5th World Lead Conference - Istanbul
19-20 March 2013

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# Past, present and future of lead battery recycling

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"The alchemist's dream comes true: lead turns into gold."

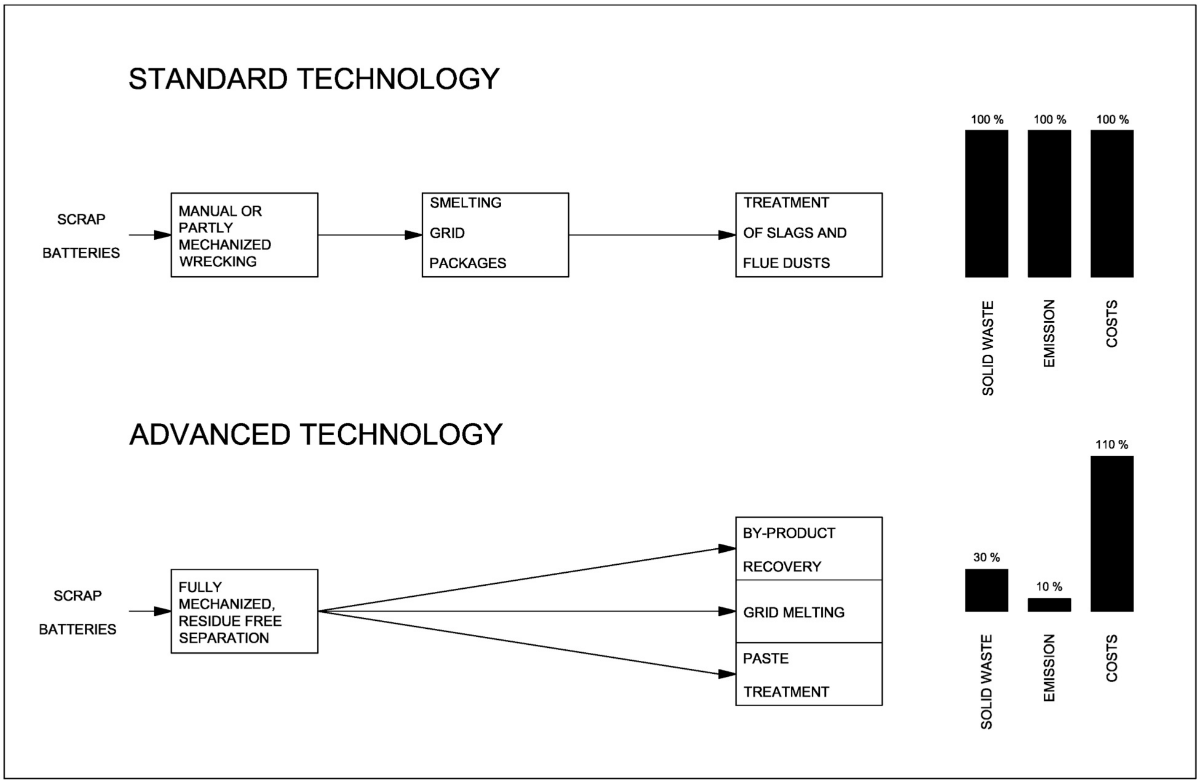
**Abstract**
Even today, the use of Lead-acid batteries is projected for the next 50 years. On the other hand, the legislative trend concerning human health and the environment makes evident the need for future innovation on recycling technologies.
For this reason, the entire world is working, in the short term, in optimizing and adapting technologies, which today we consider BAT (Best Available Technologies).
In the medium and long term, we must rather think of a radical change of technologies, including robotic technologies and futuristic scenarios with low temperature processes without emissions, for example using hydrogen as reducing agent.
In this paper we describe, STC activities in these directions, in part within a research project funded by the Italian Authorities.

## Introduction

Why is energy storage, such as the old Lead acid battery, still a leader in the market after nearly a century, with interesting prospects for the next 50 years? Certainly, for the very high reliability achieved in its use even in the most severe conditions, but also for the relatively easy recyclability of its component materials.
Over the past hundred years, the business of battery recycling, in the developed countries, has evolved from a simple, small junkyard's activity, in complex industrial activities, concurrently with the growing of automotive industry and, consequently, with its larger economic interest. This rapid evolution has highlighted all the major environment related problems.
The crucial aspects of recycling and recovery activities are not just a matter of process technology, but concern also the collection, selection, storage and transport of exhausted lead acid batteries. During the 1980s and 1990s, in Europe, the Authorities established public-private Consortia for the collection of batteries and their redistribution to secondary lead smelters.

In the late 80's, technologies, that today we consider up to date, were already available, but this is an unstable situation because new restrictions are foreseen in the next future. One example is the recently proposed REACH (Registration Evaluation Authorization and restriction of Chemicals) candidate listing for authorization by the EU Commission of many lead compounds, including compounds used in the manufacture of lead-acid batteries and contained in the lead battery recycling materials. This means that, in the near future, we will need process innovation to adapt them to the new rules.
As in all industrial sectors, also in the metal recycling activities the world is sharply divided: on one hand the industrialized countries, where production processes developed a whole range of knowledge relating to the specific industrial impact on human health and the environment. On the other hand the developing countries, which are rapidly aligning using the available knowledge. In a short time, they must necessarily conform to common rules on respect of man and the environment: precisely because, due to the existence and availability of all the developed knowledge, no Authorities in the world can justify the absence of compliance with these rules, nor politically, nor ethically. The technological scenario of the future is essentially based on this statement.

**The past**
In the past, the aim of metal recycling activities was always to gain profit and economic returns linked (determined) all innovations. At the end of the '60s, in secondary lead plants, technologies were implemented to separate the various fractions, metal, plastic and lead sulfate-oxide powders, contained in the crushed product after a pre-drying treatment. This approach has produced an unsustainable pollution, mainly dust, in the work places.
In the seventies, during the first energy crisis, these activities were re-evaluated in terms of preserving resources and energy saving and consequently a higher attention to environmental problems has triggered a process of innovation in recycling activities. In this period, the efforts to adapt the process to the increasingly stringent laws and to control the risk of these activities on the human health were significant and expensive. During this period, a new process based on wet separation technologies was implemented and in Italy, at the beginning of the '80s, TONOLLI started, with the breaker system, the first fully mechanized and automated secondary lead plant in Paderno Dugnano, a historical site where the industrial recycling activity began in 1938.
At the beginning of the nineties, a significant increase in treatment costs, related to an improved process based on paste desulfurization and the use of oxygen in the furnace burner, was well accepted because it led to a drastic reduction in pollution and waste.




R. Guerriero - *Resources, Conservation and Recycling*, 10 (1994) 129
Elsevier Science B.V.

The heart of the process, the source of the most significant environmental problems, is the furnace. Various kinds of smelting furnaces were tested: shaft and reverberatory furnaces, long rotary kiln for continuous operations, etc. Based on the results of all these experiences, the most extensively used furnace has been the short rotary kiln, which presented many advantages, among them:
- It was not dependent on the type of fuel: the burner could be fired with gas, oil or any pulverized fuel with enriched air or pure oxygen.
- Its batch operations allowed a great flexibility of the process changing parameters and composition of the charge.
- The very low thermal capacity allowed shutting down the furnace without important losses of energy and productivity.

Fundamentally, technologies considered, until today, the best available were carried out in the nineties.
Speaking about the past, for us is impossible not to remember a great Italian engineer Marco Olper founder and leader of ENGITEC: Marco was a star in the world of lead metallurgy, and many innovations produced in this and in successive periods are connected to his name.

**The present**
Respecting rules means to have under control, in subcritical conditions, gas emissions, dust emissions and the quality of slag.

The present technological situation seems to be stable. In the industrialized countries, lead recycling plants do not present large differences in the mechanized first part of the process: emptying from acid, crushing the batteries in a hammer mill and separating the different materials (polypropylene, polyethylene, metallic Lead and Lead paste) by wet sieves and gravimetric, hydrodynamic devices.
After this point, the processes are divided into two different types: in some plants, the control of Sulfur dioxide emission is obtained by treating the gas stream from the kiln; in others, such control is obtained eliminating the sulfates in the kiln feeding.

*Flue gas treatment*
The main technology is to treat the flue gas by Sodium bicarbonate: the Solvay process. The thermal decomposition of Sodium bicarbonate produces Sodium carbonate in a very active form which, with fast kinetics, reacts with the Sulfur dioxide in the hot gas, producing Sodium sulfite and then, by direct air oxidation, Sodium sulfate.

$$2\ NaHCO_3 = Na_2CO_3 + CO_2 + H_2O$$

$$Na_2CO_3 + SO_2 + 1/2\ O_2 = Na_2SO_4 + CO_2$$

The solid Sodium sulfate filtered contains the excess of Sodium carbonate and the dust coming from the kiln. Normally this product, which presents a high concentration of Lead, is recycled in the feed of the furnace. From a simple material balance, it is clear that all Sulfur is eliminated through the slag as Iron sulfide or Sodium sulfide.
The smelting reactions related to a charge containing Sodium carbonate as flux and Iron scraps, are:

$$2\ PbSO_4 + 5\ C + 2\ Na_2CO_3 = 2\ Pb + 2\ Na_2S + 7\ CO_2$$
$$PbSO_4 + 2\ C = PbS + 2\ CO_2$$
$$2\ PbS + C + 2\ Na_2CO_3 = 2\ Pb + 2\ Na_2S + 3\ CO_2$$
$$PbS + Fe = Pb + FeS$$
$$PbO_2 + C = Pb + CO_2$$
$$2\ PbO + C = 2\ Pb + CO_2$$
$$Na_2CO_3 = Na_2O + CO_2$$
$$Na_2SO_4 + 2\ C = Na_2S + 2\ CO_2$$

Above 550 °C, the working conditions, the reaction, $CO_2 = CO + 1/2\ O_2$, is fully displaced to the right side.
This process is very critical and the slag becomes a problem for its high Lead concentration and high reactivity and, consequently, for the difficulty to overcome the new European leaching test for waste disposal: no longer will Authorities accept this process. The same considerations apply to the alternative similar but more complex process in which Calcium carbonate

remove the Sulfur dioxide from flue gas: not always, the final product, gypsum, presents acceptable and useful quality.

*Paste desulfurization*

This approach consists in a pre-treatment of the Lead paste to transform Lead sulfate in Lead carbonate and corresponds today to the best available technology for the lower criticality.

The Lead paste is suspended in water to form slurry and then treated with Sodium carbonate. The reaction products, other than (besides) Lead carbonate, PbCO3, are Lead carbonate hydrate, $Pb_3(CO_3)_2(OH)_2$, and Lead and Sodium carbonate hydrate, $NaPb_2(CO_3)2OH$. The byproduct is a solution of Sodium sulfate, which is recovered by crystallization and, after a purity control mainly referring to Lead content, sold to paper or detergent industries. Anhydrous, crystalline Sodium sulfate is normally obtained under vacuum evaporation. For this specific, STC prefers to follow another way to obtain the anhydrous Sodium sulfate, through the crystallization of decahydrate salt (Glauber salt), obtained by cooling the solution, and followed by a melting operation.

The advantages of this choice are:

- slightly lower investment costs,
- further purification of the solution, which permits to obtain a high-grade Sodium sulfate,
- significant energy savings in countries with a cold climate,
- An economic interest connected to the skill to sell directly the Glauber's salt whenever possible.

For these reasons, the last plant built by STC is designed with Sodium sulfate crystallization via Glauber salt.

The desulfurization process can be carried out with other reagents than Sodium carbonate, for example with Sodium hydrate in similar conditions and with similar chemistry; in this case, the main final product is Lead hydrate and the control of impurities in Sodium sulfate solutions is more critical, due to the higher possibility to form soluble plumbate. Whenever it is difficult to commercialize Sodium sulfate, it can be wise to use Ammonium carbonate to obtain, as byproduct, Ammonium sulfate, a fertilizer used, also in solution, on soil.

$$PbSO_4 + (NH_4)_2CO_3 = PbCO_3 + (NH_4)_2SO_4$$

In this case, the chemistry of the desulfurization process is very similar: the solid product is only Lead carbonate because double Ammonium-Lead salts do not exist. Conversion yield is higher and the Ammonium sulfate can be crystallized in the traditional way or, as in the STC process under development, by spray drying. On the other hand, the Ammonium carbonate process needs more controls, related to the solubility of Lead in Ammonium salts solutions. Besides, this process has higher investment costs related to the impact of the new reagents on the working environment that implies the use of closed, controlled reactors.

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In conclusion, the desulfurization process has permitted to control the Sulfur dioxide emissions in subcritical conditions and further, feeding the kiln with carbonated paste, the smelting temperature is lowered of about 200°C, the Iron scraps added in the charge are reduced of 90%. The produced slag is reduced to over 70% in weight, and is less reactive (lower content of sulfide) than that produced without desulfurization.

It is important to know that, for a plant of 15000-20000 t/y, the economical advantage deriving from the insertion of a desulfurization stage in the process, with an investment cost as proposed by STC, produces a payback of investment of two, three years.
As shown above, it is clear that the major pollution problems arise from paste smelting. In some plants, the control of dust emission has been implemented feeding the furnace with pre-pelletized paste. This way it is possible to reduce the dust emitted from kiln up to 50%, lowering the criticality of the dust filtering section.
The yield of the desulfurization process is about 90%, which allows, today, to meet the law limits for Sulfur dioxide emissions. On the other hand, in the near future, these limits are expected to be lowered, especially for those activities operating in areas with high population density. For this reason, many efforts are addressed to reach higher desulfurization yields: achieving this goal would permit to obtain lower quantities of less reactive slag.
In the desulfurization process the conversion yield is not a thermodynamic limit, but mainly a kinetic limit; in fact, the limiting factor is the diffusion of carbonic ion and the back diffusion of sulfate ion in the solid layer of the
Lead carbonate formed on the grain surface of Lead sulfate during the reaction, growing in the time.
Based on this evidence, STC is now testing a new reactor in which the grain surfaces are continuously renewed by milling, to reach higher conversion yield. The new type of reactor is also designed for the use of Ammonium carbonate instead of Sodium carbonate and permits continuous operations, reducing in this way the dimensions of the full plant respect to the traditional one with stirring reactors. The first STC results, obtained with Ammonium carbonate in the "milling reactor", show conversion yield close to 100%.
The full process also includes a pre-treatment of the metallic grid fraction to eliminate last residues of impregnated paste; the operation consists in a washing treatment of this fraction by a solution of Ammonium salt in a drum ultrasonic washing machine.
In any case, the final product feeds a furnace and it is known that the environmental impact is directly correlated to process temperature. For this reason, a big interest is addressed to hydrometallurgy.
Hydrometallurgy is generally considered cleaner than pyrometallurgy and hydrometallurgical processes are really an alternative approach to produce and purify Lead without Sulfur dioxide and Lead dust emissions. On the other hand, hydrometallurgical processes, producing waste solutions containing soluble Lead salts, can be very harmful. Besides, Lead hydrometallurgy

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implies a quite different cultural approach: this could hinder a radical change in a short time.

In this field, STC is moving on two parallel lines: the production of pure Lead oxide to be recycled directly for new paste or for the production of electrowinned Lead.

STC started some years ago the production of pure Lead oxide from Lead battery paste carrying out patented hydrometallurgical processes, proved up to industrial level, characterized by the high level of purity reached and the easy and economical recovery of the leaching reagent, acetic acid.

The pure nanostructured Lead oxide obtained by STC process is battery grade. It can be recycled to substitute, partially or totally, the Lead oxide used in the production of new electrodes.

On the second line, STC studied a hydrometallurgical process to produce electrowinned Lead. Lead electrochemistry is well known: the electrorefining of Lead bullion has been practiced at industrial level from the beginning of last century and, since then, we all know hydrofluosilicic, fluoboric, sulfammic, methane sulfonic electrolytes and the physical, chemical and hydrofluodinamic conditions to manage the cathodic reduction of Lead. Many proposals were presented and tested up to pilot scale to transform primary Lead pyrometallurgy into hydrometallurgy. Many technical problems arose, mainly in the choice of anodic materials and in controlling the anodic reactions to avoid Lead oxidation to Lead dioxide. In order to control this last phenomenon, many additives have been proposed (mainly elements of the fifth group such as Arsenic) achieving an acceptable process with oxygen anodic evolution, but creating new criticality, for example, the possibility of the accidental arsine production from an Arsenic containing electrolyte.

The anodic materials must be chemically inert and present a low oxygen overvoltage; beta Manganese dioxide, precious metals, as Rhodium coated on Copper, special Titanium DSA and many others were proposed.

The results of all these experiences have been blindly transferred to the hydrometallurgical process to treat Lead paste, considering always a problem the anodic Lead oxidation during electrowinning.

On the contrary, STC carried out a new hydrometallurgical process following a very different approach stemming from the conviction that, for the specific case of Lead battery production, the contemporary production of Lead dioxide can be interesting and useful. In fact, the limited quantity and the good quality of the Lead dioxide produced allow its easy recycling. This way, with a traditional cell, it is possible to produce, with the same operative cost, the same quantity of Lead metal and a stoichiometric quantity of pure Lead dioxide, which can be transformed in pure Lead oxide by a simple thermal treatment. In the STC process, the design of the cell allows to separate Lead dioxide slimes and the geometry of the anodic system is studied to obtain the right anodic current density for a good quality of Lead dioxide. STC process uses, as in the traditional process of electrorefining, the additives (glue, etc.) for a good current distribution on the cathode.

STC is also considering new economical uses of the interesting oxidizing power of Lead dioxide.

**The future**

How can new technologies eliminate all the operating risks for the recovery and recycling of Lead batteries?
The future of Lead batteries depends mainly from the answer to this question. STC strongly thinks that a believable answer to such a question will be possible only if battery design satisfies all the conditions for its recyclability; even more, the problem involves the entire system, including production and collection of exhausted batteries.
Many are operating towards this goal, also STC that, to this purpose, has organized a series of collaboration with private and public research institutions. In the next few lines, we will introduce the ambitious research project, partially founded by Italian Authorities, of which STC is the leader. The main STC objective is the full robotization of dismantling and sorting of various fractions of the batteries, avoiding to mix them all together as it happens in the traditional process where batteries are crushed in bulk with a reciprocal pollution of all the components. The second objective, of the same importance, is the elimination of the smelting operation that means no high temperature processes, no gas and dust emissions and no slag.
This technology consists in following steps: an optical system, which uses a data bank containing battery information about the typology and geometry, recognize the batteries; laser cut the cover, at the proper height, to separate the Lead-Antimony alloy of the connectors from the Lead-Calcium alloy of the grids. The cases are emptied, washed and crushed in a hammer mill, together with the covers, obtaining, by simple separation, two products: directly recyclable polypropylene and Lead-Antimony alloy, which can be, after melting, directly marketed.
On the other side, the emptied content is crushed by a knife mill and the grid metal, the paste and the polyethylene are wet separated in traditional way. The metallic fraction, after washing and a pretreatment with Sodium hydroxide or other flux, is compacted by a press and melted. The polyethylene fraction is pyrolized to produce clean fuel gas.
The paste, 100% desulfurized by the STC process in milling reactors, can be converted by a simple thermal treatment or by an hydrometallurgical process, into a very pure Lead oxide, battery grade; this process permits to skip two environmentally critical operations: the smelting and the Barton process.
The robotized process will be operated, at pilot scale, in MECA SpA, an Italian secondary Lead industrial plant, next year.
Within the research project, STC carried out experiments on Lead oxide reduction at low temperature, below the Lead melting point, by Hydrogen.
In principle, Hydrogen can be used as reducing agent for the production of many metals: commercial applications in the synthesis of some metals do exist. The Authors have experience in the production of some rare metals,

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such as Germanium, up to industrial level, where thermodynamic difficulties, higher than those to be encountered in the relatively simple Hydrogen reduction of Lead oxide, are found. The economy of the process is primarily a function of the Hydrogen quantity used: for the reduction of Lead oxide, this quantity must be not far from stoichiometry and this result can be reached only by a proper reactor design. The reactor designed by STC is an expanded bed reactor, thermostated, with gas recycling.
STC is transferring the laboratory results to pilot scale, with two main objectives: the first one is limited to a partial reduction of Lead oxide to reach a stoichiometric ratio Pb-O as in the oxide produced by the Barton process, (battery producers had better accept this lead oxide). The second objective is the complete reduction of Lead oxide, followed by a raise of temperature up to the melting point: a new smelting process with no pollution!
Reaching these goals means not only to have carried out a super-clean process, but also an economically competitive one!
Despite the demonization, Lead is still an irreplaceable material for batteries, as said before, with good prospects for the next 50 years, until now, no other energy storage system is able to show the same reliability of Lead-acid batteries. It is clear that the competition will be very tough and that forecasts are based on the assumption that over the next 50 years strong innovations will be implemented throughout the entire life cycle of the Lead acid battery system and not only at the recycling level.
Over the next 50 years, the competition will be focused on energy storage systems for electric car: battery weight will play a key role and the density of Lead will be the weak point.
In this futuristic scenario, a new Lead material could be interesting, the "light Lead", a metal matrix composite. This new material is produced by powder metallurgy or pressure infiltration of liquid Lead on ceramic powders or vacuum infiltration of liquid resin in Lead foam. This technology has been developed by the Authors many years ago in Venezia Tecnologie SpA, who has a broad know how deriving from its activities in the metallurgical sector and in general in that of new materials from the eighties and experimental facilities for the most advanced technological developments, also in Hydrogen applications.
The properties of this new material are very interesting: the density can reach 50% of that of Lead, electrical and electrochemical properties very similar, the ductility of Lead disappears and the composite has high toughness characteristics, while retaining anyway the ability to be deformed hot plastically: a candidate for the replacement of the traditional material that should permit an interesting weight reduction, better mechanical properties and, therefore, higher performance of the system. On the other side, the substitution of materials requires a review of both, the battery design and of waste battery recycling process: this puts a strong impediment, even psychological, to change.