New Approaches on Non Ferrous Metals Electrolysis

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Engitec Technologies is a relatively young company active in the field of non ferrous metals recovery from diverse sources. Since the beginning, the company has studied systems based on innovative hydrometallurgical processes trying to avoid, when possible, the use of pyrometallurgical techniques.
In particular, the company has developed two systems based on very different and unusual electrolytes:

- Fluoboric acid: for primary and secondary Pb and Cu
- Ammonium chloride: for primary and secondary Zn and Pb

For the fluoboric acid system, a demo plant campaign on primary Pb concentrate was recently completed and we are currently preparing proposals for industrial plants. This electrochemical system is based on a diaphragm divided cell were Pb metal is plated at the cathode and Fe^{3+} is produced at the anode instead of evolving oxygen. The Fe^{3+} produced is then used to leach the Pb from the mineral concentrate closing the process loop.

For the ammonium chloride system, the electrolysis is run in a more traditional open cell. Unlike other chlorine electrolysis systems, this cell has no chlorine gas emissions. Instead, where chlorine is produced at the anode it is immediately converted to nitrogen by a chemical reaction with ammonia in the bulk solution. A small industrial plant was operated for several years in Italy producing Zn from electric arc furnace dust generated during the production of steel from steel scrap.

In addition, we are electrowinning Pb from ammonium chloride electrolyte in a bi-polar flow cell working at 8,000-10,000 A/m^2 without any need for cathode stripping. This is currently being piloted at our facility in Milan, Italy.

This paper will describe these industrial electrochemical approaches in more detail.

1. Introduction

Engitec Technologies is acknowledged as the world market leader in the design and construction of plants for the recycling of lead acid batteries. In the early nineteen nineties, Engitec started studying processes for the production of lead with hydrometallurgical technologies to replace the old pyrometallurgical processes. This was also the start of development of other potential approaches for the production of non ferrous metals through hydrometallurgical technologies. This caused us to consider non-traditional technologies by taking advantage of the experiences of some metallurgists working with the company, and before with Tonolli Group, since the forties. This work led us to the development of three lines of processes with original solutions: the Fluoborate technology, the EZINEX process and the FAST Pb Process. The processes, as well as the electrolysis cells, will be described in this paper.

2. Fluoborate technology: recovery of Pb (FLUBOR® Process) and Cu (ECUPREX® Process) from primary and secondary sources

The processes based on this technology are relevant to the production of Cu and Pb from primary and secondary materials. Both metals, as well as their sulphides, are leached in a fluoborate solution under the action of ferric fluoborate which takes metals in solution according to the following reactions:

$$Me + 2\,Fe(BF_4)_3 = Me(BF_4)_2 + 2\,Fe(BF_4)_2 \qquad (Me = Pb,\ Cu) \qquad [1]$$
$$MeS + 2\,Fe(BF_4)_3 = Me(BF_4)_2 + 2\,Fe(BF_4)_2 + S° \qquad (Me = Pb,\ Cu) \qquad [2]$$

As far as the copper sulphides are concerned, only chalcopyrite ($CuFeS_2$) is not directly leachable by this system. It has to first be converted in covellite (CuS) or chalcocite (Cu_2S).

The leachate is then fed to the cathodic compartment of a diaphragm divided cell where, at a stainless steel cathode, metals are plated according to the following reaction:

$$Me(BF_4)_2 + 2\,e^- = Me + 2\,BF_4^- \qquad\qquad (Me = Pb, Cu) \qquad\qquad [3]$$

At the graphite anode, the ferrous fluoborate is oxidized to ferric fluoborate according to the following reaction:

$$Fe(BF_4)_2 + BF_4^- = Fe(BF_4)_3 + 2\,e^- \qquad\qquad\qquad [4]$$

The overall cell reaction is:

$$Me(BF_4)_2 + 2\,Fe(BF_4)_2 = Me + 2\,Fe(BF_4)_3 \qquad\qquad (Me = Pb, Cu) \qquad\qquad [5]$$

The plated metals are very compact with a very fine grain-size. The overall processes are:

$$Me_{(Feed)} = Me_{(Plate)} \qquad\qquad (Me = Pb, Cu) \qquad\qquad [6]$$
$$MeS = Me + S° \qquad\qquad (Me = Pb, Cu) \qquad\qquad [7]$$

The cell is equipped with a fabric diaphragm where the catholyte is fed into the cathodic compartment creating a height differential with the anolyte. This gap has to be sufficient for the electrolyte flow through the diaphragm to overcome the ferric diffusion from the anodic compartment to the cathodic compartment. The anode material is graphite, which is fully stable with the iron oxidation reaction from ferrous to ferric. To increase the diffusion rate, the cell is equipped with an air sparging system. Both the electrolytic systems work at temperatures in the range of 40-50 °C and current densities in the range of 250-500 A/m^2. The cell voltage, at 300 A/m^2, is about 1.5-1.6 V for Cu and 2.0-2.1 V for Pb. The plating time is 6 days for Cu and 2 days for Pb. The plating current efficiency is > 97 %. The reactions 1-6 refer to an electrorefining system in which the feed is a dirty granulated metal leached in a continuous rotary reactor and not a metallic anode. This avoids all of the problems relevant to the traditional methods that require a thermal steps with heavy internal recycling of solids.

Any precious metals that are present in the feed will be left in the final leaching residue for further recovery. The following Figures 1 and 2 summarize the concept for both copper and lead.
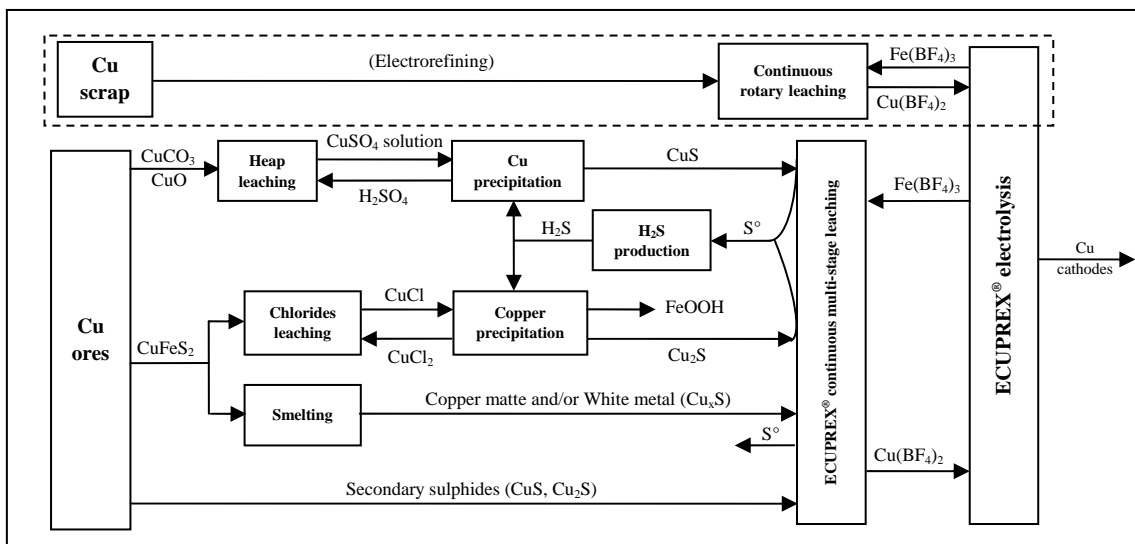

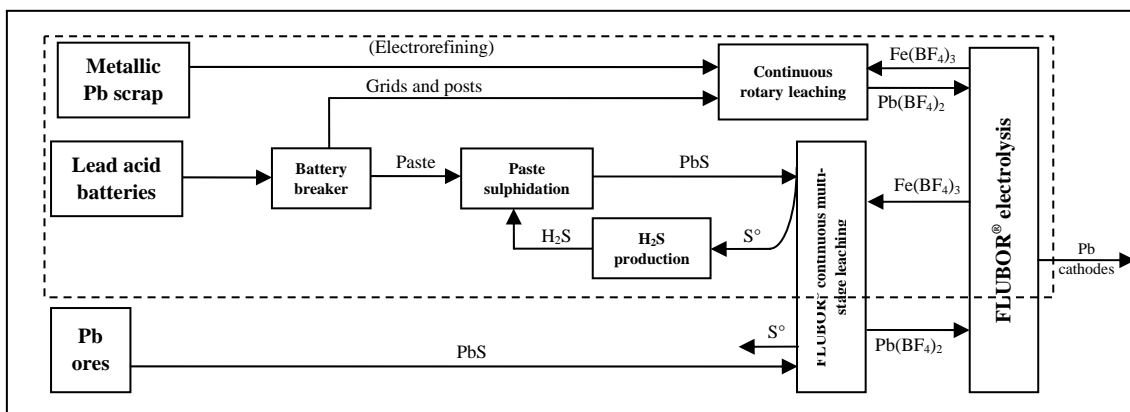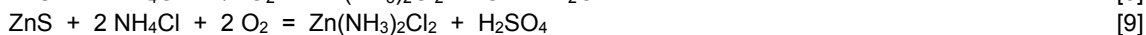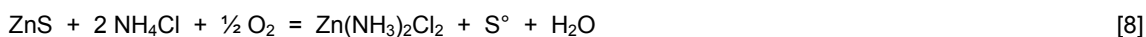Figure 1 – ECUPREX[®] Process: copper recovery from ores and scrap

Figure 2 – FLUBOR® Process: Lead recovery from ores and scrap

3. Ammonium chloride technology: recovery of Zn (EZINEX® Process) from primary and secondary sources

The process based on this technology is relevant to the production of Zn from primary and secondary materials. Zinc primary sources (ores) are based on sulphides and the main compounds are blenda and sphalerite, which are both zinc sulphide. Zinc secondary sources are waste and by-products coming from production of other metals and/or from hot-dip zinc galvanizing. The two materials require different leaching procedures, but the electrowinning process is the same. Zinc sulphide is leached in a pressure leaching reactor pressurized with oxygen, according to the following reactions:

$$ZnS + 2\,NH_4Cl + \tfrac{1}{2}\,O_2 = Zn(NH_3)_2Cl_2 + S° + H_2O \tag{8}$$
$$ZnS + 2\,NH_4Cl + 2\,O_2 = Zn(NH_3)_2Cl_2 + H_2SO_4 \tag{9}$$

This second reaction has to be limited because if this is the preferred reaction, the oxygen consumption will overwhelm any project. To avoid this, cupric ion is added to control the potential of the solution. In this case the reaction is the following:

$$ZnS + 2\,NH_4Cl + 2\,CuCl_2 = Zn(NH_3)_2Cl_2 + 2\,CuCl + 2\,HCl + S° \tag{10}$$

The cupric ion, present in a very low concentration, is continuously regenerated by the oxygen:

$$2\,CuCl + 2\,HCl + \tfrac{1}{2}\,O_2 = 2\,CuCl_2 + H_2O \tag{11}$$

The sum of the reaction 10 and 11 is the reaction 8 but in this case the kinetics are faster and the solution potential is controlled. The copper compounds are working as an oxygen carrier.
The leaching of secondary sources are quite easy and rapid at atmospheric pressure:

$$ZnO + 2\,NH_4Cl = Zn(NH_3)_2Cl_2 + H_2O \tag{12}$$
$$ZnCO_3 + 2\,NH_4Cl = Zn(NH_3)_2Cl_2 + CO_2 + H_2O \tag{13}$$

The leachate is purified and fed to the electrowinning cell. The cell is an open one equipped with a graphite anode and titanium cathode. At the cathode, zinc is plated according to the following reaction;
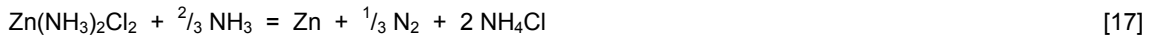
$$Zn(NH_3)_2Cl_2 + 2\,e^- = Zn + 2\,NH_3 + 2\,Cl^- \tag{14}$$

At the anode, chlorine is produced according to the following reaction:

$$2\,Cl^- = Cl_2 + 2\,e^- \tag{15}$$

immediately followed by the following fast reaction:

$$Cl_2 + \tfrac{2}{3}\,NH_3 = \tfrac{1}{3}\,N_2 + 2\,HCl \tag{16}$$

The overall cell reaction is:

$$Zn(NH_3)_2Cl_2 + {}^2/_3\,NH_3 = Zn + {}^1/_3\,N_2 + 2\,NH_4Cl \qquad [17]$$

The solution leaving the cell contains the ammonium chloride to be used in the leaching unit. To increase the diffusion rate, the cell is equipped with an air sparging system. Because of some solubility problems, the system works at temperatures in the range of 65-75 °C and current densities in the range of 300-400 A/m^2. The cell voltage, at 300 A/m^2, is about 2.6-2.8 V. The plating time is 1-2 days. The plating current efficiency is > 97 %.
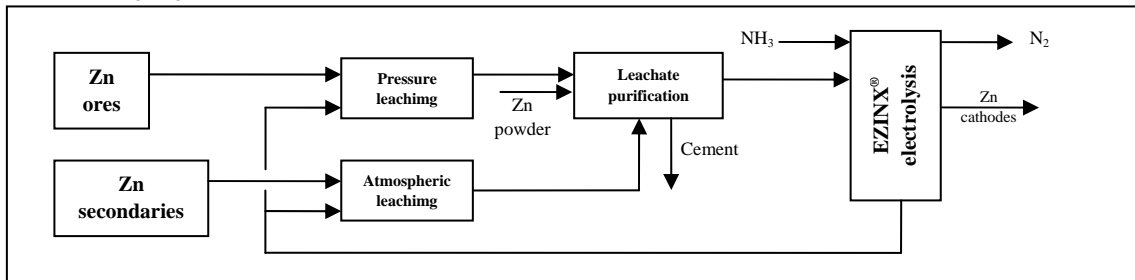The following Figures 3 summarizes the concept.

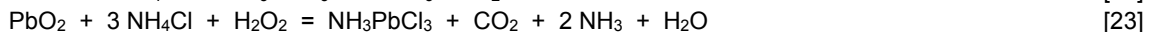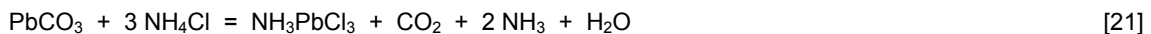Figure 3 – EZINEX® Process: zinc recovery from ores and secondary materials

The EZINEX® technology is the only one handling primary and secondary sources without any pretreastment for one of ythe two possible feeds

4. Ammonium chloride technology: recovery of Pb (FAST® Pb Process) from secondary sources

The process based on this technology is relevant to the production of Pb from secondary materials. Lead secondary sources are typically coming from battery recycling. The first step of battery recycling is the breaker where the battery component are separated, The two fractions containing Pb are the metallic fraction (battery grids and poles) and the paste (active mass containing some Pb salts). This process coverts this second fraction, after its desulphurization or the conversion of lead sulphate to lead oxide or carbonate, according to one of the following reactions:

$$PbSO_4 + Na_2CO_3 = PbCO_3 + Na_2SO_4 \qquad [18]$$
$$PbSO_4 + 2\,NaOH = Pb(OH)_2 + Na_2SO_4 \qquad [19]$$
$$PbSO_4 + (NH_4)_2CO_3 = PbCO_3 + (NH_4)_2SO_4 \qquad [20]$$

These are simplified reactions: the reality is more complex. In the desulphurized paste, after the desulphurization, PbO, PbCO$_3$ and PbO$_2$ are present. They are leached according to the following reactions:

$$PbCO_3 + 3\,NH_4Cl = NH_3PbCl_3 + CO_2 + 2\,NH_3 + H_2O \qquad [21]$$
$$PbO + 3\,NH_4Cl = NH_3PbCl_3 + 2\,NH_3 + H_2O \qquad [22]$$
$$PbO_2 + 3\,NH_4Cl + H_2O_2 = NH_3PbCl_3 + CO_2 + 2\,NH_3 + H_2O \qquad [23]$$

Also in this case the chemistry is more complex, but we will focus on the electrochemistry of the process. The leachate is purified with lead flakes (produced by the cell) and fed to the electrowinning cell. This cell is very unconventional when compared with the other cells used to win metals. It is a flow-cell where the solution is passing through two electrodes at a very high linear velocity to strip the flakes of lead produced at the cathode instead of producing a sheet.

The cathodic reaction is the following:

$$(NH_3)PbCl_2 + 2\,e^- = Pb + NH_3 + 2\,Cl^- \qquad [24]$$

The anodes have the same reactions (15 and 16) of the EZINEX Process. To have strippable dendrites, we work very close to the limit current. To reduce the ohmic drop through the electrolyte the gap between the electrodes is very narrow. Also in this case, the solution leaving the cell contains the ammonium

chloride to be used in the leaching unit. To increase the diffusion rate the cell is equipped with an air sparging system. Because of issues of solubility, the system works at temperatures in the range of 65-80 °C and current densities in the range of 8000-10000 A/m^2. The cell voltage, at 8000 A/m^2, is about 3.0-3.1 V. The stripping is continuous and doesn't require stripping equipment or a stripping crew. The plating current efficiency is > 85 %.

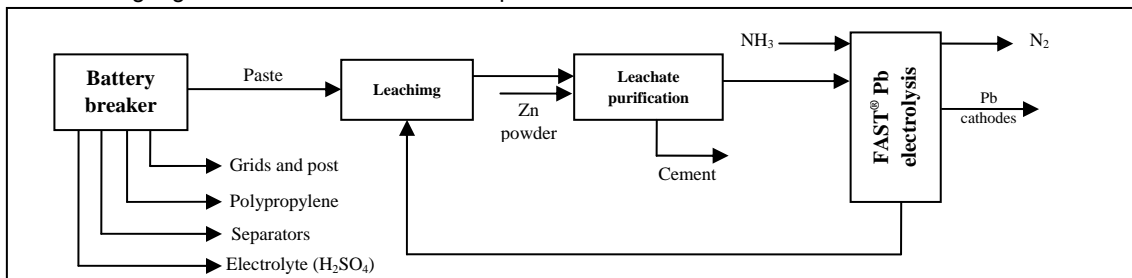The following Figures 4 summarizes the concept.

Figure 4 – FAST® Pb Process: lead recovery from secondary materials

The treatment of lead paste in the traditional lead recycling process is problematic, both in terms of production and of environmental impact. We think that this new approach can significantly improve the quality of the battery recycling process.

5. Electrolytic cell description

The cells used for the previously described technologies are not typical. Figure 5 is a simple description to help to understand.
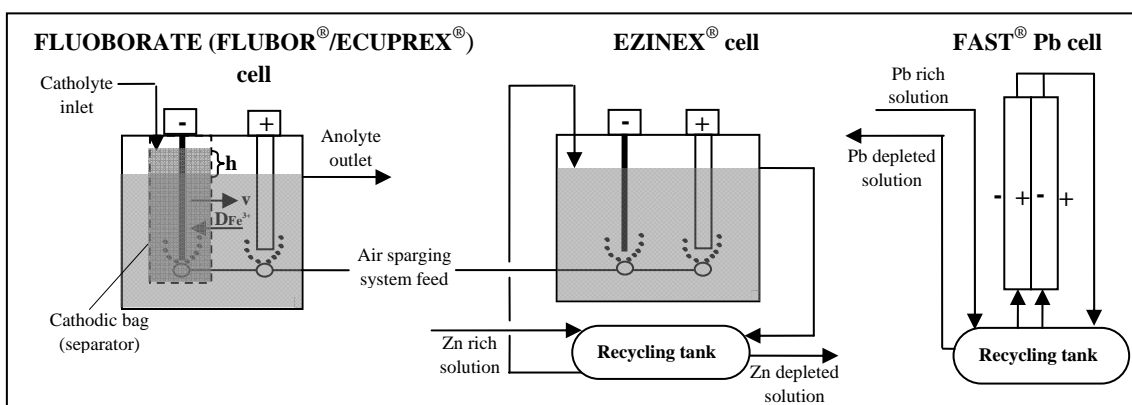

Figure 5 – Cells drawings

The FLUBOR®/ECUPREX® cell is quite similar to the one of the Ni electrolysis. The titanium cathode is positioned in the cathodic compartment, which is equipped with a separator that we call the "*cathodic bag*". The catholyte is fed in this bag, and because of the porosity of the separator, the gap **h** is formed. This gap has to be high enough to generate a flow through the separator having a velocity **v** higher than the diffusion of Fe^{3+} (**DFe^{3+}**) generated by the concentration difference of Fe^{3+} (20 g/l in anolyte, 0 g/l in catholyte).

When **v < DFe^{3+}**, Fe^{3+} enters the cathodic compartment and is reduced to Fe^{2+} before plating Pb and reducing the Pb plating efficiency. Both compartments are equipped with an air sparging system to increase the diffusion rate of chemicals to the electrodes. For the anode, this is very important because if the Fe oxidation doesn't happen, the competing water oxidation reaction occurs with oxygen production inducing the corrosion of the graphite anode.

The EZINEX® cell is an open cell. No separators are required even if chlorine is the anodic product. In fact, as already mentioned in the process description, chlorine immediately reacts with ammonia producing nitrogen. The cell has to be sealed and scrubbed because some ammonia vapours could leave the cell. The cell is equipped with titanium cathodes and graphite anodes but some recent experiences with DSA type anodes showed good results. This cell is working with low zinc concentrations due to solubility issues, so it is equipped with an air sparging system to increase the diffusion rate of chemicals.

The FAST® Pb cell is really unconventional. It is a bipolar flow cell filterpress type design. The current density used are much higher than the ones commonly used in metals electrowinning and the Pb concentration is very low (a few g/l) because we want to produce dendrites and avoid a flat deposit. The formed dendrites are stripped and taken out of the cell by the electrolyte flow which passes through the electrodes at a very high linear velocity. The gap between the electrodes is very narrow to have a low ohmic loss through the solution but wide enough to avoid the particles making contact with the anode and being re-dissolved.

6. Conclusions

These new electrolyses systems have been developed in recent years while trying to replace old pyrometallurgical processes. The development stages are quite different: The EZINEX® cell was tested in an industrial plant producing 2000 t/y of zinc from the electric arc furnace dusts produced in a steel plant, the Fluoborate cell has been tested in a demonstration plant producing 2000 t/y of lead from lead concentrates, the FAST® Pb cell is quite recent and under development in a pilot plant operating at our lab. These technologies raised some commercial interest and we are now working on some projects for their industrial application.