

# INDUTECH<sup>®</sup>/EZINEX<sup>®</sup> Integrate Process on Secondary Zinc-Bearing Materials

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Published online: 20 April 2016

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**Abstract** Steel used for many different applications is more and more often coated with zinc for corrosion protection purposes. The growing amount of Electric Arc Furnace Dust (EAFD) generated during the production of steel requires treatment that is able to convert this dust into usable materials. The current state of the art for the treatment of these wastes is based on the use of a Waelz Kiln, or any other zinc fuming system, where the zinc contained in the EAFD is concentrated in Crude Zinc Oxide (C.Z.O.), which is then fed to sulfate electrowinning or to the Imperial Smelting Process to produce zinc metal. These two processes require that the C.Z.O. be pre-treated, or at least washed, to meet the requirements of the processes. Engitec developed the EZINEX<sup>®</sup> Process that is able to convert C.Z.O. and other zinc oxides directly to metallic zinc cathodes. Engitec also studied the INDUTECH<sup>®</sup> Process, a pyrotechnology competitive to the Waelz Kiln. The INDUTECH<sup>®</sup>/EZINEX<sup>®</sup> Integrate Process will be described.

**Keywords** EAF · Dust · Zinc · Recycling · Electrowinning · Ammonium · Chloride

## Introduction

Zinc is contained in numerous wastes and secondary raw materials that can be considered high-zinc concentrate mines that are easily exploitable. However, only parts of

these materials are currently processed, while most of them are landfilled with or without previous stabilization processes. In recent years, some processes—mainly pyrometallurgical—were developed to convert the 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 vaporized and re-oxidized producing (C.Z.O.) which also contains relatively high concentrations of heavy metals and halides. Many potential C.Z.O. sources, such as electric arc furnace (EAF) dust, galvanizing ashes, brass foundry, and converters fumes, contain chlorides, fluorides, and alkali metals that will then be found in the produced C.Z.O. This is also true of the Waelz oxides [2]. This C.Z.O. has to then be transformed into zinc metal and, until now, it is done in two main processes: the sulfate leaching and electrowinning system and the Imperial Smelting Process (ISP). ISP is facing a crisis for technical and economic reasons that led to the closure of most of the existing plants. But before being fed to one of these processes, the C.Z.O. has to be treated to eliminate or reduce the contained impurities, in particular halides, which are harmful to these processes.

Any chlorides fed into the zinc sulfate electrowinning (E.W.) lead to anodic chlorine evolution causing labor health problems and increase the anode corrosion rate, compromising the zinc quality. The fluorides, even at very low concentrations of a few hundreds of ppb, seriously compromise the cathode stripping. The halides content also causes problems in the ISP because of issues induced at the condenser.

In recent years, some processes for C.Z.O. treatment were studied and installed. These processes are based on a water (or Na<sub>2</sub>CO<sub>3</sub> solution) wash and are having some difficulties. For these reasons, a chloride-based zinc

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The contributing editor for this article was Shinya Kitamura.

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recovery system, directly producing metallic Zn, would be valuable [3–5].

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

The Zn chloride E.W. was intensively studied because of the high conductivity of the electrolyte and the lower anodic voltage ( $\text{Cl}_2$  instead of  $\text{O}_2$  evolution) resulting in energy savings compared to the sulfuric E.W. [7].

The major drawback in the zinc chloride E.W. is the  $\text{Cl}_2$  anodic evolution instead of  $\text{O}_2$  [8, 9]. This problem was overcome by introducing a cationic perm-selective membrane using  $\text{H}_2\text{SO}_4$  in the anodic compartment obtaining  $\text{O}_2$  evolution at the anode. This conceptually elegant solution allows the process 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 the EZINEX<sup>®</sup> Processes [10] to treat zinc-bearing materials such as EAF dust. In 1993, a pilot plant producing 500 t/y zinc from EAF dust was erected and operated. After 1 year of operation, an industrial plant producing 2000 t/y of zinc cathode was designed, erected, and operated. During the industrial plant operation, a thermal pilot plant for the conversion of zinc-bearing materials to C.Z.O. was also built and operated. This thermal process, called INDUTE<sup>®</sup>, is based on an induction furnace.

EZINEX<sup>®</sup> [11] is a hydrometallurgical process, based on an  $\text{NH}_4\text{Cl}$  electrolyte, capable of producing metallic zinc directly from C.Z.O. The first industrial scale EZINEX<sup>®</sup> plant [12] was designed to produce zinc directly from EAF dust. Several campaigns using a C.Z.O. feed instead of EAFD were run in this plant and obtained very good results. These tests oriented Engitec towards a new approach: the EZINEX<sup>®</sup> Process was considered the perfect terminal for the direct treatment of C.Z.O., because it is virtually insensitive to the impurities that are detrimental for other processes. In addition, feeding C.Z.O. simplified the most problematic operations of the EZINEX<sup>®</sup> Process.

### The INDUTE<sup>®</sup> Process

During the management of the EZINEX<sup>®</sup> plant, Engitec studied its own thermal treatment to produce a crude zinc oxide when the advantages obtained feeding ZnO instead of EAF dust directly into the EZINEX<sup>®</sup> Plant were evaluated.

Engitec evaluated this process with several tests performed in a 150 kW induction furnace pilot unit installed at the Ferriere Nord facility.

Tests were carried out on the following materials:

- EAF dust,
- Mill scale, and
- Blast furnace lead slag.

The products of the fuming in the Induction furnace are as follows:

- Zinc oxides fume with Pb, Cd, and Ag,
- Pig iron of saleable quality, and
- Inert slag.

The fuming of zinc and simultaneous production of pig iron from zinc ferrite-bearing materials by a specially designed induction furnace was patented and called INDUTE<sup>®</sup> process.

The flowsheet of the pilot plant used is shown in Fig. 1.

The recovery of zinc and other metal values is almost complete, while the pig iron is of marketable quality. The slag (40 % of the feed) is inert and meets the standards of EPA TCLP test.

Figure 2 shows the average quality of the obtained product coming from 1 year of tests on different starting materials.

The crude zinc oxide we obtained from the INDUTE<sup>®</sup> Plant was fed into the EZINEX<sup>®</sup> Plant. We achieved very good results, comparable to the ones obtained when the Waelz oxides were fed.

As a comparison, Fig. 3 shows the different pathways followed by crude zinc oxides when metallic zinc is produced.

Processes other than EZINEX<sup>®</sup> require, at a minimum, a washing of the crude zinc oxides. These treatments have high-operating costs and induce environmental problems.

We evaluated the consumption for the INDUTE<sup>®</sup> treatment and Table 1 below is a summary of the results obtained from the pilot plant tests.

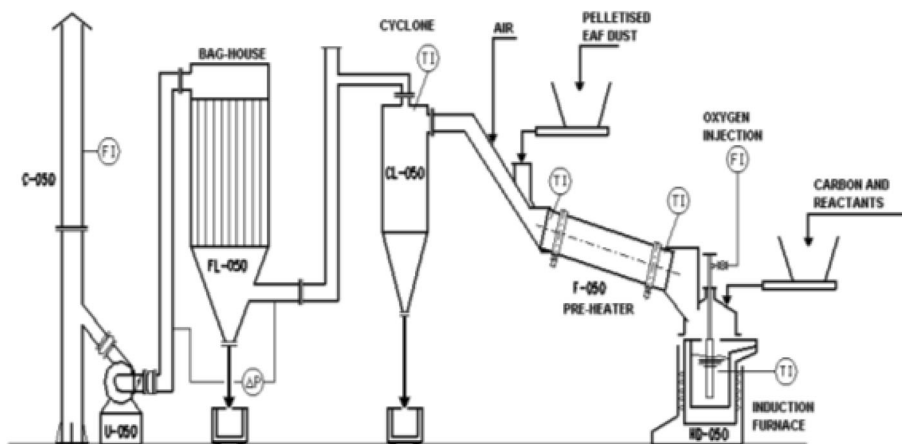
### The EZINEX<sup>®</sup> Process

The EZINEX<sup>®</sup> Process, described in Fig. 4, is an electrowinning system based on a chloride leaching able to leach materials containing oxidized zinc and consists of five main operations:

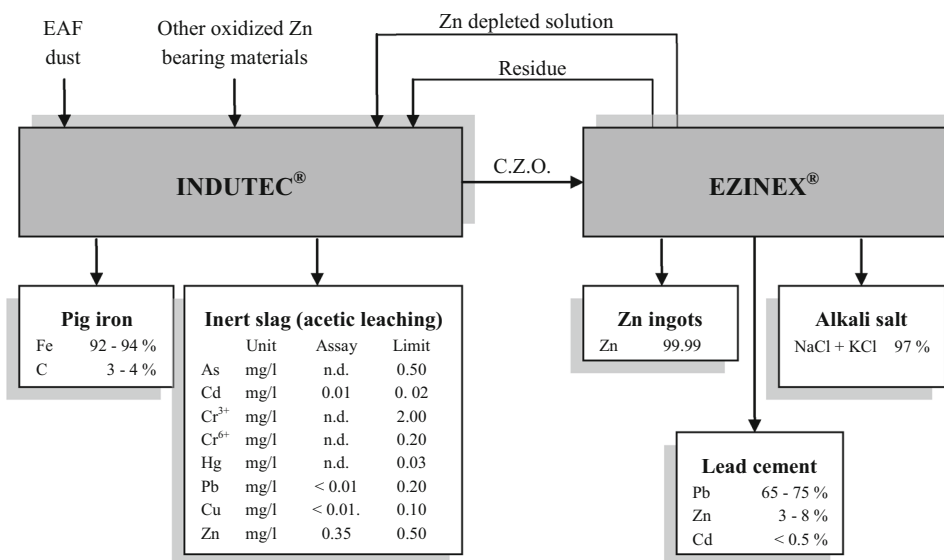
- Leaching of Zn-bearing materials,
- Solution purification,
- Zinc electrowinning,
- Evaporation/crystallization, and
- Purification of elements less noble than zinc (Carbonation).

Here below each single operation and the relevant technical aspects will be described and discussed.

**Fig. 1** INDUTECH® pilot plant flowsheet

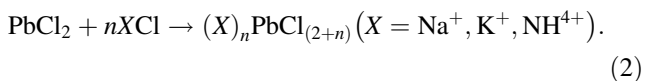
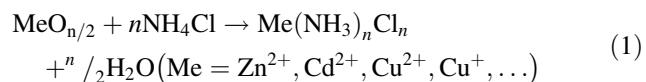


**Fig. 2** INDUTECH®/EZINEX® combined process: products quality



**The Leaching**

This new technological approach is based on the use of a neutral pH solution containing a quite high concentration of ammonium chloride in which also alkali and alkaline-earth chlorides are present. In this environment, Zn and the other contained heavy metals are easily leached and taken in solution together with alkaline chlorides and part of the alkaline-earth salts. The leaching mechanism is as follows:



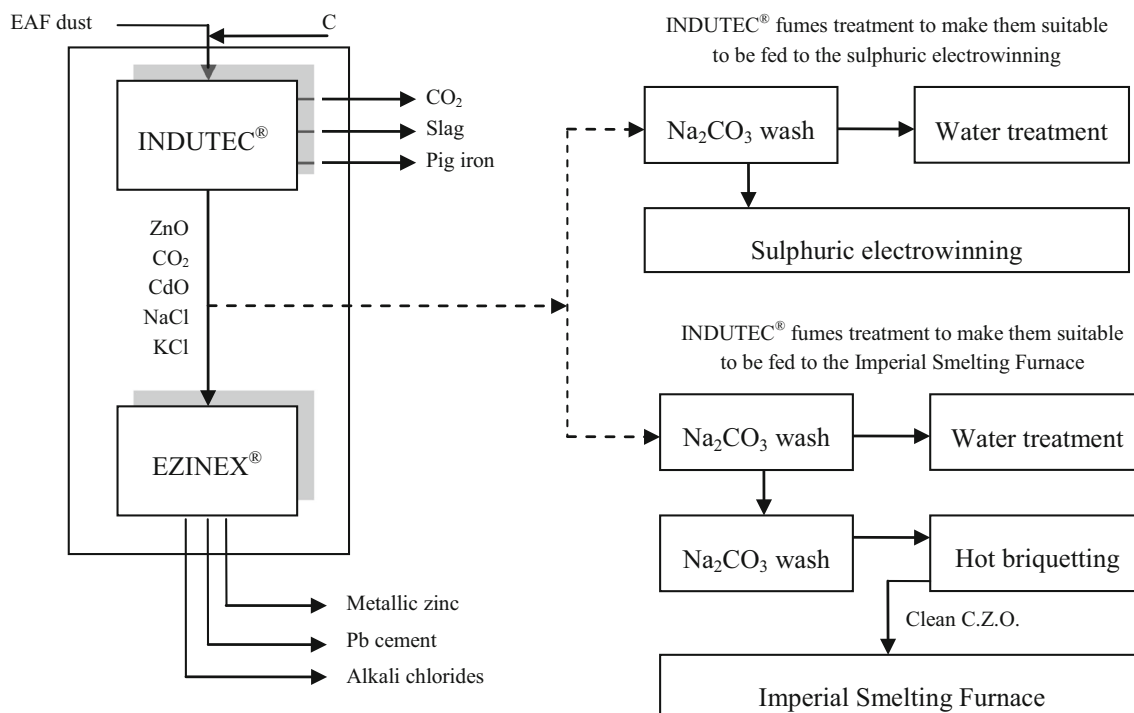
The zinc oxide leaching efficiency is practically 100 %, but the zinc ferrite is not leached at all.

For solubility problems, the leaching is operated at temperatures in the range from 70 to 80 °C and it is a very fast operation having the advantage, because of the neutral pH, of not leaching the iron.

The leaching residue, containing all the iron and the zinc ferrite, is recycled back to the thermal system which generated the C.Z.O.

**The Leachate Purification**

The leachate contains minor concentrations of metals more noble than Zn that could be co-deposited with Zn into the cathode. Their removal is very important for the quality of the plated zinc and it is achieved by adding zinc powder or granules which causes the precipitation of these metals in metallic form according to very well-known cementation or displacement reaction reported here below:

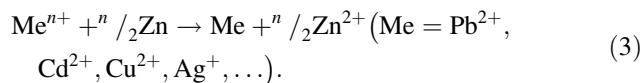


**Fig. 3** Zinc metal production from crude zinc oxides—methods comparison

**Table 1** INDUTECH<sup>®</sup> plant consumption

Expected consumption (per 1 t of dust) for an INDUTECH<sup>®</sup> Plant treating 15.000 t/y of EAF dust

|                |                    |
|----------------|--------------------|
| Electric power | 600 kWh            |
| Carbon         | 50–100 kg          |
| Flux aids      | 20 kg              |
| O <sub>2</sub> | 90 m <sup>3</sup>  |
| Natural gas    | 20 Nm <sup>3</sup> |



The chemical Zn dissolution is kinetically slow at the operative pH, being, for this reason, not a serious competitive reaction for the cementation. The complete removal of these impurities, optimizing the zinc powder consumption, influences the final quality of the plated, so the design of this unit needs a particular attention. We learned that the higher the Zn cathode purity requirement, the greater has to be the number of cementation stages. In any case, a multistage system is necessary if some notable quantities of valuable metals, such as Ag and Cu, have to be recovered in a relatively pure form.

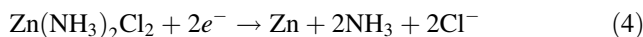
The purified solution leaving the cementation unit is suitable for being fed to the E.W. unit.

### The Zinc Electrowinning

The core, and the real novelty, of this process is the EZINEX<sup>®</sup> E.W. unit. As anticipated, one of the issues of the conventional chloride E.W. is the anodic evolution of chlorine which requires a complex cell design and a complicated and troublesome chlorine handling.

The EZINEX<sup>®</sup> E.W. occurs in an open cell with permanent titanium cathode blanks and graphite anodes. The electrolysis has to be run at temperatures higher than 65 °C, because of the zinc solubility problems, and it has to be assisted by an air sparging system which optimizes the diffusion rate and provides a very effective mixing of the solution. This means that the electrolysis can be run at relatively high current densities (300 A/m<sup>2</sup>) even with relatively low zinc concentrations (5 g/l).

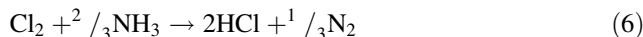
The zinc deposition occurs at the titanium cathode, according to the following mechanism:



The chemistry at the anode is slightly more complicated. The electrochemical reaction

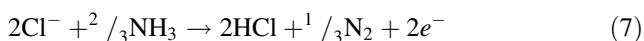
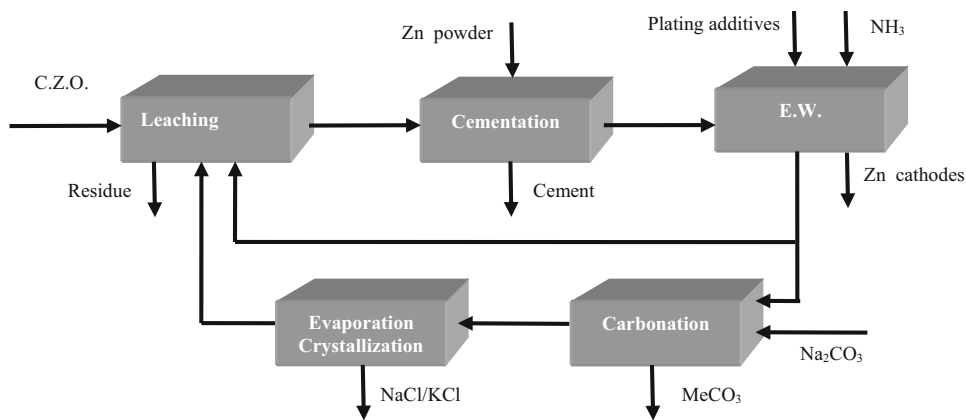


is followed very quickly by the chemical reaction:



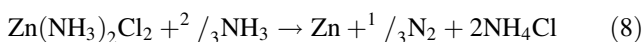
which leads to the following overall anodic reaction:

**Fig. 4** The EZINEX<sup>®</sup> process—block diagram



Because of the possible formation of chloro-amines, the electrolyte pH must be maintained in the range of 6–7. The pH control is achieved by adding ammonia solution to replace what is consumed by the chemical reaction (6). Maintaining the pH in the right range is quite easy because the solution is buffered by the zinc-amino complexes.

The overall cell reaction



is obtained summing reactions (4) and (7).

The Zn concentration in the cell is in the range of 5–15 g/l and this allows to operate the E.W. at a current density that is in the range of 300–400 A/m<sup>2</sup>. The deposition time is in the range of 24–48 h.

The cathodic H<sub>2</sub> evolution, the real competitor of zinc plating in the sulfate E.W., is practically absent. The cathodic current efficiency of EZINEX<sup>®</sup> is in the range of 94–98 % and the plate can also accept the co-deposition of metals having a low hydrogen overvoltage which is not as dramatic as in the case of the sulfuric Zn E.W. because the hydrogen evolution is not possible.

The EZINEX<sup>®</sup> cell voltage is lower than the one of the sulfuric E.W., and this means a lower energy consumption. The benefit of this energy savings is partially reduced by the ammonia consumption. The ammonia eventually released in the plant is scrubbed and recycled back to the process.

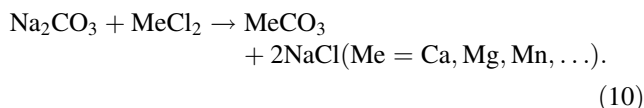
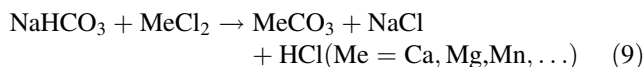
### The Evaporation/Crystallization

The main impurities building up in the leachate are alkali chlorides and fluorides, calcium and magnesium. They are not affecting the plating but, apart from the fact they can slightly modify the electrolyte conductivity reducing the ohmic drop, they have to be removed to avoid unwanted crystallization of salts in the process.

This unit has two main goals: the evaporation of the water fed to the plant (moisture of reactants make-up, electrochemical additives, cake washes, and cathode washing) and the elimination of alkaline chlorides from the electrolyte. The mother liquor, containing zinc-amino complex and ammonium chloride, is recycled back to the plant.

### The Carbonation

Calcium and magnesium build up in solution is particularly problematic for the zinc plating because they likely interfere with the zinc migration to the cathodic surface. To avoid this problem and unwanted crystallization, Ca and Mg are precipitated by adding Na<sub>2</sub>CO<sub>3</sub>/NaHCO<sub>3</sub> according to the following mechanism:



Feeding C.Z.O., some fluorides are also fed. Fluorides need to be removed and kept under control. The presence of calcium helps because fluorides are precipitated during the leaching according to the following reaction:

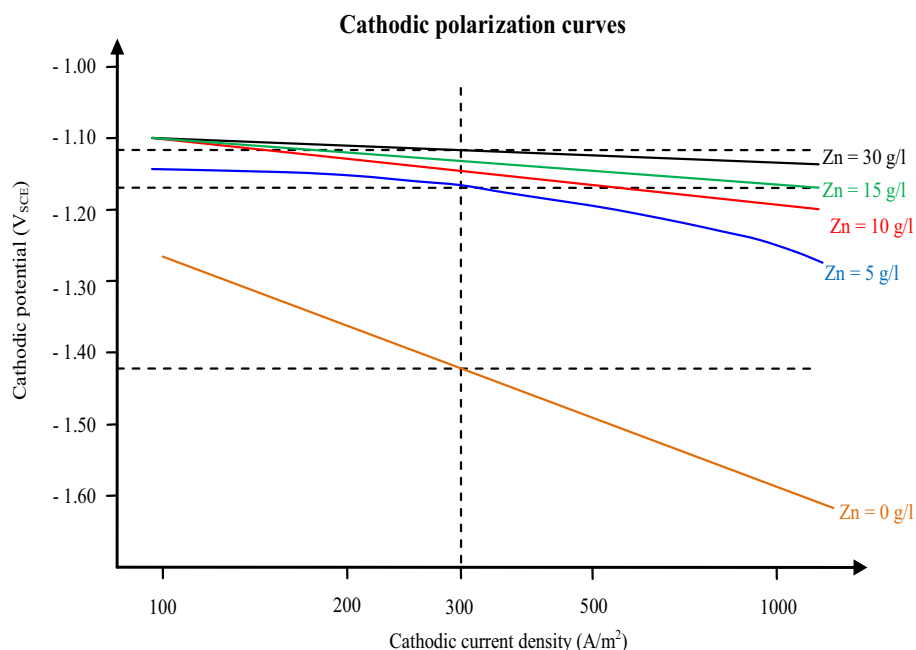


### The Electrowinning Unit

After presenting the process in general, we would like to go a little deeper in details about the electrochemical cell [13] which is the real novelty of the process.

The industrial cell underwent to a lot of changes and the latest version is an undivided one equipped with titanium cathodes and graphite anodes and an air sparging system,

**Fig. 5** Cathodic polarization curves



under the electrodes, to homogenize the solution while increasing the diffusion rate.

At the Ferriere Nord facility (Osoppo, Italy), the first industrial tank house in the world based on zinc ammonium chloride electrolysis for the production of zinc cathodes, as an alternative to the traditional zinc sulfate electrolyte, was built and operated. The process underwent to some changes during more than 3 years of operations involving operating parameters such as cell temperature, electrolyte zinc content, current density, and impurity loading in the solution. The viability and reliability of the process were proven also in extreme operating conditions (cell temperature up to 80 °C, zinc concentration as low as 5 g/l, impure electrolyte with total impurities up to 500 mg/l!). These unfavorable conditions did not affect the current efficiency which was affected only by short circuits between cathodes and anodes due to a combination of accidental misalignment of the electrodes and premature detachment of the zinc deposit because of an excessive cell temperature (>75 °C). Even the presence of high concentration in the electrolyte of elements like Sb, Ni, Co, etc., problematic for the sulfate E.W., did not affect the current efficiency and the only consequence was the co-deposition of these metals with zinc lowering the quality of the produced cathodes.

In fact, because of the neutral pH, the hydrogen competition is practically negligible even in the presence in the plate of the above-mentioned elements that normally lower the hydrogen overvoltage and do not allow the zinc deposition.

In the following figures, the cathodic (Fig. 5) and the anodic (Fig. 6) polarization curves for the EZINEX® Process are shown.

Figure 5 clearly shows that, at the operating current density (300 A/m<sup>2</sup>), the hydrogen evolution (Zn = 0 g/l curve) is at least 250 mV far from the zinc deposition potential and that 5 g/l of zinc are enough to run the electrolysis up to 500 A/m<sup>2</sup>. What shown in the graph was then fully demonstrated during the plant operation.

Figure 6 shows that the anodic potential is basically not affected by ammonia/ammonium salts addition but what we have is only a small depolarization. This probably means that the anodic reaction is not changing but likely the rate determining step is being influenced by the chemical reaction.

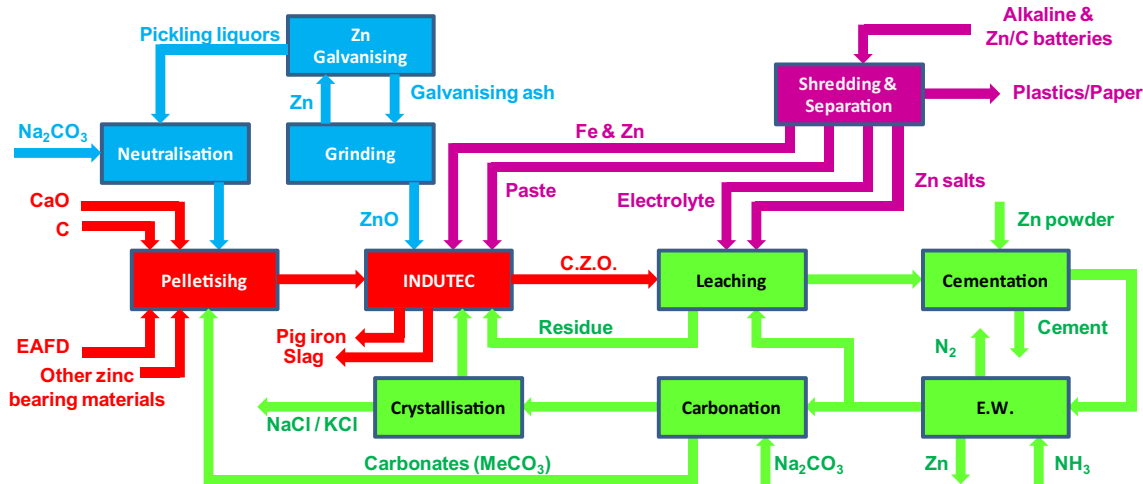
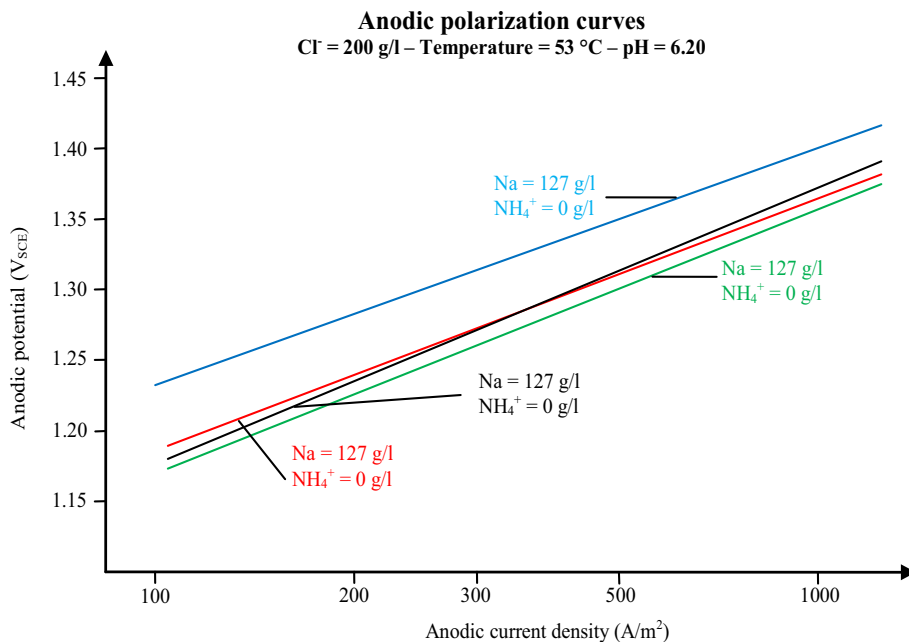
### The Integrate INDUTECH®/EZINEX® Process

If the EZINEX® Process is fed with the C.Z.O. produced in any kind of fuming process, a very powerful system to deal with a variety of wastes and/or secondaries in a very simple process is created. A conceptual plant flowsheet, based on Engitec's INDUTECH® thermal process [14, 15], is shown in Fig. 7 where diverse materials coming from different industries can be processed. Most of these materials do not have a dedicated treatment process and sometimes are disposed besides their values content.

Of course, this is an example and other feeds can be processed according to this approach with limited or no modifications to the flowsheet.

We also successfully investigated the possibility to convert zinc concentrate into zinc without any pyrometallurgical operation by combining EZINEX® and ammonium chloride pressure leach. This is a very attractive technology

**Fig. 6** Anodic polarization curves



**Fig. 7** Integrated INDUTECH®/EZINEX® process—conceptual block diagram

because it allows examination of all the raw material that can bring zinc to the system, but this needs additional investigation.

**Conclusion**

Through the EZINEX® Process, zinc contained in secondary sources can be directly converted to zinc metal. This process is a very attractive and versatile alternative to the classic sulfuric E.W. by solving some of the old drawbacks of this traditional technology.

When combined with any thermal zinc fuming process, it is particularly suitable to deal with a great deal of

materials that are nowadays at least partially landfilled even though they contain some interesting metal values. It produces a commodity directly while avoiding the problem of having to commercialize a product, such as C.Z.O., which has technical and economic problems for its marketing. For commercial reasons, some C.Z.O. producers have to improve the quality of their product, for instance by washing it, and they are facing some technical and economic troubles.

Finally, the EZINEX® unit is industrially proven and, regarding Engitec’s thermal fuming process, the INDUTECH® unit has been extensively tested as it is based on the application of a very well-known smelting procedure in the steel industry. When compared to the existing



other thermal treatments, INDUTECH<sup>®</sup> not only produces C.Z.O. but also converts the rest of the feed in reusable materials, as inert slag and pig iron, deeply changing, simplifying, and making more environmentally sounding their management.

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