A CLEAN-LEAD FACTORY IS AVAILABLE FOR LEAD-ACID BATTERIES RECYCLING BY MEANS OF THE “CLEANLEAD PROCESS”

Carlos Frias[1], Nuria Ocaña, Gustavo Diaz, Tony Piper, Brunon Bulkowski,
Andrzej Chmielarz, Peter Claisse, Steve Hemmings, Luisa Abrantes,
Herman Jansen, Joost van Erkel, Ton Franken, Zdenek Kunicky, Teodor Velea

[1]Técnicas Reunidas, S.A.; Calle Sierra Nevada, 16
San Fernando de Henares, 28830 Madrid, Spain

Keywords: Lead, Lead-acid battery, Recycling, Cleanlead, Tecnicas Reunidas

Abstract

The lead-acid battery recycling is a major industrial activity (more than four million tonnes recycled lead per year) that generates large amounts of toxic wastes such as lead slag, mattes and acidic sludge, besides airborne emissions. This is a waste-producer industry that needs a definitive solution to avoid its negative environmental impact and getting a sustainable lead production. That is the principal target of the CLEANLEAD technology, which properly combines both hydrometallurgical and pyrometallurgical routes aiming to get zero-waste production, reducing the use of energy and resources in all phases of battery reprocessing, and consequently, greatly decreasing the operating cost. There will be no toxic emissions to land, water or air, and obtained products are pure lead metal or pure lead oxide, and commercial gypsum instead of waste sludge.

Achievements after pilot plant trials of this new process were quite satisfactory, and preliminary economic estimate gave positive results, opening the way to further developments and potential applications.

Introduction

Above one hundred secondary lead smelters devoted to lead-acid battery recycling are in operation in the world [1], and a major part of them are discarding significant tonnage of toxic slags or mattes to landfill, which represents a serious environmental problem and a lack of sustainability in that important industrial sector.

Usually, the conventional pyrometallurgical process applied for lead-acid battery recycling comprises a breaking and classification unit, followed by drained acid neutralisation to generate a sludge to be disposed of, paste and metallic components smelting which produces toxic and unstable slags (sodium-based slag in most of the cases) and air emissions, and eventually a refining stage to get pure lead ingots for further alloyed lead production (see Figure 1).

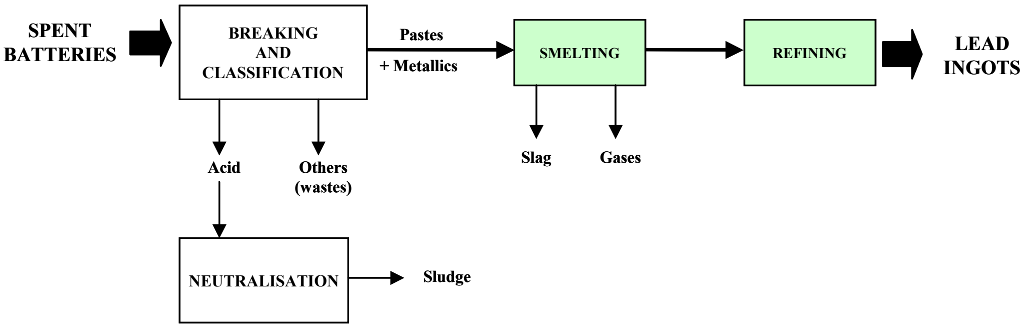

Figure 1. Conventional battery recycling process

For instance, above 200,000 t/y of toxic slags (and mattes) to landfill are produced by secondary lead industries in Europe [2] and disposal of those wastes is being forbidden by European Union environmental regulations due to its leachability and unstable nature of the sodium-based slag.

In some secondary lead smelters battery paste is (partially) desulphurised by addition of sodium hydroxide or sodium carbonate to decrease the SO_2 emissions and to simplify the smelting operations. However, the desulphurisation process is very frequently uneconomic due to reagent cost and energy consumption required for crystallisation of generated sodium sulphate.

Objectives

The CLEANLEAD process has been developed from lab scale to pilot scale by an European consortium composed of battery recycling companies, technology developers and universities. Aim of the project has been to overcome the current environmental limitations and deficiencies of lead battery recycling industries. The developed technology pursuits the following objectives:

- No toxic slag would be produced
- No acid sludge from drained acid treatment is generated
- Minimum SO_2 emission, and any dust or fume is internally recycled
- Metallic parts are smelted at low temperature (<500 ºC), presenting low energy consumption.
- Lower operating costs, less energy requirements, and less consumables
- Commercial gypsum production by turning actual wastes into valuable products
- Safer and more healthy environment for the workers

Main Innovations of the CLEANLEAD Technology

The CLEANLEAD technology deals with all battery components, therefore, three main research lines have been developed within this project, including treatment of drained acid, optimisation of the smelting process, and hydrometallurgical treatment of the battery pastes.

Drained Acid Treatment

In the conventional route, battery acid is neutralised, and obtained waste sludge is disposed of. Matching the objective of no waste production, the proposed new process aims at drained acid purification to yield commercial gypsum by-product. That way, distinct membrane techniques as well as chemical precipitation proved to be suitable for sulphuric acid purification. In addition, diluted acid can be purified through biological treatment by means of H_2S bio-generation.

For acid reuse, electrodialysis techniques have been developed aiming to concentrate the diluted sulphuric acid. Membrane electrolysis was the technique used for drained acid recovery to reuse it in battery refilling. Experiments applied on drained acid of nominal composition led to achieving a purified and concentrated sulphuric acid of concentration around 30% and with very low impurities content (see Table I), being antimony the only impurity that reported values slightly over specifications; nevertheless, antimony is not detrimental for this application.

Table I. Results of membrane electrolysis applied on drained acid

	H_2SO_4 mol/l	Cd mg/l	Cu mg/l	Ni mg/l	Pb mg/l	Fe mg/l	Zn mg/l	Sb mg/l
Feed	1.13	28	67	20	0.2	980	150	74
Anolyte	4.74	<0.02	0.04	<0.1	<0.1	0.3	0.8	78
Catholyte	0.32	97	47	660	<0.1	830	161	0.5

For acid purification and further commercial clean gypsum production, different techniques were tested, and nanofiltration and chemical precipitation led to most promising results.

Nanofiltration. Aim of Nanofiltration piloting was to produce several cubic metres of purified sulphuric acid able for clean gypsum production containing minimum amount of metals. A series of nanofiltration membranes were checked and commercial size Type-D membrane was chosen for testing at the pilot plant (8 m^2 membrane area). The experiments were carried out in the batch configuration. Each time a batch of about 800-1000 litre was concentrated to about 30-40% of the original volume. During this concentration process, the flux, the pressure drop across the module and the pressure were monitored. After concentration, samples were taken from permeate (product) and concentration in the tank (concentrate). Obtained results were very positive, showing a high retention (> 98%) for most of the metals present in the drained acid. Compared to the starting situation, the concentration of the purified acid is a little bit lower than the original drained acid.

Table III - Recovered acid after five nanofiltration cycles in the pilot plant

	H_2SO_4 mol/l	Cd mg/l	Cu mg/l	Ni mg/l	Fe mg/l	Zn mg/l	Ca mg/l
Feed	1.10	180	135	165	3000	1000	1100
Acid product after NF	0.98	1	2	0	9	7	5
Concentrate	1.30	185	141	173	3300	1120	1200

Chemical Precipitation. It was found that NaHS is a suitable reagent for impurities removal such as As, Sb and Cu to avoid contamination of the gypsum by-product. A continuous small pilot plant was set up including chemical precipitation, solid-liquid separation, and oxidation of residual sulphide. The plant operation was about 100 hours under steady state conditions. Experimental results were according with the expectations and shown that treated acid containing less than 1 ppm of As, Sb and Cu can be obtained with a dose of around 1000 g of NaHS.

Commercial Gypsum Production. The gypsum produced out of the treated drained battery acid must fit some physical and chemical specifications concerning morphology, crystals size and shape, density, etc. A complete pilot plant for gypsum production using purified acid after diffusion dialysis (DD) and nanofiltration (NF) was installed and tested. The pilot facility included the following equipment: precipitation reactor with working volume 300 litres, two heaters able to maintain the right temperature, pH control devices, one cubic metre feed acid tank, limestone preparation tank, and two stages of hydrocycloning including pumps and piping.

As for the results, the following data were logged for the different treated acids. Most relevant conclusion was that gypsum samples contain very low amount of impurities as can be observed in Table III, which allows to be applied as a by-product for some commercial applications.

Table III. Gypsum products obtained form different acid sources

Type of acid	Concentration in gypsum, ppm						Apparent density, g/dm^3	d_{50}, µm
	As	Ni	Cu	Zn	Cd	Pb		
Purified by NF	5	0	8	10	2	3	0.73	33
Purified by DD	8	0	3	0	1	5	0.78	30

The gypsum product is a mixture of rhombic and needle forms of crystals. Crystal shape was determined using Optical Microscopy and Scanning Electron Microscopy (SEM). Some representative microphotographs are shown below.

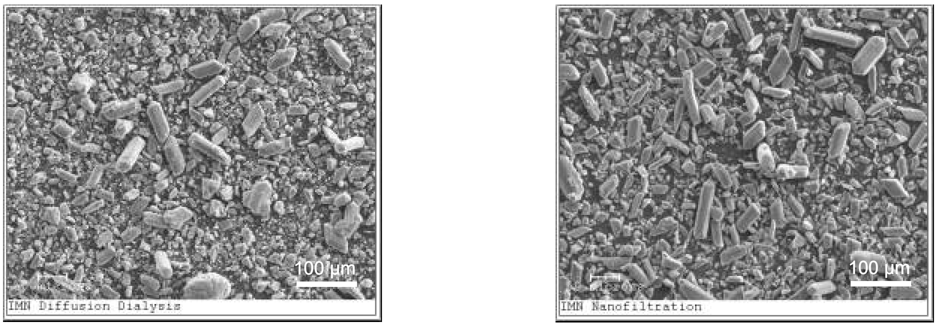

Figure 2. Microphotographs of gypsum from DD (left) and NF (right) purified acids

Optimised Smelting Process

The research work aiming at secondary lead smelting optimisation has been focused on no waste generation as well as lower fluxes and energy consumptions. Besides, stabilisation of slag materials has been studied too.

Different smelting methods have been tested in 15-ton rotary furnace based on previous data obtained in 500 kg capacity pilot furnace. The finally selected smelting method enables direct obtaining of lead bullion and silica slag at relatively low energy consumption (natural gas, 100 Nm^3/t Pb; oxygen 200 Nm^3/t Pb) and high productivity (97% feed lead yields in metal phase). A silica slag of low lead content (2.9 %) was generated.

Slag re-smelting in electric arc furnace was tried to check whether unstable slag could be transformed into stable non-toxic slag, that is, ferrosilicate type slag. The pilot installation for this work included an electric furnace of 1.5 m^2 hearth area, equipped with a 500 kW electric power transformer and 3 graphite electrodes as the main items. Obtained results showed that non-toxic ferrosilicate slag of very low heavy metals content can be successfully produced. The optimal parameters of slag treatment for obtaining non-toxic slag are as follows: sand addition ensuring 40-45% SiO_2 content in silica slag; iron addition stoichiometric amount with PbS content in primary slag; coke addition 2 % of slag mass; slag tapping temperature 1250-1350 ºC.

Hydrometallurgical Treatment of Battery Paste

The aim of this new hydrometallurgical process is to get a cheap and clean alternative to conventional pyrometallurgical route, thus integration with any battery recycling factory would allow a more efficient battery reprocessing, in such a way that the metallic components are directly sent to melting and casting, while battery paste is treated in the hydrometallurgical line to yield either pure PbO by crystallisation or pure electrolytic Pb.

Various techniques have been checked, desulphurisation by means of lime, solvent extraction, and salt splitting. Relevant results are as follows.

Battery Paste Desulphurisation. Pastes desulphurisation by means of lime was tested in a pilot plant having a capacity of 5 kg/h battery paste. Two campaigns of 100 hours each have been performed, and operation was focused on obtaining gypsum by-product from battery paste. In the first trial, the feed was raw paste. As for the second campaign, the plant feed was reduced paste. Obtained desulphurisation efficiency was in the range 95-99%. As main point, it is concluded that paste desulphurisation yield largely depends on residence time. It is estimated that two hours are necessary to reach yields over 95%. Also, regeneration yields are mainly influenced by the sulphate-to-lime molar ratio, a parameter value balancing the regeneration yield and the regenerated OH^- concentration.

Pastes Desulphurisation by Amines. The pilot facility to test this procedure comprises a three-stage counter-current leaching with circulating tri-ethyl tetra amine solution. Inlets are the battery paste and the make-up amine solution and the outlets the desulphurised paste and the spent amine solution charged with extracted lead. This solution is saturated in carbon dioxide to get the lead precipitated as carbonate. The amine solution is regenerated by means of adding lime. When adding lime, gypsum is produced simultaneously. After sedimentation and phases separation, a gypsum suspension as well as a regenerated amine solution is obtained.

Regeneration of NaOH by Membrane Electrolysis. This work studies the possibility of splitting the sodium sulphate solution into sodium hydroxide and sulphuric acid by a membrane electrolysis technology with bipolar membranes. Laboratory tests were done with synthetic solutions to assess the technical and economic feasibility. The electrolytic cell includes two sets of membranes present in the reactor; each set was composed of 1 bipolar Membrane (BPM), 1 anion exchange membrane (AEM) and 1 cation exchange membrane (CEM) and thus creating 3 compartments: one for the sodium sulphate solution, one for the sulphuric acid solution and one for the sodium hydroxide solution. On the basis of the lab tests results, a preliminary estimation is performed for three cases, including the production of 4 N NaOH in one stage EDBM, 2 N NaOH in one stage EDBM and 4 N NaOH in two stages EDBM. It is found that lowest costs per ton lead produced have to be paid when 1 mol/l Na_2SO_4 solution is split into 2 mol/l NaOH and 1 mol/l H_2SO_4.

Electrolytic Lead Production. The stages of the hydrometallurgical pilot plant having a capacity of 400 kg/d electrolytic lead were battery paste leaching and subsequent lead electrowinning, both in alkaline media. The hydrometallurgical pilot plant includes a control system allowing on-line information obtaining of the operation parameters such as levels, flowrates, temperature, etc., and also enables the operator to take actions over the process parameters in real time.

Three campaigns of 100, 100 and 200 hours respectively were carried out. Aim of first campaign was to check behaviour of the equipment and prototypes and the process itself. During initial run, the plant was conducted to reach a continuous operation and trying to get proper adjustment of the control system and instruments. Second campaign was changed to run in a single step due to low level of impurities yielded in first run. Aim of the third campaign was to sound the proposed hydrometallurgical process by running at steady state conditions. The leaching stage average data offer 95% yields. In the commercial plant the leaching residue would be recycled to battery breaker; therefore, no waste is generated in this application. Current density in the range 200 to 1000 A/m^2 was checked (see Figure 3); finally current density was set at 650 A/m^2, which allows obtaining an energy consumption of around 0.6 kWh/kg Pb and a current efficiency close to 100%.

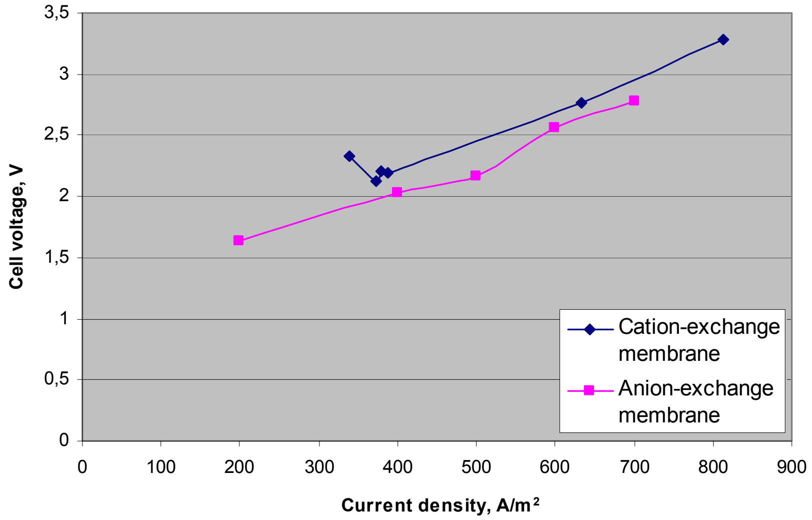

Figure 3. Pilot cell results regarding cell voltage vs. current density

Tracked impurities as Sb, As, Sn, Bi and Cu did not exceed from 5 ppm in the lead deposit when treating well desulphurised paste. In general, pilot plant results have been quite satisfactory, and the fundamentals and performance of lead electrowinning in alkaline media have been soundly proved at pilot cell scale with industrial size electrodes. Nevertheless, some operational deficiencies were detected that would require additional effort in the future, such as membrane selectivity and mechanical resistance.

Pure Lead Oxide Production. A pilot facility including a leaching vessel with system for mixing and heating, a centrifugal pump, a nuche filter, a vacuum pump and a settler for drops, was installed to produce pure PbO crystals. The reduced and desulphurised paste goes to leaching in concentrated NaOH mother solution coming from the settling of PbO by crystallization from the previous step (the initial mother solution was obtained in six experiments made with fresh solution and fresh paste and homogenized). The recycling of the mother solution obtained after the settling of PbO crystals, at the next step of leaching, has a significant influence on the leaching and crystallization process efficiency. After three continuous cycles, the content of impurities in crystals of PbO remained constant. Silica content was higher than expected likely due to the glass vessels used for experimentation.

Table IV. PbO crystals obtained at the pilot plant

Step of recycling	Ag ppm	Si ppm	Fe ppm	Bi ppm	Sb ppm	Ca ppm	Cu ppm
Initial	-	540	7	3	32	-	5
Third cycle	3	595	10	6	32	-	6

Preliminary CLEANLEAD Process Evaluation

After piloting of the main process steps, the developed technologies have been integrated into a whole CLEANLEAD Process and a preliminary evaluation has been performed based on environmental, technical, and economical parameters.

A conceptual process diagram is shown in Figure 4 and main results and conclusions of this work are presented below.

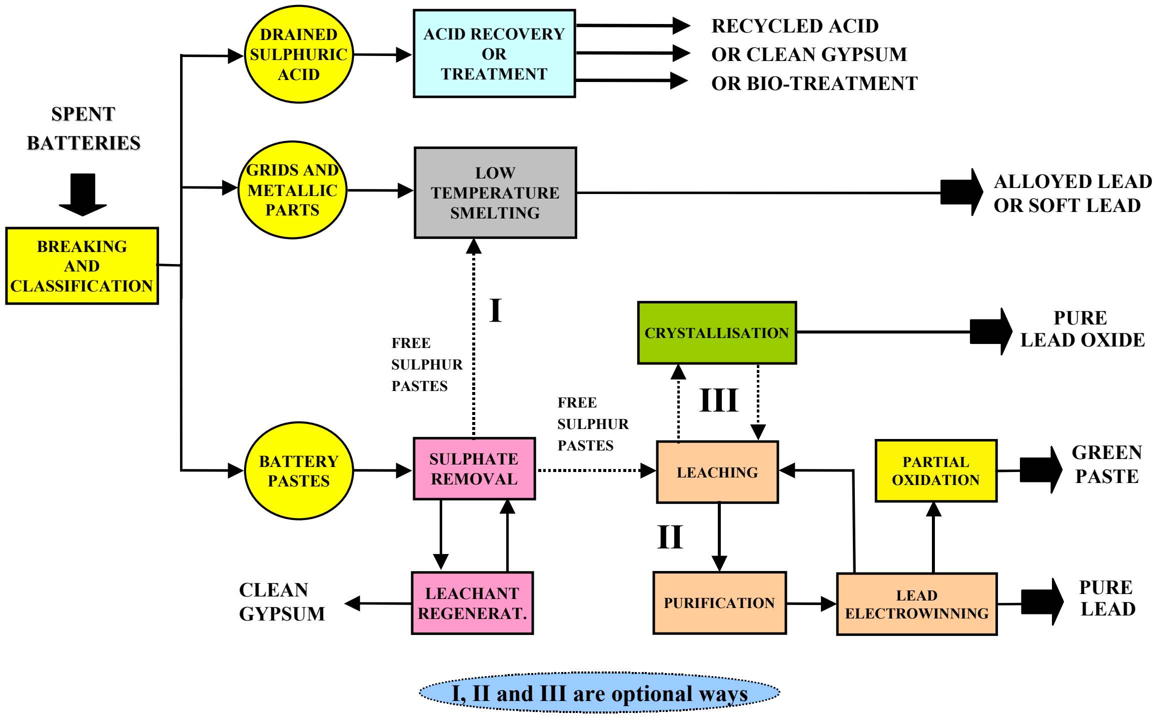

Figure 4. Conceptual diagram of integrated CLEANLEAD Process

Preliminary Environmental Analysis

Comparative analysis of the new proposed technology against conventional technology for lead batteries treatment is shown in the following table based on Life Cycle Analysis results.

Table V. Environmental parameters of conventional process vs. CLEANLEAD process

Parameter	Unit	Conventional Process	CLEANLEAD Process
Energy consumption	MWh/t Pb	1.5	1.0
Battery breaking wastes (plastics, separators)	t/t Pb	0.1	0.1
Toxic slags	t/t Pb	0.3	0
Exhausted gases	Nm^3/t Pb	70,000	5,000
Drained acid sludge	t/t Pb	0.2	0
Gypsum commercial products	t/t Pb	0	0.4

It is remarkable the good potentiality of the CLEANLEAD technology to get zero-waste generation in lead battery recycling.

Preliminary Economic Evaluation

A preliminary economic evaluation was carried out to get the proposed technology compared with the conventional technology. To perform this assessment, nominal capacity has been set at 50,000 t/y of spent batteries. The lead batteries composition would be as follows.

Table VI. Battery components fed to the process

Component	Weight, t/y	Content lead, t/y
Drained sulphuric acid (10-15% H_2SO_4)	14,000	---
Plastic box, cover and separators	4,000	---
Metallic parts: connectors, grids…	12,000	12,000
Battery pastes	20,000	14,667
	50,000	26,667

Evaluation procedure was based on conceptual design and economic estimate of the three sections of the whole plant, including drained acid treatment, smelting process, and hydrometallurgical treatment of the pastes. A summary of obtained results compared with conventional battery recycling process is presented in Table VII.

Table VII. Comparative costs of the CLEANLEAD process vs. conventional process

Process Step	Conventional Process	CLEANLEAD Process
Breaking & Classification	25 €/t Pb	25 €/t Pb
Drained Acid Treatment	10 €/t Pb	0
Smelting/Hydrometallurgical	170 €/t Pb	118 €/t Pb
Melting and Casting	32 €/t Pb	32 €/t Pb
Waste or By-products	Wastes: Slag, 300 Kg/t Pb Acid Sludge, 200 Kg/t Pb Disposal cost: 20 €/t Pb	By-product: Gypsum, 550 Kg/t Pb Associated cost: 19 €/t Pb
Total Operating Cost	257 €/t Pb	194 €/t Pb

The engineering work covered process flowsheeting; material and heat balance; equipment pre-design; estimate of capital cost; estimate of operating cost based on gathered information and real data provided by industrial partners of the project. It can be pointed out that the new CLEANLEAD Process presents, at least, 25% lower operating cost than conventional technology, avoiding at the same time any waste generation.

Investment cost varies in a range of 8.0 to 10.5 million Euro, depending on the different process stages combined in the new battery recycling plant. Anyway, depreciation cost has fewer relevancies than operating cost on the project profitability.

Conclusions

The CLEANLEAD process stands as an innovative and global solution that faces the current limitations of secondary lead industry. The advantages that present this new technology can be summarised in the following points:

- Main aim is getting a sustainable lead battery recycling activity for the 21st century.

- Other important target is zero-waste emission process, avoiding environmental damage and disposal costs, and producing reusable valuable products.

- Getting energy saving in the improved smelting operations, and producing stable and reusable slags rather than toxic slags as usual in conventional battery recycling industries.

- Sustainability thanks to consumables cost savings since very small amount of raw materials is used.

- Development of a novel and low-energy hydrometallurgical process in alkaline media to obtain either pure lead oxide or pure electrolytic lead.

- Process flexibility, adapted to local market conditions and needs.

Acknowledgment

This project is partially funded by the European Community under "Competitive and sustainable growth" Programme within V Framework Programme. The authors wish to acknowledge the support and help they got from the European Commission to afford this project.

References

1. International Lead and Zinc Study Group, *Annual Lead and Zinc Statistics Report*, January 2005.

2. European Commission, IPPC Directive, *Reference Document on Best Available Techniques in the Non Ferrous Metals Industries*, December 2001.