

Environmentally sound technologies for recycling secondary lead

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Abstract

Advances in hydrometallurgy are providing increasingly simple means for controlling the entire lead chain from concentrate to recycled lead. Used in parallel with pyrometallurgy, these processes allow furnace temperatures to be reduced to the minimum, which is essential for casting or alloying. Fumes and atmospheric pollution are minimized, furnace slags are digested, and most residues (other than purification cements) are non-toxic and convertible into marketable products. These new processes provide the cleanest and healthiest practicable means for recycling lead from batteries. By substituting melting for smelting, the heat requirement and cycle time per charge are reduced by more than half. A new hydrometallurgical plant could be installed alongside an existing pyrometallurgical plant without interference, doubling its potential capacity when operational (and more, if electrowinning is used). Over 99.5% of the lead originally present is recovered in tests of a combined PLACID–pyro plant. The average purity of electrowon PLACID lead is 99.995%. Results from the PLINT process should be similar. The purity of the lead chain can thereby be sustained through recycling. Perfect solid/paste separation is not mandatory, and PLINT-type plant units can be of any size. Such processes constitute a good basis for development of clean processes, which are suitable for use in Asian societies. © 2000 Elsevier Science S.A. All rights reserved.

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1. Background

This paper describes advances in the recycling of secondary lead that appear to be opportune for lead industries in general, and for those now being created ab initio in Asia in particular. They have all been identified by recent and current work in the Research and Development Centre ('R & D Centre') of Técnicas Reunidas ('TR') at Torrejón de Ardoz near Madrid in Spain. Because this has been an evolutionary process, several of the steps described have been tested only in bench-scale pilot-plants, and opportunities are still being sought for commercial demonstrators. By virtue of this cumulative experience, however, TR believes that its predictions will be vindicated. Nevertheless, there is a call here on the reader's confidence.

Because the credibility of any claim made depends on who makes it, one cannot avoid describing here the background experience on which it is based. The Commission of the European Union ('CEU') also demands a mention for its support at an early stage.

Although unknown to most English-speaking engineers, TR is a substantial private company, founded in 1959 to undertake the design, procurement and construction of industrial and process plants as well as fossil fuel and nuclear power plants. The company has worked in 25 countries (mostly Spanish-speaking) on more than 350 major projects with a combined value exceeding US\$20 billion. It is now the largest company in Spain, and among the top 10 contractors worldwide in its field. The R & D Centre was founded in 1972 as a self-contained, semi-autonomous unit, to develop a new industrial capability based on hydrometallurgy. In the intervening quarter century, it has undertaken pilot-plant demonstrations of more than two dozen hydrometallurgical extraction processes for cadmium, cobalt, copper, gold, lead, mercury, nickel and zinc. Many of these demonstrations have proceeded to full

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commercial exploitation. The ‘Modified ZINCEX’ process, in particular, is acknowledged to be a front runner in its class.

In the 1980s, TR was asked to develop a process for the recovery of lead from low-grade lead concentrate mined south of Spain. The pilot-plant of the ‘LEDCLOR’ process, described below, was successful, but at that time there was a crisis in the lead market and the market price of lead had already started to fall. Accordingly, the client abandoned the project. Some time later, an ion-selective membrane became available that permitted the use of acid brine as electrolyte. TR recognized the significance of this for lead recovery from scrap batteries, and encouraged the formation of an English-speaking consortium — LeRe-fLeOS — to develop this concept. The partners are: TR (the project manager), TNO (The Netherlands), University of Lisbon (Portugal), University of Alicante (Spain), Quimitecnica (Portugal), and David Andrews Projects (UK). Application was made for support to the CEU, who acknowledged the significance of this development by awarding it the largest Brite EuRam grant ever made at that time (1993). This was to cover half the research and development costs incurred over a 3-year period. A 4-month extension was later granted to cover the preparation of reports. The shortfall was made up by the partners. It was soon found that the initial expectations of TR have been justified, and the ‘PLACID’ project was completed on time, within budget, and with all technical objectives surpassed.

As is usual in hydrometallurgy, lead was extracted from the PLACID process by electrowinning. While electrowinning is generally acceptable for the extraction of valuable metals, however, the high capital cost of the electrical installation and electrolytic cells appeared disadvantageous to established smelters when compared with the existing (and possibly the future) market price of lead. Electrowinning is superior for plants producing more than about 20 000 t a year of electrolytic lead, but before such a plant can be started, someone must first be persuaded to provide a small demonstration plant.

One smelter, who had witnessed the operation of the pilot-plant at Torrejón in 1995, suggested that it might be possible to process the electrolyte to precipitate a lead compound that could be fed into a furnace for decomposition or reduction. TR has since worked on this concept for 3 years, and this has resulted in the definition of the ‘PLINT’ process described below. The confidence engendered by this success has caused TR to review its conception of the scope of hydrometallurgy for lead processing. No longer is the aim to promote a ‘best’ hydrometallurgical process, as measured against conventional standards, but to design processes that best take account of the constraints within which users operate. The emergence of this confidence can be seen in the discussion that follows, and the effect of this transformation can be seen in the choice of topics for future research.

2. Elements of process design prior to lead extraction

2.1. Hydrometallurgy vs. pyrometallurgy

The essential characteristic of hydrometallurgy is that the metals to be processed are dissolved in liquids and then processed as in other chemical operations. In espousing hydrometallurgy as its specialty, TR is not contemptuous of pyrometallurgy — the processing of materials in furnaces — the advantages of which are fully recognized. Hydrometallurgy is, however, more exact, more predictable, and more easily controlled. Hydrometallurgical processes are also cleaner in themselves, and in combined-cycle plants, they can be used to reduce furnace temperatures. This will reduce the energy demands and environmental impact of smelting, and increase the productivity of existing pyrometallurgical plants.

Pyrometallurgy is more limited in its application, because furnace contents must be essentially mobile for impurities to float to the surface and metal product to be pourable. Hydrometallurgy makes no such demands.

2.2. Leaching

This is the initial step in a hydrometallurgical process in which all accessible soluble metals in the feedstock are dissolved. The metal content in the feedstock can be quite low. In the LEADCLOR process, for instance, the design requirement was to extract lead from concentrate containing only 40 wt.% lead, but the process would have extracted lead from much lower grades. When, in a PLACID-pyro process, the measured extraction rate was 99.5% overall, this was because the leaching process extracted available lead from slags already rejected by the furnace operation. Hydrometallurgical processes can be used to purify slag mountains or even contaminated earths.

The composition of the solvent liquid — the leachant — can be varied. For instance, in the original PLACID process it was dilute hydrochloric acid brine, which is a reducing agent, while in the LEDCLOR process it was a dilute solution of ferric chloride, which is an oxidant. The result, in a given time, does depend significantly on the accessibility of the metals. This can be seen in a comparison of the measured efficiency, when leaching concentrate having 40% to 45% lead content but only 250 to 400 ppm of silver, with the efficiency when leaching battery pastes/fumes with a lead content of 70% to 75%. In pilot-plant operation of the LEDCLOR process, after 300 h of treating concentrate for an output of 10 kg of lead per hour, 97% to 99% of the lead was dissolved, but only 80% to 82% of the silver. In the final two campaigns of the PLACID pilot-plant operation, leaching from representative battery pastes/fumes mixtures showed an efficiency of 99.4% to 99.7%. Leaching efficiency may perhaps be influenced by the penetrating capability of the leachant,

but it is not dependent on the nature of the subsequent process.

It is worth mentioning that the leachants used by TR in these PLACID PROCESSES are almost entirely common place. At no time did TR find the need to use vicious leachants like fluosilicic acid or fluoboric acid, which other researchers seem to have tested for this purpose [1].

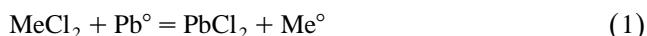
2.3. Desulfurization

Several desulfurization processes have been used. In the LEDCLOR process, for instance, lead sulfide is reacted with ferric chloride to release elemental sulfur. In cases in which sulfur is present in lead sulfate, the preference usually is for a reaction with lime (about the cheapest material suitable for this purpose) to form gypsum, which is then extracted by filtration. In 1992, when the development of the PLACID process was first proposed, it seemed reasonable to suggest that this gypsum should be distributed in landfill; but circumstances have changed. Gypsum is slightly soluble — about one part in 450 in cold water — so as landfill, it must be contained. This has raised the cost to an uneconomic level, which will rise further.

TR has since developed techniques where the gypsum can be produced pure in any mix of its three morphologies (hydrated, hemi-hydrated and anhydrous) to suit market demands. Coventry University assisted in defining the commercial requirements — in particular for its use as a moderator in cement to control the setting rate. There is so much surplus gypsum, however, that its enforced sale keeps the market price low — the real benefit in this is not having to pay for its disposal.

2.4. Purification

A typical purification technique involves injecting lead powder into the leachant or electrolyte to enable a radical, which is attached to the molecule of an impurity metal, to be transferred to a molecule of lead. This frees the impurity molecule and allows it to bond to a residual unattached lead molecule to create cement. In the PLACID process, for instance, if Me is taken to represent an impurity metal, the purification reaction is:



The leachant is then filtered to remove the cements.

The efficiency of the process is governed by several parameters, so the purity of the electrolyte remaining is under the control of the system designer or operator to some extent. It is noteworthy that the residual impurities in the catholyte in the LEDCLOR pilot-plant tests were less than 5 ppm of silver, and less than 1 ppm each of

antimony, copper, magnesium, arsenic and bismuth. Zinc and iron, which were present in large quantities in the original concentrate, were removed without trace.

Of course, the concentration of impurities in the catholyte does not translate directly to the concentration of impurities in the lead. In the last campaign of the PLACID pilot-plant tests, the impurities in the lead product were: copper at 9 ppm, antimony at 19 ppm, arsenic at 2 ppm, tin at 1 ppm, and bismuth at 2 ppm. Impurities removed by filtration are contained in lead cements, whose value depends on the constituents of the feedstock. In the LEDCLOR trials, for instance, the silver grade was between 1% and 2%, which was sufficiently valuable to justify extraction by refining.

Normally, in secondary smelting, the production of lead of primary quality (99.99%) is not the aim, and impurities present in the feedstock are passed to the product. If, however, lead of the highest purity is produced from pastes, it may be necessary to absorb the rejected cements into secondary or other commercial grades of lead in parallel smelting operations. If the processes being used are designed like PLACID or PLINT, i.e., to provide high purity lead, and it is considered unnecessary to produce this primary quality lead at some time, the purification step can be disabled simply by cutting off the supply of lead powder. Purification steps are included in all these processes, except the CLEANLEAD process. CLEANLEAD is the simplest of these processes, but it is not supposed that this deficiency is irremediable.

2.5. Regeneration

In all these processes, reagents are regenerated and re-used, sometimes by the use of quite sophisticated procedures. Only lime is used in any quantity; the amount is directly proportional to the quantity of lead sulfate present in the feedstock. Small quantities of reagents are consumed in some processes for clean-up circuits and to replace reagents passed as impurities.

2.6. Sophistication

The demonstrated effectiveness of the PLACID PROCESSES results from the fact that the chemical reactions employed are simple, positive, and complete at each step. This makes for stability and dependability. Meaningful measurements can be made, and the operator in the control room can monitor plant behaviour at each point in the process and make adjustments if needed. Whether processes will go or not may depend on factors such as temperature, concentration, residence time, sequence, rate of mixing, mode of mixing, acidity (pH), and catalysis. These factors are mostly determined by the decisions of the system designer, and do not require improvisation.

3. Lead extraction processes

3.1. Electrowinning

In only two of the processes discussed here is electrowinning relied upon in the extraction of pure lead. Mechanically, the cells used in these two processes are rather similar (as mentioned above), but the electrolytes and recombination processes are different.

The description of the PLACID process given by Pngaman [1] is inaccurate in several respects [2], particularly with respect to the electrowinning cell. A single PLACID electrowinning cell is illustrated diagrammatically in Fig. 1. The electrolytes for the two electrodes — the anode and the cathode — are different, and are separated by a membrane that is permeable only by proton ions (H^+). Because an electron is said to be a negative charge, a proton ion is said to be ‘positively charged’ because it is a hydrogen atom stripped of its electron. On the cathode, lead chloride is stripped of its lead atom, which leaves two chlorine atoms that are ‘negatively charged’ (having additional electrons). These negatively charged chlorine atoms combine with protons passing through the membrane to reform hydrochloric acid, which is returned to the leaching bath for reuse.

The designs of these cells are unusual. Instead of depositing lead on to metal plates, as is conventional, electrolysis deposits lead as dendrites, which are subsequently shaken off and collected on a conveyor belt, as shown. Immediately after leaving the electrolyte, the dendrites are rolled to express the liquid and to form platelets of pure lead, which can then be conveyed to a kettle for casting into ingots.

There is no special virtue in the conventional practice of depositing the lead on to the plates: the plating process must be interrupted periodically while plates are replaced, and there is no application for lead in the form of discrete thin flat plates. There are important cost and convenience virtues, by contrast, in depositing lead as dendrites because then the amperage can be increased by a factor between 4 and 10, which greatly reduces the number of electrolytic cells that must be provided for a given throughput of lead product. And the whole of the extraction process can be run continuously, without interruption.

Unlike most processes in hydrometallurgy, electrowinning is scale-sensitive. Electrolyte must be brought into

contact with both the anode and the cathode, and must then be removed from those surfaces once the chemical changes have been effected. These mass-transfer processes are hydraulic, and fluid streams, vortices and gravity have important effects. The individual electrolytic cells (i.e., each corresponding to the diagram in Fig. 1) used in both the LEADCLOR and PLACID process pilot-plants were full-scale, and output can be adjusted only by changing the number of such cells in use.

Electrowinning is a capital-intensive process — largely because of the electrical transformers and rectifiers needed — and although direct operating costs are lower than for pyrometallurgical extraction processes, the amortization costs are not insignificant. Electrowinning is most advantageous for large plants.

It is strongly recommended that advantage be taken of the cost reduction made possible by use of a combined-cycle generating plant. Waste heat from an engine can then be used to maintain leachant temperatures at appropriate levels (typically about 80°C) and effect drying and evaporation where required.

3.2. Pyrometallurgical extraction

Lead can be extracted from battery pastes by smelting, but the temperature required for decomposition of lead sulfate is very high — typically 1100°C or above. The problems that such high-temperatures entrain are well understood.

Even with electrowinning — whether by deposition to plates or as dendrites — it is ultimately necessary to melt the lead product in order to cast ingots or to create alloys. This provides an opportunity for an alternative approach that eliminates the capital costs associated with electrowinning. If the pure electrolyte can be converted into a solid, like lead carbonate or lead hydroxide, by hydrometallurgical means, the final kettle can be relied upon to isolate the lead by pyrometallurgical means. This combination has a double benefit. The kettle then has only solids to deal with, for which a temperature of around 500°C is probably adequate. Because this temperature is half what it would have been, the amount of energy that must be provided to heat a charge is halved, and the time taken to smelt this charge is reduced by a half or more. The kettle is then able to accommodate the additional mass of lead compound supplied by the hydrometallurgical process, which allows throughput to be increased by a factor of two or more.

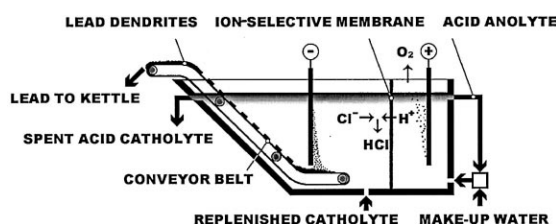


Fig. 1. Schematic of PLACID lead-electrowinning cell.

4. Existing and available processes

4.1. LEADCLOR process

At the head of the lead chain, and the first of this series to be developed, is the LEADCLOR process (originally

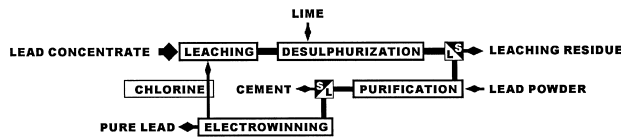


Fig. 2. Block diagram of LEADCLOR process.

entitled the LEADCLOR process). It was developed under contract to recover lead from low-grade concentrate (40% to 45% lead content) from a prospective lead mine. A pilot-plant, which produced 10 kg h^{-1} of pure lead, was erected and tested successfully in the yard of the TR R&D Centre in 1988.

A block diagram of this process is shown in Fig. 2. The leachant in this case is a dilute solution of ferric chloride, which reacts with lead sulfide to form ferrous chloride and elemental sulfur. Electrolysis dissociates the residual lead chloride into its elements, and the chlorine is collected and used to oxidize the ferrous chloride, thereby reforming ferric chloride for re-use as leachant. The process has a purification step enabling lead of 99.99% (or higher) purity to be obtained, which meets the accepted requirements for primary lead. Details were published in the Tenth International Lead Conference in Nice in 1990 [3].

An important element of this development was the new METCLOR electrowinning cell, on which the initial design of the PLACID electrowinning cell was based. The design of this process has now been updated to take advantage of lessons learned in the development of the PLACID process. This emphasizes the benefit of parallel development once processes have become mature. The client decided not to proceed with the project, and the concept has been ‘mothballed’. Nevertheless, it is still a good process, valid for any similar application.

The LEADCLOR process is not compatible with the PLACID process, and it is therefore not possible to use the PLACID electrowinning cell for recovering the lead from concentrates. TR recognized, however, that there may be an interest in associating these two processes, and designed a chemical step to enable this, but so far has not been called upon to develop it.

4.2. PLACID process

Much about the PLACID process has already been described in previous sections. The block diagram is shown in Fig. 3. The name comes from PLomo + ACIDo. The leachant in this case is dilute acid brine, and the desulfur-

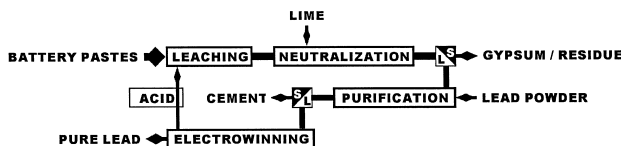


Fig. 3. Block diagram of PLACID process.

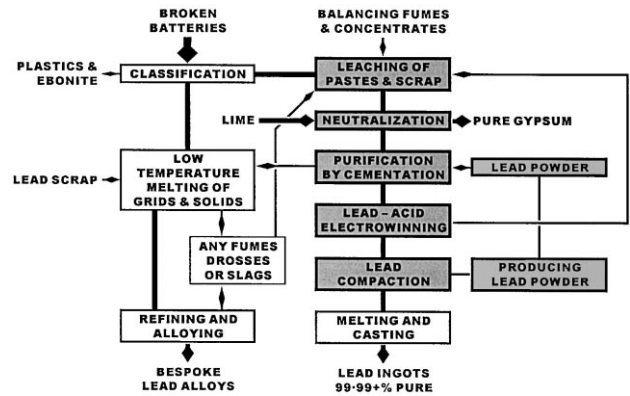


Fig. 4. Block diagram of PLACID process used in parallel with a pyrometallurgical smelter.

ization sequence is quite interesting. The lead sulfate reacts with salt to form lead chloride and sodium sulfate, and the lead sulphate then reacts with hydrochloric acid to yield the gypsum, at the same time reforming salt ready for re-use in the leachant.

Pilot-plant development in the laboratories of the TR R&D Centre was carried out in four 12-day campaigns in the first half of 1995, during which 10 t of lead were produced. In May of that year, the International Lead–Zinc Study Group held a Conference in Madrid, and 15 delegates to that conference went to Torrejón de Ardoz to witness the process in operation in the final campaign.

On conclusion of the pilot-plant operation in the laboratories of the TR R&D Centre, several papers were published [4–6].

4.3. PLACID–pyro combined cycle

Early in the first year of the project, consultation between TR and a Spanish smelter revealed that the PLACID process could be improved if it were used in parallel with a pyrometallurgical smelter. The arrangement is shown schematically in Fig. 4 where ‘boxes’ showing the steps in the PLACID process are shaded. A study of this diagram reveals that the fumes, drosses and slags (if any) from the pyrometallurgical line can be passed to the leaching bath of the PLACID line, and the cements from the purification step are fed into the furnace.

4.4. PLINT process

By 1998, the TR R&D Centre was satisfied that it knew enough about the PLINT concept to justify proceed-

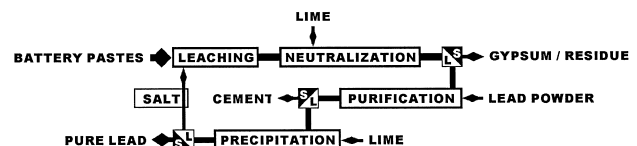


Fig. 5. Block diagram of PLINT process.



Fig. 6. Block diagram of CLEANLEAD process.

ing with development on laboratory bench scale (note PLINT = PLACID + INtermediate). As can be seen by comparison of the block diagrams in Fig. 3 and Fig. 5, the only difference in principle between this process and the PLACID process is in the substitution of a precipitation step for electrowinning. In the subsequent kettle, the lead hydroxide product is first decomposed and then reacted with hard coal to obtain pure lead. All that takes place at a temperature no higher than is required for casting or alloying. Because the leaching and purification processes are unchanged, the leaching efficiency of this process and the purity of the lead produced should be the same as in the PLACID process.

Obviously, it would be possible to integrate a PLINT process line with a pyrometallurgical line to create a system similar to that in the PLACID–pyro process, but to give the division of 99.99 + % purity lead and recycled lead it would then be necessary to have separate, dedicated kettles. Development of this has proceeded to the stage where a demonstration plant is needed.

4.5. CLEANLEAD process

As a separate development, the TR R&D Centre has explored the possibility of using alkaline media for leaching. This makes it rather easier to get high purity gypsum as a by-product. So far, means for purification of the precipitate have not been tested. As can be seen in Fig. 6, this is a very simple process, one that is easy to operate. It has been tested successfully in continuous operation of a pilot-plant, which processes 0.5 kg h^{-1} of battery pastes. Scaling is considered practical because only conventional

equipment is required, but obviously testing at a larger scale would be valuable.

5. Future developments

It appears probable that the CLEANLEAD process could be adapted to meet the requirements for simple plant to remove the worst of the hazards associated with battery reconditioning and unlicensed smelting in various parts of Asia.

One of the major disadvantages of all processes concerned with the recovery of 99.99% purity lead is that this lead is most readily obtained from desulfurization of battery pastes, and separation is needed. On a large scale, recourse is to battery breakers, but these are expensive, and separation is often carried out by hand. The TR R&D Centre is considering means whereby this separation could be avoided in small-scale operations. In short, the availability of this technology has opened a window of opportunity, and inquiries are invited.

References

- [1] R.D. Prengaman, Recovering lead from batteries, JOM (US TM-MMS) (1995) 31–33, January.
- [2] G. Díaz, Lead recycling, letter, JOM (1995) 3–4, June.
- [3] J.L. Alvarez, E. Hermana, D. Martin, F. Martin, LEDCLOR process for low grade concentrates and wastes, in: Tenth International Lead Conference, Nice, France, May 1990.
- [4] G. Díaz, C. Frias, L.M. Abrantes, A. Aldaz, K. van Deelen, R. Couchinho, Lead-acid battery recycling by the PLACID process — a global approach, in: TMS Third International Symposium on the Recycling of Metals and Materials, Point Clear, AL, 12–16 November 1995.
- [5] G. Díaz, D. Andrews, Placid — a clean process for recycling lead from batteries, JOM (1996) 29–31, January.
- [6] G. Díaz, D. Andrews, Batteries International (1996) 73–74, April.