U4Lead: A new innovative process for the desulfurisation of lead paste

STC compares their new innovative process for the desulfurisation of lead paste from used lead-acid batteries (ULABs) to other processes currently available on the market.

For a long time ULABs have been, and still are, the best available solutions for power supply with several applications in many fields including automotive and energy storage, which are constantly growing markets.

One of the greatest strengths of lead-acid battery recycling technologies lies in the possibility to recycle lead and its compounds almost entirely and infinitely. As a matter of fact, today the world lead production from recycling (secondary lead) is higher than from mining operations (primary lead).

At present, pyrometallurgy represents the main approach to lead recycling from ULABs: the process, shown in ***Fig 1***, presents some issues mainly related to SO_2 emissions and formation of slags (matte), that are normally considered hazardous waste.

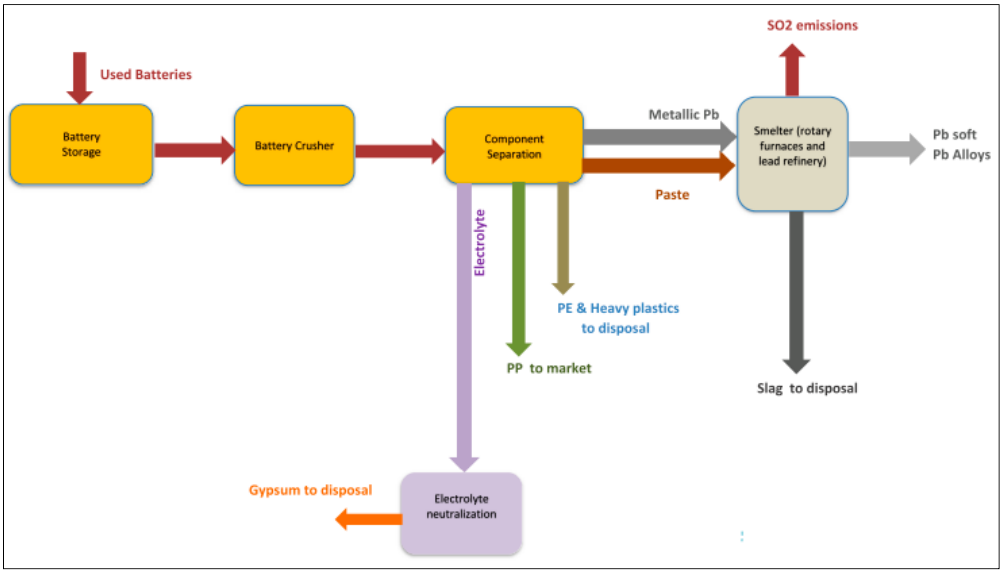

Fig 1: Standard battery recycling process

In order to reduce the environmental issues caused by the traditional pyrometallurgical process, cope with the pressure of local environmental authorities and with the costs increase for transportation and landfilling of hazardous waste, the hydrometallurgical desulfurisation of the lead paste is widely used especially in Western Countries.

Advantages of traditional desulfurisation process

The main benefits resulting from the implementation of the paste desulfurisation process in a battery recycling plant derive from a series of advantages concerning the following areas:

Process optimisation

- Lower smelting temperature of desulfurised paste
- Lower sulfur in the desulfurised paste (typically 0,5-0,6%)
- Easier formation of iron-soda matte
- Good quality of obtained slag
- Easier refining operation (time reduction)
- Reduction of dross and ashes from refinery to be recycled

Savings in production costs

- Reduction of slags generated (-65%) – hazardous waste to be transported and disposed of in special landfill sites at high cost
- Less fluxants required and particularly iron consumption is reduced by 90%
- Less fuel required (-15%)
- Less oxygen required (-15%) when using oxy-fuel burners
- Higher productivity
- Faster cycle
- Smaller furnace
- Less lead lost with slags
- Revenue from sodium sulfate covers some of the additional costs (chemicals and energy)

Environmental impact reduction

- Drastic reduction of generated hazardous waste to be transported and disposed of in special landfill sites
- 90% reduction in SO_2 emissions
- Less fossil fuel consumption (oil or natural gas etc.)
- Less CO_2 generated due to reduced fuel consumption
- No liquid effluents as the process is zero liquid discharge when crystallisation is adopted: the condensate is reused inside the plant
- No need for an external electrolyte-neutralisation system as the sulfuric acid can be converted into sodium sulfate in the same equipment used for paste desulfurisation

Basis of the traditional desulfurisation process

The chemistry of the traditional desulfurisation is relatively simple and consists of the reaction between an alkali chemical (Na_2CO_3 or NaOH) and the lead sulfate ($PbSO_4$) that is converted into lead carbonate ($PbCO_3$) or lead hydroxide $Pb(OH)_2$.

The simplified overall reactions involved are the following:

$$PbSO_4+Na_2CO_3 \dashrightarrow PbCO_3 + Na_2SO_4$$

$$PbSO_4+2NaOH \rightarrow Pb(OH)_2+ Na_2SO_4$$

The sodium sulfate solution Na_2SO_4 obtained as by-product from the reaction, after a purification step (necessary to remove the contamination from heavy metals), can be crystallised to produce pure sodium sulfate that can be sold to detergent, glass, textile and paper industries.

The sulfuric acid contained in the electrolyte is also transformed into sodium sulfate according to the following reactions:

$$H_2SO_4+Na_2CO_3 \rightarrow Na_2SO_4+H_20+ CO_2$$

$$H_2SO_4+NaOH \rightarrow Na_2SO_4+H_20$$

The equipment required for the desulfurisation process consists of stirred reactors, pumps, chemical dosing system, filter press.

In few cases, depending on location and local authorities, the sodium sulfate solution, after purification step, can be directly discharged into the sea or reused in certain mining operations but generally the sodium sulfate solution is afterwards crystallised in a crystallisation unit. The system configuration is shown in ***Fig 2***.

A great deal has been written about the desulfurisation process via $(NH_4)_2CO_3$ but, to our knowledge, there are no existing plants operating on an industrial scale employing ammonium carbonate to carry out the desulfurisation reaction. Therefore, no real data is available for performance comparison.

The main disadvantages of using $(NH_4)_2CO_3$ as chemical for the desulfurisation reaction are: the higher price of the chemical and the environmental consequences, pollution and safety issues related to production, transport, storage and handling of this compound. Due to the ammonium carbonate high volatility and subsequent NH_3 released toxicity, procurement and transportation may become difficult specifically because the production of ammonium carbonate is only concentrated in few countries (mainly China and India).

The possible onsite self-production of ammonium carbonate starting from ammonia and CO_2 has some drawbacks— high cost and safety problems related to ammonia transportation and storage.

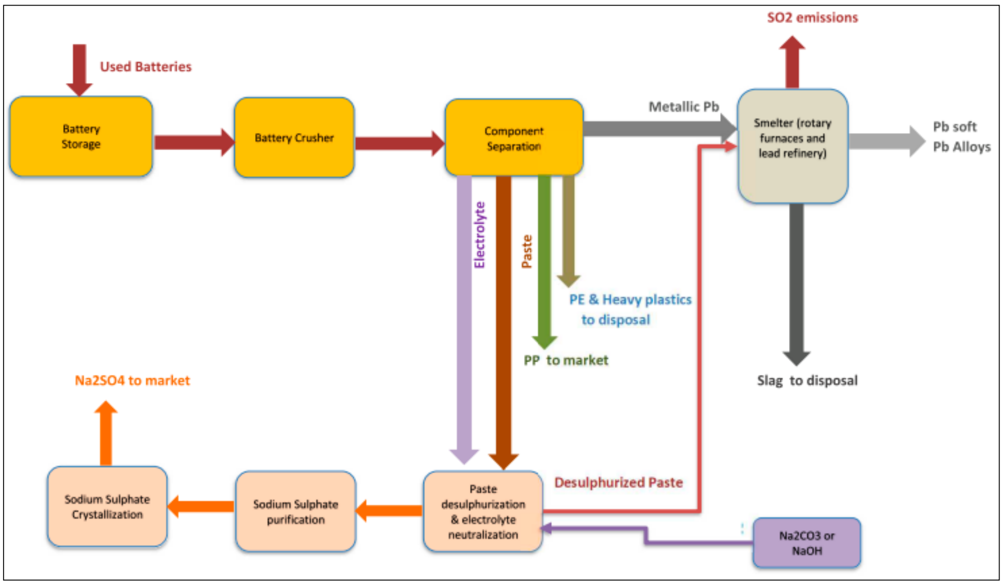

Fig 2: Battery recycling with a traditional desulfurisation process

Problems related to traditional desulfurisation process

Beside the waste disposal problems, there are three other aspects to be considered:

1. With the advent of liquid detergents the demand for sodium sulfate, one of the main filler components used in washing powder production, has become weaker and consequently the sale price has slightly decreased although still presenting positive revenues.
2. The quality of the chemicals (especially when using sodium carbonate with chloride content) impose the use of special construction materials like AISI 904L or DUPLEX for heat exchanger and crystallisers in order to avoid the corrosion problems caused at high temperature in presence of chlorides.
3. The cost of the chemicals sometimes makes the overall process more expensive (NaOH is a by-product of the chloro-alkali process and with the reduction of chlorine uses the cost of caustic soda in certain countries increased).

STC improvements through U4Lead process

STC has developed and patented an innovative desulfurisation process, in order to overcome the problems of the chemicals cost/quality, and the relatively poor market for sodium sulfate. At the same time , this ensures all the advantages of the desulfurisation process.

The **U4Lead** process by **STC** uses an amino compound, namely urea, for the desulfurisation of paste and the electrolyte neutralisation process.

The simplified reaction can be summarised as follows:

$$CO(NH_2)_2 + PbSO_4 + H_2O \rightarrow PbCO_3 + (NH_4)_2SO_4$$

$$CO(NH_2)_2 + H_2SO_4 + H_2O \rightarrow (NH_4)_2SO_4 + CO_2$$

As by-product, pure ammonium sulfate is obtained: this chemical has a very good market and can be sold, in liquid form or in crystals, as fertiliser for agriculture.

STC can provide either a full crystallisation system to produce pure ammonium sulfate crystals, or just an evaporation system in order to produce a concentrated solution of ammonium sulfate 'ready-to-use'. The graphic of the process is represented in ***Fig 3***.

Advantages of the U4Lead process by STC

All the advantages of the traditional desulfurisation are maintained and in many cases further improved and in particular:

- A higher degree of conversion of the lead sulfate into lead carbonate (more than 97%, is achieved)
- The process is faster than using other chemicals thus allowing reduction of reactors volume
- The desulfuration level obtained is higher than the traditional process (0,2-0,3% of sulfur remaining)
- Further reduction of slag generation (only 5-6% on Pb produced) and associated lead losses are achieved
- Further reduction of iron usage in the charge
- Further reduction of fuel and oxygen consumption
- Using UREA, there are no undesired side-reactions during desulfurisation such as formation of double salts
- UREA is normally cheaper than other reagents and is largely available worldwide
- The by-product obtained is ammonium sulfate that could be used and sold easily as fertiliser in liquid or crystal form: the selling price is normally higher than sodium sulfate

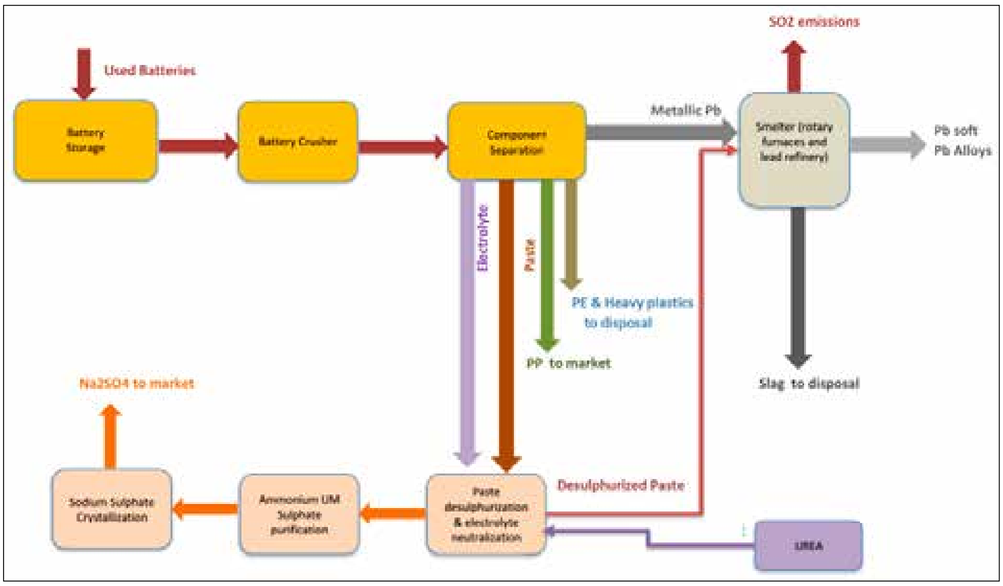

Fig 3: Battery recycling with the innovative 'U4Lead' process

- UREA does not involve any environmental, pollution and safety problems for workers related to transport, storage and handling

Comparative desulfurisation design options
The three desulfurisation design options are compared in ***Table 1***: (the data are partially empirical based on the practice and experience and therefore unrelated to scientific rigor).

Conclusions
Hazardous waste and disposal costs are increasing all around the world and permitted emission levels are under continuous revision by environmental authorities.

Paste desulfurisation allows smelting process optimisation, cost reduction and better metallurgical results: these benefits are amplified using the **U4Lead by STC** desulfurisation process.

Smelting desulfurised paste improves the overall environmental performances particularly because of the minimisation of hazardous waste production and SO_2 emissions.

Data *Referred to 1 ton of SLI batteries treated full of electrolyte (15% of H_2SO_4) with a total average Pb recovery of 56%*	**No desulfurisation***	**Desulfurisation with Na_2CO_3**	**Desulfurisation with NaOH**	**Desulfurisation with U4Lead process by STC**
Paste characteristics				
Insoluble sulfur %	6,2%	0,5%	0,5%	0,3%
Na content	--	2,5%	2,5%	--
NH_4 content	--	--	--	0,3%
Chemicals consumption				
Na_2CO_3 kg/t	--	130	--	--
NaOH kg/t (100%)	--	--	100	--
$(NH_2)_2CO$	--	--	--	75
By Products production				
Na_2SO_4 kg/t	--	150	150	--
$(NH_4)_2SO_4$ kg/t	--	--	--	145
Smelting parameters and chemicals for paste smelting (soda slag)				
Iron kg/t	50	10	10	5
Coal kg/t	20	20	20	20
Soda ash kg/t	20	15	15	10
Batch time h	6	5,5	5,5	5
Fuel consumption (CH_4) Nm^3/t	45	37	37	34
Oxygen consumption Nm^3/t	90	74	74	68
Environment impact				
Typical SO_2 concentration at stack mg/Nm^3	600-800	100	100	80
Slag generated	ab.17%	Ab.7%	Ab.7%	Ab.3,5%
Pb losses with slag (5%)	0,85%	0,35%	0,35%	0,18%
Impact at refinery				
Drosses/ashes to be recycled	5%	3,5%	3,5%	3%

**When no desulfurisation process is adopted the recycling plant needs a dedicated section for the neutralisation of the sulfuric acid contained in the electrolyte that is not considered here. In the desulfurisation cases, the electrolyte treatment is an integral part of the process and is neutralised together with the paste in the same equipment.*

After the initial tuning of the U4Lead process at the industrial plant, STC confirmed the excellent results already obtained in the lab-scale testing.


Desulfurisation reactors


Urea converter/activator

For the first time, the possibility of industrial-scale desulfurising of lead paste via UREA has been demonstrated.

The process can be easily implemented and integrated into existing plants. While, from the environmental and process point of view, the desulfurisation process is always convenient, the real impact on production costs is more evident where the cost of disposal of the slag is high, or when the availability of landfill for hazardous waste is limited. Therefore, the real economic advantages of the process have to be verified case-by-case and calculated carefully for each specific situation.

STC has developed a model for calculation of the process feasibility and return of the investment that is available for **STC**'s customers.

STC is able to provide all kinds of desulfurisation systems as described in this article, using the chemicals available on local markets, coupled with different kinds of evaporation and crystallisation systems including: direct steam, cold and hot crystallisers, mechanical vapour recompression and heat pump.