PB BATTERY RECYCLING. NEW FRONTIERS IN PASTE DESULPHURISATION AND LEAD PRODUCTION

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Abstract

The change in regulations and the strong attention to the environment have suggested some changes in the traditional processes for the recycling of lead acid batteries. Engitec Technologies, marketing the Integrated CX® System, is continuously updating and improving its technology to fulfil the technical, economical and ecological requirements coming from the market and from the environmental authorities. In this paper Engitec Technologies will present the latest technical innovations introduced in the Integrated CX® System.

1. Introduction

The price of lead is reaching unexpected high values that nobody was able to forecast as well as nobody probably knows how long this “Eldorado” will last. As a matter of fact the lead stocks are rapidly decreasing and the Far East Countries consumptions are rapidly increasing and this is considered the driving force for the present price situation.

The Chinese market is the most representative of this situation. In Figure 1 we can see the figures for lead market showing a big production increase in the last 7 years while the export is practically not changed if not decreased.

Figure 1: Chinese refined lead exports and production (data: GTIS)
The reason for this big increase is not only the fast growing car market, but also the even faster growing of the electric bikes market. In fact, in 2006 more than 19 millions of electric bike were produced using 400,000 of lead for their batteries that have a life time of one year only!

Being the secondary lead production (4,400 t/y) higher than the primary (3,500 t/y), used batteries result to be the most important raw material for lead production. Processes for recycling batteries underwent big changes in the last years trying to combine the need of producing lead and the solution of some environmental problems typical of lead production processes. These environmental issues are becoming every day more and more important.

The CX® Technology, commercialised by Engitec Technologies and considered the B.A.T. [1,2,3], is nowadays the most diffused and trusted technology in battery treatment.

This process is continuously technically updated to meet the continuous change proposed by Environmental Authorities.

In this paper we will go through the technological changes introduced along the years and we will discuss some future projects to improve the battery recycling technology.

2. Lead acid batteries recycling development

The first battery breaker technology was based on a direct fired rotary dryer, fed with the previously crushed batteries, where the paste was dried and separated from the grids and then, after a final screening, discharged into containers, ready to be fed to the rotary furnaces. The grid metal was separated from the rest of the plastics in a special sink and float unit based on heavy media circulation (paste slurry at a density of 1,8 t/m³).

This type of technology had a lot of throughput that can be summarised here below:

- a heavy pollution (lead dust) in the work place, compromising the in plant air quality
- grid metal and plastics produced were heavily contaminated with paste
- the exhausts from the dryer were heavily contaminated with SO₂ and lead dust
- the produced paste was not suitable for desulphurisation because through the dry screening good separation of the coarse fraction (plastics and grids) was not achieved and then its suspension in water would have produced a slurry very difficult to be pumped.

The first big improvement to the process was the development of a new process based on a wet screening of the ground batteries avoiding in the mean time the use of high polluting and poor efficient heavy media for plastic separation. A dynamic flotation was applied, taking advantage from the mining technology, and an hydro separator was introduced too to achieve the initial goal: the separation of paste from the rest of the battery components, avoiding any further contact with them.

At the beginning of 1982 Engitec developed and constructed the CX® automated battery breaker system.
The new generation of battery breaker (the wet type) has been developed not only because there have been a change in the environmental rules but simply because almost all the secondary lead Plant where not complying with the existing rules in terms of in plant air quality and environmental impact (mainly for SO\textsubscript{2} emission).

As a result of these modifications, the impact on the environment and on the in plant air quality was highly reduced. A survey conducted at Tonolli of Canada showed that the full wet process minimised the SO\textsubscript{2} emissions and, sucking air from all the machinery and washing it in a special wet scrubber, the Pb concentration in the air leaving the chimney, passed from the previous 50 mg/m\textsuperscript{3} to less than 1 mg/m\textsuperscript{3}. The introduction of the paste desulphurisation process, on the other hand, allowed a dramatic reduction of the SO\textsubscript{2} emissions to the chimney of the smelter: the average SO\textsubscript{2} concentration in the fumes from the furnace dropped down from 800 to 80 ppm.

The dispersion model, and the relevant analysis, showed a reduction of the SO\textsubscript{2} concentration, in the area surrounding the smelter from 470 to 67 µg/m\textsuperscript{3}. The in plant air quality had a sudden improvement: the Pb concentration was reduced from 0,15 - 0,3 mg/m\textsuperscript{3} down to 0,05 or less mg/m\textsuperscript{3}.

Another important fact was the introduction of the 100 % oxyfuel burners in secondary lead smelter. Contemporarily to the development of the new CX\textsuperscript{®} system generation, most of the secondary lead smelters introduced the use of the oxyfuel technology. At the beginning it was only an enrichment of the combustion air, but soon after a 100 % oxygen burner was used making evident the following advantages:

- Reduced fuel consumption (from 30 to even 40 % reduction per unit of produced raw lead)
- Reduced NO\textsubscript{X} and CO emissions
- Higher productivity (average 30 % increase)
- Higher flexibility during the smelting operations
- Reduced fumes formation, resulting in better working condition for the bag house
- Complete combustion, inside of the furnace, of the small plastics chip still present in the paste, because of the either higher temperature of the flame and higher residence time of the exhaust inside the furnace
- Easier formation of slag and mattes because of the higher temperature achievable and consequently a better separation from the molten lead when tapping
- Lower production of flue dust
- Easy regulation of the furnace atmosphere (oxidizing, reducing ..)

Another step ahead was the introduction of the desulphurisation of battery paste. The desulphurised paste smelting in furnaces equipped with oxyfuel burners introduced some more advantages:

- Lower paste smelting temperature resulting in a saving of fuel
- Lower SO\textsubscript{2} emissions due to either low sulphur content of the paste and higher and easier smelting rate with formation of the iron soda matte, which keeps the residual sulphur into the slag
Higher productivity achievable by summarizing the advantages of oxyfuel technology and of lead paste desulphurisation allows the use of smaller furnaces, which are more environmental friendly, requiring in total a lower volume of process and sanitary air to be filtrated before being released to the atmosphere.

The slag produced by smelting desulphurised paste with the oxyfuel burners is only 25% of the one produced by smelting sulphurised paste and its composition satisfies the most restrictive regulation.

The Integrated CX® System includes the battery crushing and component separation, even if industrial batteries are fed, paste desphurization, sodium sulphate manufacturing and lead production.

The Engitec Technologies Integrated CX® System for lead recycling is now the most innovative process available in the world to produce lead alloys and soft lead from SLI and industrial scrap batteries full of acid.

One of the most important process issue is related to water utilisation. In this process all the water is continuously recycled and no liquid effluents are produced.

Nowadays the Engitec’s CX® Units are processing more than 2,000,000 tpy of batteries all over the world.

3. **The CX® Plant**

![The Integrated CX® System – Block flow diagram](image)

The CX® Integrated System is designed for the crushing and processing of whole SLI and industrial batteries with plastic or ebonite cases. The plant can be divided in three units (see Figure 2):
The basic unit, where the batteries are crushed and the different components are separated. The high purity of product is very helpful for their commercialisation (PP), for their treatment (grids and poles, paste, electrolyte) or for their disposal (separators).

The paste desulphurisation and sodium sulphate production, where the paste is desulphurised and the electrolyte is neutralized. The sodium sulphate solution, resulting from this operation, is then crystallized producing high purity $\text{Na}_2\text{SO}_4$ crystals.

The smelting and refining unit, where high purity soft lead and lead alloys are produced from lead containing fractions.

4. The last generation

Some modification in the process were necessary to meet the new and strict regulation and to demonstrate that it is possible to produce lead in a efficient way tasking in consideration the environmental issues.

A particular care have to be taken as far as concerns $\text{SO}_2$ emissions and slag production also the quality of the slag is assuming a big importance because in Europe, for instance, a new leaching test for the waste disposal was introduced and this is making slag disposal quite difficult.

Another issue was relevant to the quality of the $\text{Na}_2\text{SO}_4$ to enlarge its market suitability. The requirement for a very pure salt is often coming from our potential customers. All these request coming from the market were converted in new units, or old units modification, ready marketable.

4.1 The improved desulphurisation. An effective way of reducing $\text{SO}_2$ emissions and slag production

The traditional desulphurisation design run in one stage has a couple of issue that can be further improved:

- the desulphurisation rate, that is around 90 %
- the Na content, that for a good desulphurised paste is in the range of 1.8 – 2.5 %.

This two parameters highly impact the slag in term of cost (high S and Na content means need of chemicals), of quantity (the higher are S and Na, the higher is the amount of produced slag) and in term of quality.

For these reasons, a new approach to desulphurisation was studied to try maximising the sulphur removal. In the mean time we also checked the possibility of removing Na, contained in the desulphurised paste because of the formation of alkaline lead salts during the desulphurisation process.

The new approach, tested in the lab and validated in an industrial scale test, is based in a double stage counter-current design using $\text{Na}_2\text{CO}_3$ as desulphurisation reactant. The excess of one of the two reactants speeds-up the reaction rate. The removal of Na requires some $\text{CO}_2$ that extracts it converts it in NaHCO$_3$ that can be recycled to the desulphurisation reactor and used as a desulphurisation agent.
A block diagram of the new improved desulphurisation is given in Figure 3.

Figure 2 – New desulphurisation process – Block diagram

As far as concerns the chemistry of the process, the double stage desulphurisation reactions are the following:

\[
2 \text{PbSO}_4 + 3 \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} \rightarrow \text{NaPb}_2(\text{CO}_3)_2\text{OH} + 2 \text{Na}_2\text{SO}_4 + \text{NaHCO}_3 \quad (1)
\]

\[
3 \text{PbSO}_4 + 4 \text{Na}_2\text{CO}_3 + 2 \text{H}_2\text{O} \rightarrow \text{Pb}_3(\text{CO}_3)_2(\text{OH})_2 + 3 \text{Na}_2\text{SO}_4 + 2 \text{NaHCO}_3 \quad (2)
\]

According to the reaction conditions we have some paste reacting according to reaction (1) and some other reacting according to the reaction (2) fixing the concentration of Na in the final paste. The produced NaHCO₃ partially reacts according to the following reaction:

\[
\text{PbSO}_4 + 2 \text{NaHCO}_3 \rightarrow \text{PbCO}_3 + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O} + \text{CO}_2 \quad (3)
\]

In the final paste we have a mix of NaPb₂(CO₃)₂OH, Pb₃(CO₃)₂(OH)₂ and PbCO₃. The Na removal and the conversion of basic lead salt to PbCO₃ is achieved reacting the desulphurised paste with CO₂ according to the following reactions:

\[
\text{NaPb}_2(\text{CO}_3)_2\text{OH} + \text{CO}_2 \rightarrow 2 \text{PbCO}_3 + \text{NaHCO}_3 \quad (4)
\]

\[
\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2 + \text{CO}_2 \rightarrow 3 \text{PbCO}_3 + \text{H}_2\text{O} \quad (5)
\]

The produced NaHCO₃ is recycled to the first stage reactor to start the desulphurisation.

This desulphurisation way, doesn’t produce an excess of carbonates and doesn’t require any acid for their neutralisation. This is very important for the design of plants treating drained batteries because in case of the traditional design they need to buy some H₂SO₄.
A typical desulphurised paste produced through this new approach has the following characteristics (compared to the traditional approach):

<table>
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<tr>
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<th>Super-desulphurisation</th>
<th>Traditional desulphurisation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Insoluble sulphur</td>
<td>&lt; 0.2 %</td>
<td>&lt; 0.5 %</td>
</tr>
<tr>
<td>Na</td>
<td>&lt; 0.2 %</td>
<td>1.5 – 2.5 %</td>
</tr>
</tbody>
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The smelting of the super-desulphurised paste, compared to traditional desulphurised paste, is very easy and shows the following advantages:

- **SO\(_2\)** emissions are minimised:
  - because insoluble S < 0.2 %
- Chemical to fix sulphur in the slag are minimised
  - Less slag is produced
    - Less material to be disposed
    - More room in the furnace to produce lead increasing the furnace productivity
  - Less energy to heat the slag
  - Less matte is produced
  - Less lead is lost

Also the Na removal causes a decreasing of the produced slag. Practically the smelting can be achieved, in a short rotary furnace, with addition of the coal necessary to reduce the lead at the metallic state and 0.5 % of additives. A rough estimate let us say that the furnace production can be increased by 20- 30 % and an energy saving in the same range can be achieved too. The produced slag amount is reduced and this allows to play with the slagging additives to stabilise it and dispose it safely, overcoming the problems induced by the last introduced regulation for waste disposal.

### 4.2 Grids desulphurisation

Also grids contribute to the **SO\(_2\)** emissions. In fact, because of the corrosion, some lead sulphate is present in the grids and poles fraction, specially in the finer fractions in which the sulphur content can also reach the same concentration of sulphur in paste.

Some ways of desulphurising the grids were investigated and a unit dedicated to this issue can be designed. Of course, the operating condition depend on the chosen desulphurisation technology and can be installed also in the existing plants.

### 4.3 The purification of Na\(_2\)SO\(_4\) solution

The Na\(_2\)SO\(_4\) crystals purity depends on the purity of the solution sent to the crystallisation. In this solution a few ppm of heavy metals are present and their presence can contaminate the final salt. In any case, till now the salt produced was pure enough to be sold to the glass or detergent industry.

The request for a superior purity raised by the possibility to sell this product to other industries widening the market possibility for this product.
The solution can be very highly purified through the application of the sulphide chemistry.

Most of the heavy metals, reacting with a sulphide source, are precipitated as sulphides. As and Sb, unfortunately, are soluble in an alkaline environment and also in excess of sulphide ions. For the complete removal of these elements we must play with the solution pH and Na$_2$S addition.

The process has been patented and industrially applied. The composition of the final solution has a heavy metal content very low that takes to the production of a very pure salt where the total heavy metals content is $<$ 5ppm and the lead content is $<$ 1 ppm.

5. The next generation

Trying to be on the top of the battery recycling technology, some new technical approaches are under evaluation. Here below we would like to give some information about the innovations that Engitec is studying for the future plants

5.1 A new alternative desulphurisation approach.

In some countries, specially some Eastern Countries, the market for Na$_2$SO$_4$ is quite difficult and some alternative desulphurisation technique have to be used. A product with a very interesting market for these countries seems to be (NH$_4$)$_2$SO$_4$ to be used in agricultural applications. Even if the unit design needs a lot of care, the chemistry is quite simple:

$$\text{PbSO}_4 + (\text{NH}_4)_2\text{CO}_3 \rightarrow \text{PbCO}_3 + (\text{NH}_4)_2\text{SO}_4 + \text{NH}_4\text{HCO}_3$$ (6)

$$\text{PbSO}_4 + 2 \text{NH}_4\text{HCO}_3 \rightarrow \text{PbCO}_3 + (\text{NH}_4)_2\text{SO}_4 + \text{CO}_2 + \text{H}_2\text{O}$$ (7)

$$\text{PbSO}_4 + 2 \text{NH}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{PbCO}_3 + (\text{NH}_4)_2\text{SO}_4$$ (8)

The reactants choice is wide and make the process very flexible and some options for a desulphurisation based on ammonium compounds is under evaluation. As a results of tests run till now, we can state as follows:

- PbCO$_3$ is produced because no lead basic salts based on ammonium are formed
- The desulphurisation efficiency is comparable to the one run with Na$_2$CO$_3$
- A particular care have to be used for reactor design

5.2 New electrolysis of paste

Running tests with ammoniacal salts, we contemporarily have run some tests on a new hydrometallurgical approach for the paste treatment. The process is based on a chloride electrolytic system, run at high current density, avoiding the chlorine evolution and using a flow cell.
The flow cell can be run at very high current density having a very high productivity, but a particular care have to be used in designing it because an optimisation work has to be done to keep under control the operating cost. In any case, the use of a flow cell makes the process highly productive simplifying the lay out and reducing the required area. This process is patent pending and we are just finishing the evaluation phase. For this reason we cannot describe it in details but the first data indicate that the process seems to be both technically and also economically viable.

5.3 PVC and PE separators detoxification

Another issue coming from the battery recycling plants is the need of completely remove the lead compounds that report to the PVC and PE separators fraction. We are now working for overcoming also this problems applying some purification wash of this fraction. The main problem of designing a new unit is, as usual, to find the best way to integrate it in the existing process to maintain the main characteristics and eventually use the same reactant.

The problems seems to be solved with an alkaline wash in a dedicated unit recycling the wash in the mainstream of the process avoiding having any stream leaving the process.

6. Conclusions

The CX® Plants in operation all over the world are considered the B.A.T. (Best Available Technology) for their environmentally friendly design, for the quality of products, for the quality of design and manufacture of equipment and it is also the sole guaranteed process for the clean treatment of the industrial lead acid batteries. The most reputed secondary lead producers of the world have installed an Engitec CX® System and the Environmental Protection Agencies of a lot of countries approved the installation of the CX® facility.

The introduction of some new modification have the main task of decreasing the environmental impact making the process comfortable and safe for workers and for neighbourhood.

The new improvements under evaluation can introduce modification deeply changing the process and making the secondary lead production technology cleaner and cleaner.

7. References

[1] Prof. Dr. O. Rentz, Dipl.-Ing. Stephan Hähre, Dr. Frank Schultmann, Report on Best Available Techniques (BAT) in German Zinc and Lead Production, FINAL DRAFT, Deutsch-Französisches Institut für Umweltforschung (DFIU), French-German Institute for Environmental Research University of Karlsruhe (TH), Karlsruhe, February 1999, p. 45-47, 191-194