useful if some notable quantities of valuable metals, such as Ag and Cu, are contained in the treated C.Z.O.

The purified solution resulting from this operation is ready to be fed in the E.W. unit.

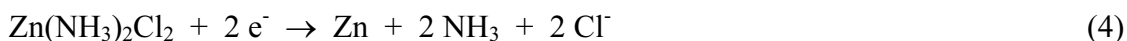
2.3 Zinc electrowinning

The EZINEX E.W. unit is the real core of this process. As already said, one of the problems of conventional chloride E.W. is the anodic evolution of chlorine that requires a complicated cell design and a particular care in its handling.

The EZINEX E.W. occurs in a conventional open cell with permanent titanium blank cathodes and graphite anodes. The electrolysis, for the zinc solubility problems, has to

be run at high temperature too (70 – 75 °C) and assisted by an air sparging system that optimises the diffusion rate to a point that the electrolysis can be run at relatively high current densities (300 A/m²) even with relatively low zinc concentrations (5 g/l).

At the titanium cathode, the zinc deposition occurs according to the following reaction:



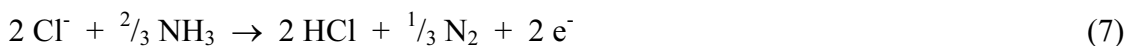
At the graphite anode the chemistry is a little bit complicated because there is an electrochemical reaction



followed by the very fast chemical reaction:



that takes to the following overall anodic reaction



The pH of the electrolyte has to be maintained in the range of 5,8 - 6,5 to avoid the formation of chloroamine. This is achieved by addition of ammonia solution and this operation is very easy because the solution is buffered by the zinc-amino complexes. Ammonia, consumed by the chemical reaction, has to be added to the electrolyte loop. The overall cell reaction, obtained summing the reactions (4) and (7), is the following:



The Zn concentration in cell is in the range of 10 - 20 g/l and the current density in the range of 300 - 400 A/m² affecting the deposition time that is in the range of 24 - 48 hours.

On the cathode, the competition of cathodic H₂ evolution is practically absent. In fact the cathodic current efficiency is in the range of 94 - 98 % and the co-deposition of other metals having a low hydrogen overvoltage is not so dramatic as in the case of the sulphuric Zn E.W.

Compared to the sulphuric E.W. the cell voltage is lower and this means a lower energy consumption. This energy saving is partially compensated by the ammonia consumption. The ammonia, eventually released in the plant, is scrubbed and recycled back to the process.

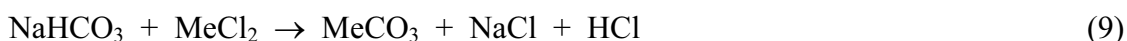
2.4 Evaporation/crystallisation

The impurities usually building up in this system are essentially alkali chlorides and fluorides, calcium and magnesium. They can slightly modify the electrolyte conductivity but, in any case, they have to be removed to avoid unwanted crystallisation somewhere in the plant.

The alkali chlorides can be crystallised obtaining two benefits: the elimination of alkaline chlorides from the electrolyte and the evaporation of the water fed to the plant with reactants make-up and electrochemical additives. The mother liquor, containing zinc-amino complex and ammonium chloride, is recycled back to the plant.

2.5 Carbonation

As already said, calcium and magnesium tends to build up in solution and, specially calcium, are problematic for the zinc deposition because they probably interfere with the zinc migration to the cathodic surface. To avoid this problem as well as unwanted crystallisation, Ca and Mg are precipitated by Na₂CO₃/NaHCO₃ addition according to the reactions:



Ca can also have a control on fluorides in solution, during the leaching, through the following reaction:



3. The Electrolytic unit

After this short presentation of the whole process we would like to spend some words about the electrochemical cell [13] that is the real novelty.

The industrial cell is an undivided cell with 33 titanium cathodes (5 mm thick having a surface of 2.13 m²) and 34 graphite anodes (40 mm thick having a surface of 1.96 m²). The electrode gap is 40 mm and an air sparging system is also provided.

The tank house installed at the Ferriere Nord facility was the first industrial application in the world of the zinc aminochloride electrolysis for the production of zinc cathodes as alternative to the traditional zinc sulphate electrolyte. During more than two years of operations, the system was subject to many changes in the operating parameters like cell temperature, zinc content in the electrolyte, current density, and impurity loading in the solution. The reliability of the process was good also in extreme conditions of operation (cell temperature up to 80°C, zinc concentration as low as 5 g/l, impure electrolyte with total impurity up to 500 mg/l!). Also in these unfavourable conditions, the current efficiency was affected only by shortage between cathodes and anodes, due to accidental misalignment of the electrodes, or to premature detachment of the zinc deposit, induced by an excessive cell temperature (> 75°C). In case of high contamination of the electrolyte caused by poor purification, the current yield was not affected even in presence of elements like Sb, Ni, ecc. that are poisons in acidic sulphate electrolyte. The only consequence was the co-deposition of those metals together with zinc lowering the quality of the produced cathodes. In the zinc aminochloride electrolysis the operating pH of the cell is around 6. In this conditions

the hydrogen competition is practically impossible also in presence of elements that normally lower the hydrogen overvoltage and do not allow the zinc deposition.

In the following figures the cathodic (Figure 3) and the anodic (Figure 4) polarisation curves for the EZINEX Process are shown.

In Figure 3 we can see that, at the operating current density of 300 A/m^2 , the difference between the hydrogen evolution and the zinc deposition potential is, at least, 250 mV and that 5 g/l of zinc are enough to support the electrolysis up to 500 A/m^2 . This last issue was fully demonstrated during the plant operation.

In Figure 4 we can see that the anodic potential is practically not affected by the addition of ammonia/ammonium salts. There is only a small depolarisation. This probably means that the anodic reaction is not changing but probably the rate determining step is changed influenced by the chemical reaction.

In figure 5 the splitting of the cell voltage is given taking advantage of some measurements run on the cell of the industrial plant.

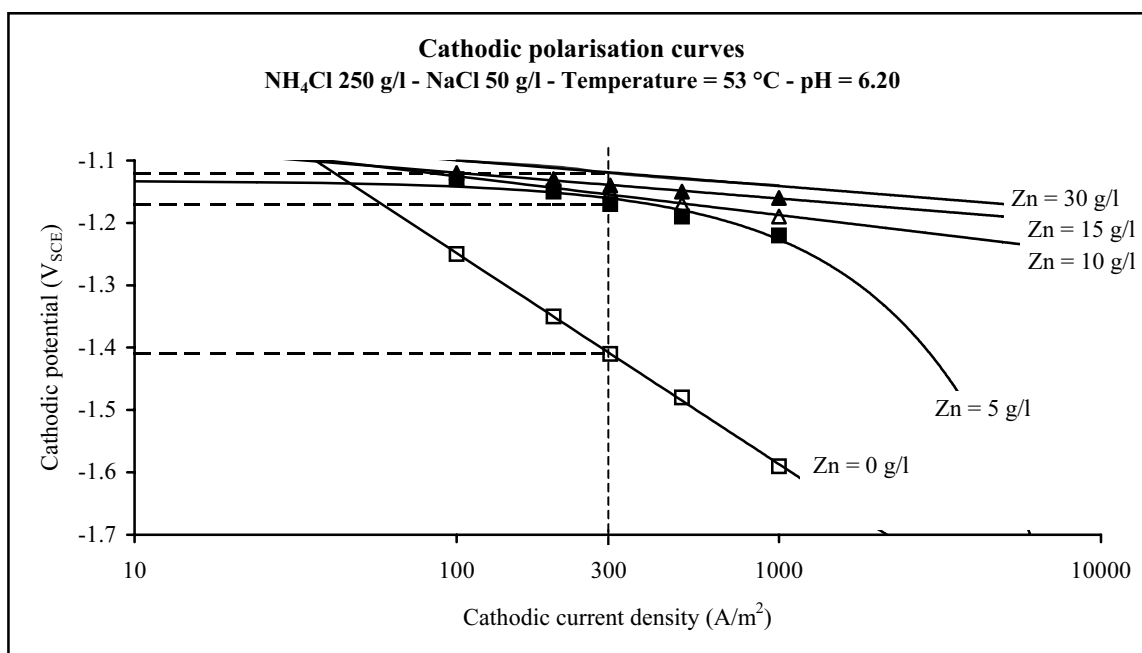


Figure 3: Cathodic polarization curves

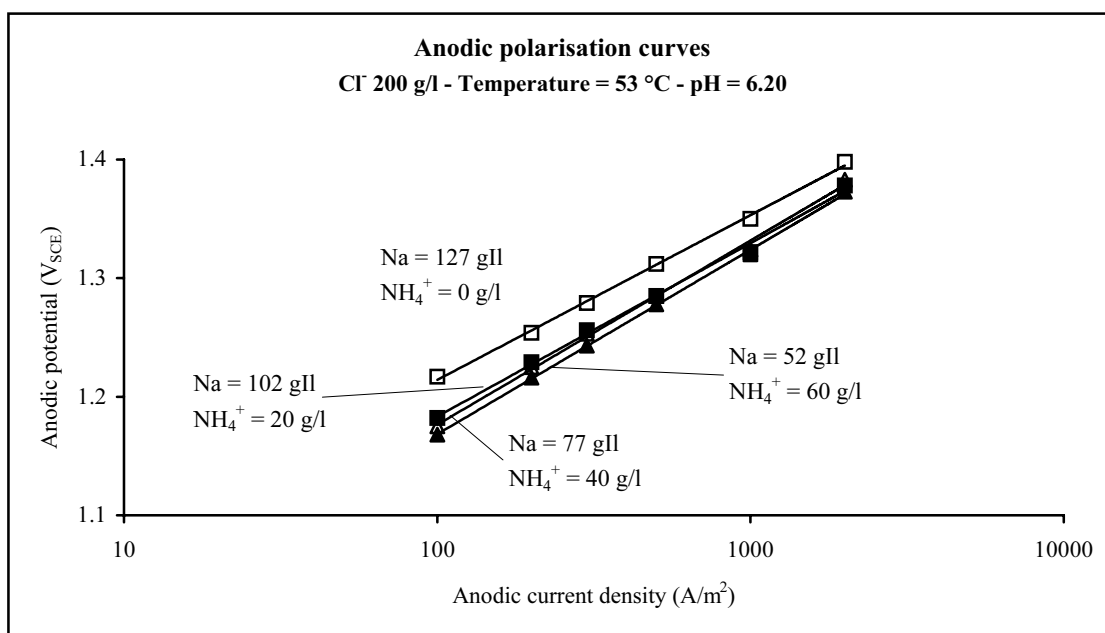


Figure 4: Anodic polarization curves

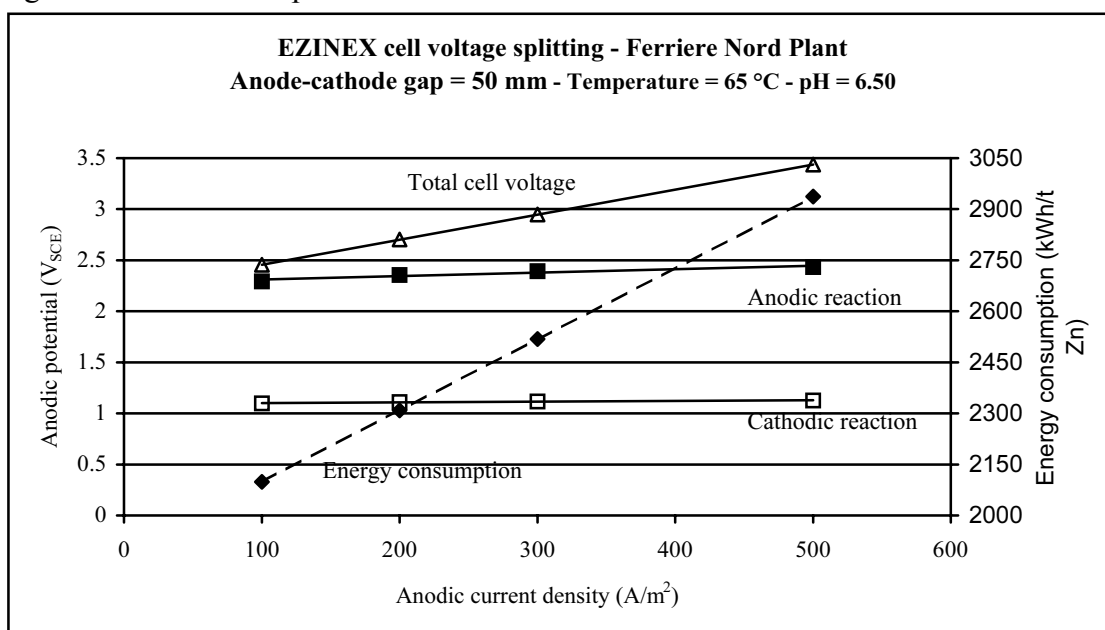


Figure 5: Cell voltage splitting of the EZINEX cell

More than two years operation of the industrial plant can be summarised by the following average figures:

- Current density 310 A/m²
- Cell voltage 2.9 V
- Zinc in electrolyte 11.8 g/l
- Temperature of electrolyte 69 °C
- Current efficiency 93 %
- DC energy consumption 2560 kWh/t zinc
- Air sparging 60 m³/h.cell

- Electrolyte circulation 10 m³/h.cell
- Zinc deposition time 48 h

Some tests were run trying to depolarise the anodic reaction. A lot of reactants were tested but the most interesting results were obtained with the other halogen ions as bromides and iodides.

These ions behave in the same way of chlorides. In fact they undergo the same anodic reactions:



causing a high decreasing of the anodic potential. The confirmation of it is shown in the graph in Figure 6 and, in particular the iodide is better than bromide.

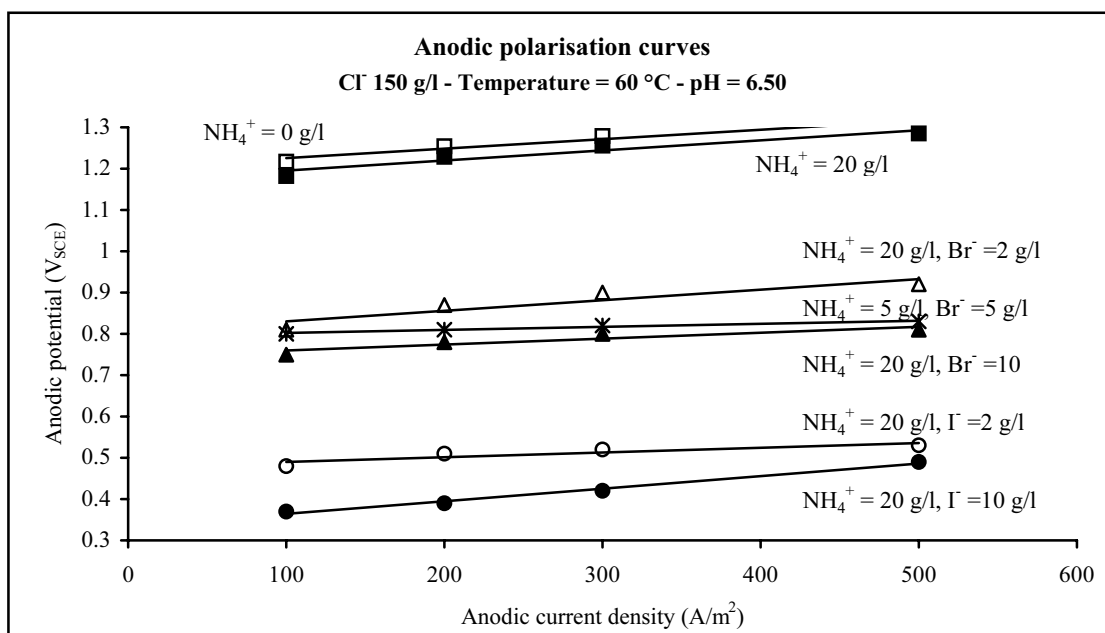


Figure 6: Anodic depolarisation with halogen ions

The chemical reaction for Br₂ reduction:



seems to work as fast as the one of chloride reduction regenerating the bromide reactant..

The case of iodide is very attractive because of the possible big energy saving, but the iodide produced is very little soluble and for this reason the chemical reduction reaction:



is very slow and not in line with the requirements of this process. In fact we see some black particles produced at the anode that take time to be dissolved. For this reasons the only possible depolarisation can be achieved by addition of bromides and it requires a very little amount of reactant

4. EZINEX vs sulphate E.W.

The electrochemical unit is very easy to operate avoiding the problems that traditional sulphuric E.W. have:

- Sensitivity to chlorides
The presence of chlorides in sulphuric E.W. causes the Cl_2 evolution inducing anode corrosion and consequently:
 - The anode release to solution, because of the corrosion, some solid particles that can be incorporated into the cathodic deposit
 - The anode maintenance is highly increased
- Sensitivity to fluorides
The presence of fluorides, even at very low concentration, makes very difficult the stripping of the zinc cathodes from the aluminium blank. In most of cases the only solution is the chemical leaching of the plated zinc to make available again the aluminium blank.
- Sensitivity to metallic impurities
The presence, even at very low concentrations, of some metallic impurities can cause the reduction of H_2 overvoltage and consequently
 - H_2 evolution can become the only cathodic reaction creating hazardous conditions in the plant
 - Lack of production
 - Nasty and long electrolyte purification process
- Mist formation causing some work environment problems
- High anodic overvoltage due to the O_2 evolution reaction

The EZINEX electrolysis, analysing the same problems, gives the following results:

- It is not sensitive to chlorides
The EZINEX electrolysis because it is based on a chloride system
- It is not sensitive to fluorides
The presence of Ca in the C.Z.O. is useful, as already said, to keep under control the fluoride presence that, in any case, is not so problematic for titanium blanks as it is for the aluminium ones.
- It is not sensitive to metallic impurities
Even in presence of some metallic impurities having a low H_2 overvoltage, working at neutral, the H_2 evolution potential is far enough to avoid H_2 evolution
- The cell is designed with a system sucking the gas leaving the cell recycling part of it to the air sparging system and bleeding the excess gas to a scrubber
- The cell voltage is lower that the one of sulphuric E.W. but part of this saving is compensated by ammonia consumption

5. Potentiality of the EZINEX Process

Coupling the EZINEX Process with any kind of fuming process producing C.Z.O. we have a very powerful system to deal with a lot of wastes and/or secondaries in a very simple flowsheet. In Figure 7 is shown as an example for a conceptual flowsheet of a plant, based on the Engitec's INDUTEC thermal process [14], processing some different materials coming from different industries. Most of these materials are very difficult to be processed and/or to be wasted and their treatment is in any case very expensive.

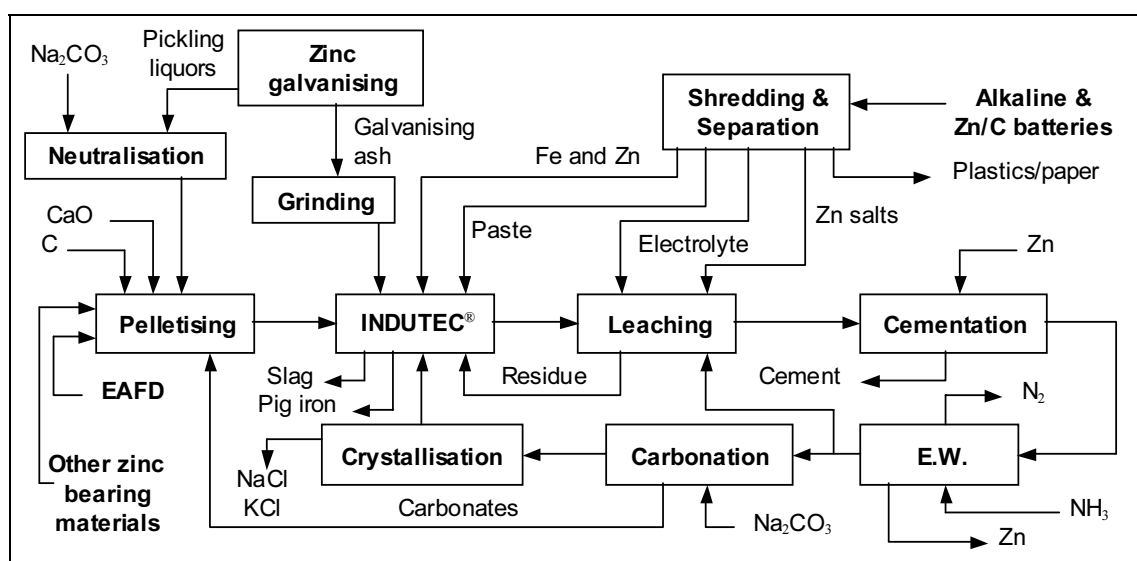


Figure 7: Combined INDUTEC®/EZINEX® Process - Conceptual block diagram

Of course, some other feeds can be evaluated and may be included in the loop with small or no modifications to the flowsheet.

We also investigated the possibility to convert zinc concentrate into zinc without any pyrometallurgical operation combining EZINEX® and ammonium chloride pressure leach. This is a very attractive technology because it allows to play with all the raw material that can bring zinc to the system, but this needs some more work.

6. Conclusion

The EZINEX process to produce directly zinc metals from secondary zinc bearing materials is a very attractive and versatile alternative to the classic sulphuric E.W. solving some of the old drawbacks of this last technology.

Its combination with a thermal zinc fuming process makes it particularly suitable to deal with a lot of material that nowadays are in part landfilled even if they contain some interesting metal values. It produces directly a commodity instead of a product, such as C.Z.O., which has some technical and economic problems for its marketing. In fact,

some C.Z.O. producers are trying to improve the quality of their product, for instance by washing the powder, facing some technical and economical troubles.

Finally, the EZINEX unit is industrially proven and, speaking about the Engitec's thermal fuming process, the INDUTEC unit has been extensively tested as it uses the application of a very well known smelting procedure in the steel industry.

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