Technical Review of the Proposed Secondary Lead Smelter at Hazelwood North, Victoria

Global Lead Technologies

Mark W Stevenson

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Executive Summary

This report has been commissioned to examine the Works Application Approval regarding the technical aspects and feasibility for a proposed secondary lead smelter at Hazelwood North, Victoria. Chunxing Corporation Pty Ltd has applied for the construction of a 28,000 tonne per annum (tpa) secondary lead smelter, which will consume around 50,000 tpa of spent lead-acid batteries from around Australia.

Secondary lead smelting is a well-established industry across the world, playing an essential role of not only recycling the lead-acid battery but being able to supply the valuable commodity back into the same product whence it came. The finished product is returned to a market that consumes 14 million tonnes per year of which recycled or Secondary lead supplies around 65% of this volume. Although it is considered a recycling operation in processing spent batteries, it is also a complex metallurgical process recovering the valuable products. Across the globe, there is a varying level of stewardship for the product and process. The aim of the industry is for continuous improvement, not only in operations but to the overall environment, health and safety of workers and to the public.

The Chunxing proposal covers the typical sections and layout of a secondary lead smelter, with the centrepiece furnace being an innovative two furnace configuration. The report examines the proposed process outlined in the documents against current operations across the world. The metallurgy and chemistry behind operations of a smelter are also detailed, giving a better understanding of the proposed process.

Three recommendations have been made based on current smelting operations across the world, including reflecting improvements continually being worked upon in the industry.
Recommendations

Although there has been a limited amount of data to analyze the proposed process, the following recommendations are made looking across the "top-level" of the proposed Hazelwood operation. Comparisons are made against current smelter operations and systems operating around the world, taking into consideration the metallurgy and chemistry behind the processes.

Area: Battery Breaker

Hazelwood proposal: To partially desulphurize the lead paste with lime (calcium hydroxide/oxide) only.

Other Options: As indicated, one of the major problems is the amount of sulphur entering the furnace system. The standard practice of the removal of sulphur in the majority of pre-desulphurization stages is via the use of sodium carbonate or hydroxide. Although in the initial proposal ammonium bicarbonate was suggested as a reagent bringing the sulphur down from 5.2% to 3.44% in the paste, this is not a method used in the industry. Sodium compounds are achieving 0.5% to 0.7% sulphur on a production basis.

Positive/Negative: One of the significant drivers in not using sodium compounds is the cost of operation of the process. The cost of crystallization and lower selling margin of the sodium sulphate all contribute to a cost against production. The benefit to the plant is the ease of smelting, higher lead percentage to the furnace, yielding higher output and much lower sulphur dioxide emissions. As Chungxing has proposed not to use the rotary furnace technology, the benefit of lower slag volumes is not valid as the slag proposed holds little sulphur. Chunxing have also stated they want to limit sodium in slag, (although evidence shows they already have upwards of 8% of the element in current operations) new processes exist where the soluble sodium compounds are removed by back-flushing techniques in the filter press, so contamination to the furnace is minimal.
**Area: Battery Breaker/Furnace**

**Hazelwood proposal:** That material produced from the battery breaker will be feed directly from the battery breaker to the furnace for the paste, and metallics to the refinery kettle.

**Other Options:** Have dedicated storage or holding area for excess production from the breaker, other sources of material in the plant, e.g. the refinery and external purchases of scrap or feed material.

**Positive/Negative:** The outline for the products from the battery breaker is an almost direct feed to the furnace or refinery, thereby no stock of feed material will be stored. In smelters around the world, areas in the plant are reserved for storing excess scrap stocks, in some cases of holding over 1,000 tonnes. It is rare for any plant to have the battery breaker running "in sync" with the furnace and refinery and at some point, there has to be excess stock build-up that has to be placed upon the floor. Items such as hot drosses from the refinery that take up to 12 hours to cool, often still fuming, are included in this stockholding. Further, if the Hazelwood plant is going to purchase external products, these materials are generally delivered in woolsack type bags and have to be stored for some period of time, even for sampling.

One other reason for storage is the reduction in water/moisture to the furnace, firstly due to the risk of explosions and secondly, the energy taken to remove the water. Although the dual furnace set-up covers the second point, the first point would be valid for the metallics directly to the kettle, as it has been indicated this material is continually fed to the refinery kettles.

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**Area: Pollution Control**

**Hazelwood proposal:** That the proposed set-up for pollution control will be a baghouse to capture the dust and particulate matter and a dual scrubber to remove the sulphur dioxide.

**Other Options:** Investigate the use of wet electrostatic precipitators (WESP's) to further reduce the emissions from the proposed Hazelwood operation.

**Positive/Negative:** The proposed baghouse/scrubber set-up could be considered the minimum requirement for a lead smelter of this type now. To improve emissions,
smelters operating the larger reverberatory furnaces have currently employed WESPS and regenerative thermal oxidizers (RTO’s) to reduce their emissions. These have generally been applied to the larger operations, typically those greater than 60,000 tpa, but there is a move to look at smaller operations. One negative is the cost of installation, and there is some difficulty in retrofitting to older plants due to room.
1. **Introduction to the Secondary Lead Industry**

Around 14 million tonnes of lead, sourced from both primary and secondary smelters is produced around the world annually. The largest consuming market for the element is the lead-acid battery, which consumes just on 85% of world production, with the remaining percentage going into diverse markets such as lead sheeting and cable sheathing alloys. The Secondary sector, (considered as the process utilizing feed from scrap batteries in comparison to Primary, which is using a product derived from ore), surpassed the production from Primary sourced material just on 20 years ago and now supplies an estimated 65% of annual global lead consumption needs. This percentage for recycling far exceeds other non-ferrous metals such as copper, zinc and aluminium, which are well below a recycle rate of 30%. The lead-acid battery is the most recycled man-made product with many countries across the world running at rates for the product of close to 99%.

The secondary industry is a very dynamic and large industry, worth around USD18 billion annually, with smelters located in over 60 countries across the world, from the United States, United Kingdom, Germany and France to places like Nigeria, Guatemala and Oman. With the size of the lead market doubling from an annual 7 million in 2003 to the current 14 million tonnes the majority of this growth has come through secondary smelting resulting in new smelters opening across the globe to meet the demand.

Whilst secondary lead smelting operations supply the majority of lead to world markets, very little is published on the smelting and processes of plants and importantly, the reporting of best practice for the treatment of batteries and the recovery of lead. One reason is due to the fragmented nature and size of the plants and secondly, the perceived simplicity of the process.

Unfortunately, the second point is often tied with the perception of "basic recycling" and "waste treatment" but spent or used lead-acid battery (ULAB's) recycling is a true metallurgical process. It cannot be overemphasized that although it may seem relatively easy on the surface, a secondary smelter is a complex operation. It has the perception of many people of being a simple process of "melting" down the old batteries and recover the lead, but this is far from the truth. Secondary lead smelting reactions are more complex than those that occur at a primary lead smelter in respect to lead. As a process, metallurgically, although stated as "quite complex" the smelting reactions take place at relatively low temperatures and go to completion quickly. (Unfortunately, this is one reason why "rogue" smelting of ULAB's occurs in areas such as India and many parts of Africa. The intrinsic value of the battery and the metallic
lead coupled with the ease of extraction and smelting, although poorly, is a driver for this operation to occur.)

The recycling of the battery has been an established practice ever since the introduction of the product in the late 1800’s and the early day’s scrap was supplemental feed at primary smelters. Secondary smelters were developed over the subsequent period, many from in-house designs and based upon blast furnace technology similar to that in the Primary arena. Around 40 years ago, the sector started to formalize plans and operations, and in recent years dedicated engineering companies began to develop and offer turn-key operations for construction of complete secondary plants. These plants now incorporate the latest technologies not only in smelting but scrap treatment and pollution control, with many of the older furnaces now phased out.

The components of a ULAB are highly valued in the metals industry and play a vitally important role in supplying lead to the world market; the product is often considered as a commodity. Significantly, most of the contents of the lead-acid battery are recovered, such as:

- 99.7% of the contained lead components are recovered as metal, refined and returned to the industry to be used in new batteries or other lead uses.

- The polypropylene casing is recovered, cleaned and sold back into the plastic market to be made into end-products including automotive parts and new battery cases.

- There are numerous processes employed for the treatment of the waste acid and the other sulphate compounds ranging from the production of food-grade sodium sulphate, gypsum and even several methods of re-cleaning the acid for further use.

Accompanying these plant developments over the years has been the intense work behind improving the environmental and worker hygiene performance of an operation. At a site level, effort goes into amongst other items, the design of faculties and the education and training of operators to minimize lead exposure. At the plant level, improvement and development of pollution control devices like the installation at the larger operations of Wet Electrostatic Precipitators (WESP’s) and HEPA (High-Efficiency Particulate Air) filters continually drive down emissions.
2. **Outline and Scope of Document**

The scope of this document studies the proposed process of the treatment of used lead-acid batteries as described in the application documents and other correspondence by Chunxing Corporation Pty Ltd for the construction of a 28,000 tonne per annum (tpa) Secondary lead smelter in Hazelwood North, Victoria.

The proposed operation will consume around 50,000 tpa of spent lead-acid batteries and is outlined in the Works Application Approval (WAA) dated December 2019, the Addendum to Works Application Approval (AddWAA) dated 29th June 2020, and subsequent correspondence to clarify the procedure.

From these documents and communications, the proposed process for the Hazelwood process would be:

i. That spent lead-acid batteries, ULAB’s, will be received onsite at the Hazelwood premises.

ii. They will then undergo breaking and dismantling via a battery breaker to retrieve the various fractions of the battery.

iii. Initially, the proposal was that the spent acid would be neutralized by agricultural grade zinc oxide to produce zinc sulphate to be sold as a liquid, but now been reverted to neutralization with lime to form gypsum.

iv. A metallic fraction will be taken from the breaker and melted in the refinery producing a hard bullion lead which will be made into lead alloys.

v. The initial proposal was for the lead paste from the battery breaker to be partly desulphurized with the addition of ammonium bicarbonate (or in some cases substituted with calcium carbonate). After discussions, the proposal now is to desulphurize the paste with lime partly.

vi. This desulphurized paste is charged to the furnace. Also added to the vessel are iron and coal, and the batch is smelted using a 36-hour smelt cycle.

vii. The bullion metal is tapped to the refinery for further refining into a soft lead product of around 99.98% purity.

viii. The resultant slag contains between 0.8 and 1% lead and a substantial amount of sulphur.
The fume and off-gases from all processes pass through to a baghouse scrubber system where the particulate matter is collected and returned to the furnace whilst the sulphur dioxide is removed in the scrubber as gypsum.

The scope of this report is to examine the above documents regarding the proposed process and technology with respect to the current operations in the secondary lead industry, along with the metallurgical and chemical background to the proposed methodology.

It is written in sections according to each plant process undertaken to clearly outline each procedure with comparison to current operations and the supporting metallurgical/chemical/process detail. The recommendations have been outlined in the Executive Summary.
3. **Operations of a Secondary Lead Smelter**

Nearly all secondary lead plants across the world operate to a general format, as outlined in figure 1 below. There are some minor variants to the flowsheet, such as the direct melting of metallic fractions, but the overall movements and operational areas are the same.

![Diagram of a typical secondary lead smelter](image)

Figure 1. Basic flow layout of a typical secondary lead smelter.

The first major step to the process is the disassembling of the battery is to extract the various components so they can be treated. Unlike other battery chemistries, the lead-acid type cells are relatively simple in construction, as shown in figure 2 and only basic engineering equipment is required to break them. (An outline of the compounds and electrochemical reactions in the lead-acid battery system is given in Appendix A).

Once the batteries have been received by the smelter, from storage, they are feed to a battery breaker which through "shear impact", breaks the batteries allowing for the liberation of the various fractions which are outlined in detail in section 5.
The next major stage of a secondary plant is the furnace, where through metallurgical reactions the lead compounds are reduced to a bullion lead with the aid of reducing agents such as iron and carbon at temperatures above 1000°C. Along with the production of the bullion lead a waste slag is produced, effectively gathering up all the gangue material in the furnace. Often considered the central part of the operation, there are numerous types of furnaces operating across the world.

Attached to the furnace is the refinery and casting section where the impure bullion lead is refined to pure lead in large steel kettles at temperatures between 350 and 550°C. Once the metal meets the required specification, it is cast into either ingots or large blocks depending upon the customer.

The final main section of the plant is pollution control, where various methods are employed to remove dust and gasses from all of the plant processes.

Although the majority of smelters possess these primary operations outlined above, where differences occur between plants is very much driven by how the contained sulphur in feed is treated and removed from the process. The extraction of sulphur, present in the battery as sulphate (see Appendix A), dictates the operation and methods used, such as the furnace used, slag matrix formed and size of scrubbing systems for example. The following sections outline each of these processes in detail, although the discussion on plant desulphurization methodologies is incorporated in the chapter on sulphur.

Figure 2. Tear-away view of a sealed lead-acid battery (from UPSPower).
4. **Purchasing and Receipt of ULAB’s.**

One of the first functions of plant operations is the purchase and delivery of ULAB’s safely to the site, which for the proposed site product will come from across Australia in around 2,500 20 tonne equivalent loads. Excellent work has been carried out by ABRI (Australian Battery Recycling Initiative) in collating and publishing the "Guidance for Packing Used Lead Acid Batteries for Recycling"\(^1\) which complies with the Australian Dangerous Goods Code – ADG 7.5 and Packaging Instruction P801. This guideline not only includes packaging and labelling requirements but also what battery chemistries cannot be accepted for transport or by the smelter. With the increased use and appearance in scrap feed of Lithium-Ion batteries, all smelters should have guidelines in place for preventing these used products onsite.

4.1. **Hazelwood Proposal for Receipt of ULAB’s**

In the AddWAA document, Section 5.3 Acceptance Criteria for ULAB’s, on page 66, the section outlines the criteria for acceptance, and penalties imposed on the delivery of batteries to the site. Whilst it rightly describes the rejection of other battery chemistries, in discussions, it was indicated that the section is extracted from the Chinese operation manual and other segments do not reflect the Australian market. This section will be re-written to reflect the local conditions using the current outline as a template.

In regards to purchasing of the ULAB’s, Chunxing will follow the method adopted by many countries across the world of a percentage of the prevailing London Metal Exchange (LME) lead price for “wet” batteries (those batteries that contain their acid against “dry”, batteries drained of their acid).

Chunxing has also indicated that they will be adopting the ABRI Guidelines as a standard practice for the delivery of ULAB’s to the site as outlined in the WAA document, Section 12.5.1., Page 126.

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5. **Battery Breaking**

There are over 60 modern secondary lead smelters operating across the globe dismantling, separating and treating the products from spent batteries. The process is a somewhat basic operation, but key in the overall successful operation of a plant as preparation of the feed for the furnace and good recovery of the various product streams is critical in a plant functioning to full capacity.

Once the used lead-acid batteries (ULAB’s) are received at the smelter, they undergo several processing stages to recover and treat the various components contained in the battery. In modern plants, automatic battery breakers are used in the first stage to process and recover the different parts of the battery. There are numerous variations to battery breaking operations throughout the world; however, the outputs obtained from each operation are generally similar, being:

i. **Battery Paste.** The paste is a fine, dense product consisting mainly of lead sulphate, lead dioxide and metallic lead that comes from the active material compounds contained on the positive and negative plates. The paste contains small fragments of metallic lead from the grid due to the pulverizing effect of the hammermill. Organic materials like floc and fibres added during the construction of the battery are also present. (This product is also referred to as "Oxide", "Paste" and "Fines")

ii. **Metallic Fraction/s.** This fraction consists of the larger, generally metallic parts of the battery such as the terminals, remnants of the grids and connectors/Cast-on-Strap (COS) fractions. Some battery breakers split this offtake into other fractions by simple size screening, removing the larger metallic terminals and connectors from the remaining smaller fragmented metallic grids. (This product is also referred to as metallics, terminals, metal fraction)

iii. **Polypropylene (PP):** This part of the battery breaker stream is the shredded battery cases which for automobile and some other batteries are made from polypropylene. This is a valued product and forms part of the profitability of the plant. (This is often referred to simply as "plastic")

iv. **Separators:** There are various types of separators used in the lead-acid battery, such as polyethylene, absorbent glass mat (AGM) and woven, but the reference in battery breaking refers to the polyethylene type. Although referred to as this polymer, it is a misnomer as they actually contain up to
65% silica. They are a mix of ultra-high molecular weight polyethylene (UHMWPE), fused silica and proprietary processing oil, creating a sheet with around 50% porosity. Because of the high silica, they have a density greater than one and cannot be recycled like the polypropylene outlined above and must be disposed of.

v. **Spent battery acid:** The spent acid is collected from the battery as it is broken through the hammermill. This acid is recycled throughout the hammermill and classification tanks until the excess is removed due to incoming batteries. Treatment of this product is outlined in section 5.

vi. **Heavy plastics and other delirious materials:** Some standby and stationary batteries are housed in plastic containers that are not polypropylene. These are often co-polymers, some containing bromine as a flame retardant for example, which cannot be recycled and must be disposed of. Other material is also collected from the breaking operation, such as labels, "magic eyes", rope handles, etc., is also destined for disposal.

It is important to note that the various lead fractions recovered from battery breakers, outlined above, can vary in the analysis due to cross-contamination from each of the individual streams. For example, the metallic fraction can contain levels of paste to upwards of 25%, and this generally comes back to the operational parameters of the battery breaker itself. This "mix" will also change over time as the simple wear-and-tear on the hammers in the hammermill can change the sizings of the various output streams. The general percentage breakdown of output streams from a battery breaker is given below in Table 1.

<table>
<thead>
<tr>
<th>Fraction</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Battery Paste</td>
<td>41 - 46</td>
</tr>
<tr>
<td>Metallic Fraction</td>
<td>20 - 28</td>
</tr>
<tr>
<td>Terminals/Posts</td>
<td>8 - 10</td>
</tr>
<tr>
<td>Separators</td>
<td>2 - 4</td>
</tr>
<tr>
<td>P.P. Plastic</td>
<td>7 - 8</td>
</tr>
<tr>
<td>Spent Acid</td>
<td>17 – 20</td>
</tr>
<tr>
<td>Other</td>
<td>0 - 1</td>
</tr>
</tbody>
</table>

Table 1. Typical product stream output from a battery breaker.
The various lead fractions are generally stockpiled and prepared for feed to the smelter furnace. This is usually done in an area of the plant adjacent to the battery breaker where conveyor belts remove the various lead feeds from the battery breaker and stockpiled for drying before adding to the furnace. The "non-lead" items, polypropylene, separators and the heavy plastics from a battery breaker are generally captured in large bags or containers making them easy to store or ship whether to be sold or disposed of offsite.

5.1. Operations of a Battery Breaker

There are around ten major battery breaker manufacturers around the world with a growing number starting to produce equipment in China and India. These companies supply "total solution" battery breaking operations or selected parts/sections of the process as required by the smelter. Previously, some 40 years ago, it was common for a smelter to design and build their own breakers including hammermills, screens and classifiers, but this is somewhat rare today. Smelters and new market players now purchase dedicated breakers and equipment from the various world suppliers, most often as a turn-key project. Importantly, there is no industry standard or design to the layout of a battery breaking plant. Engineering companies such as Engitec of Italy and Wirtz Engineering of the USA with their plant designs are becoming an unofficial model; for example, Engitec is renowned for their desulphurization units.

One of the primary catalysts to engineering companies designing and building breakers rather than smelters was the system first patented and developed by M.A. Industries in Georgia, United States, in the 1980’s. The patent outlined the design of oxide classifiers, screw and mesh screens for the sorting of the various fractions received from a hammermill. The MA oxide and plastic washing screen design had become an industry standard at that time, and many current-day operations contain parts of the original system.

All breakers across the world utilize the principle of different densities of the products along with the varying particle sizes. The first significant step at a smelter is the dismantling or breaking of the battery to free the lead components from the plastic case and top, then to gain access to the lead units and other products to sort and classify them. As previously indicated the most common approach in modern operations is processing the ULAB's via a hammer mill and in some cases roll crushers are incorporated. It is a common feature in a battery breaker design that the hammer mill is the highest part of the plant, thereby utilizing gravity to move the crushed product

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2 United States Patent 4,397,424
through to the various stages of classification. It is another common feature that long conveyor belts, generally made from a rubber compound inert from acid corrosion, are used to deliver the ULAB's into the hammermill. Numerous methods are employed to feed the conveyor belt; from unloading by hand, to vibrating hoppers and grab cranes. As the throughput tonnage of the battery breaker increases more automatic methods of loading like the grab crane is used, simply because of the more considerable load involved.

The fragmented product from the crushing/fragmentation operation of the hammermill is fed to a sink/float or hydrodynamic separator where the fractions are sorted simply by density and size. In the basic sink/float cell, the plastic fractions are floated off and removed to a plastics recovery section whilst the lead-bearing portion of metallics and compounds sinks to the bottom and removed via conveyors or other means for further classification into metallic and oxide fractions. The hydrodynamic separator method works in a similar mode, although the plastic fractions, such as polypropylene, are separated at an earlier stage. In an M.A. type system, this process is achieved in the Plastics screen and Oxide Classification Tank with the plastic being removed and washed on an inclined mesh conveyor where it is removed from the system for either bagging or storage. The system designed by Engitec of Italy uses a system of screens and upflow pumps to sort the fractions in a vessel/tank that is referred to as a "Santa Maria".

Other breaking variants do exist across the world, including systems where the top of the battery is removed by a saw and the battery cells extracted via a trommel or similar device. These cells, which includes the plates and separators, undergo no other processing other than drying and are charged directly to the furnace. The plastic case and top cover travel to a hammer mill for crushing and recovery of the lead fractions remaining, particularly any remnant lead paste, and the metallic terminal embedded in the top. The lead units are separated by various classifiers, screens and filters into the two general fractions as mentioned previously, lead paste and the metallic fragments.

The various products from the breaker, along with internal arisings such as drosses and baghouse dust, are stored in a "scrap storage area" or often referred to as the "charge preparation area" and allowed to dry further. Material for the furnace is prepared in this room along with the other reagents such as coal and iron.

### 5.2. Hazelwood Proposal for Battery Breaking

From the data submitted by Chunxing regarding the operations of the battery breaker, detailed in Section 4.4.1., page 21, WAA, the method of operation outlined is similar
to battery breakers globally; the utilization of the sink/float methodology after the batteries have been broken in a hammermill. In the examination of Figure 4, page 20, of the WAA and Figure 14, Page 42, AddWAA, the layout of the plant seems to be typical of a battery breaker set-up with equipment to extract the various fractions as outlined above. However, a larger portion of metallic feed was delivered directly to the refinery. In figure 18, page 61 of the same document, showing the flowsheet of the battery breaker whilst it does look typical, there are some variations to what would be considered normal operation. After further discussions on clarification, it is clear there are several important variants to what could be termed the standard battery breaker system. These are:

- Although it is stated as a hammermill in the documents, the ULAB's are reportedly pass through a battery "breaker" that does not cause the intense shredding of the metallic components in the battery, namely the negative plate. The plates pass through a series of mineralogical processes to clean the grids from oxide and sulphate paste. This is an advantage to a smelter, as bypassing the furnace with any fraction of the battery and directly melting it saves not only money but better plant recovery, less product to be smelted, less fume to be treated, etc.

- The other portions of the broken battery follow the sink/float process as described above.

- Once produced from battery breaker, the lead paste is fed across three conveyor belts into the furnace, whilst for the metallic feed, it goes directly to the melting kettle. There is no surge capacity or "charge preparation area" in the proposed operation, indicating that there will be no product storage and the battery breaker will run "in sync" with the furnace and refinery operations. This is not a practice done in other smelters due to issues such as moisture levels as plants prefer to build a stock of raw material as it allows drying. Moisture can have an impact right across an operation and allowing for more moisture to report the baghouse, rather than drying to the atmosphere, could impact the performance of that operation. One benefit of the proposed method is that it would reduce airborne dust around the operations of the plant as the material remains moist.
6. **Treatment of the Spent Battery Acid**

The neutralization and treatment of the spent battery are one of the vital operations conducted at all modern secondary lead smelters. There are several important drivers for the treatment of the acid, the first being the neutralization of the corrosive product to an environmentally stable form by increasing the pH of the liquid to a non-corrosive and harmless level. The second, for many countries, is the reduction of total dissolved solids (TDS) and heavy metals from the liquid end-product, particularly sulphates.

The size of the operational plant in treating acid often varies from region to region, and this is due to the amount of acid being received. Unfortunately, in many developing countries and nations in transition, ULAB's are delivered to the lead smelter drained of their acid. These are termed "dry", compared to countries such as Australia and those in North America and Europe where the used batteries arrive at the smelter still containing the acid electrolyte, designated as "wet".

The volume of acid can be upwards of 20% in a battery and varying strength, so there can be a relatively large volume of liquid that has to be treated for the average 20,000 tpa smelter, as much as 7,000 tpa. Three methods are employed in the secondary industry to address the spent acid:

i. **Neutralization with Lime.** The most common method of neutralizing spent battery acid is via the controlled addition of lime. This process has two aims, increasing the pH of the solution and forming a solid precipitate of gypsum (calcium sulphate), thereby removing most of the sulphate ion from the liquid. The reaction is:

\[
H_2SO_4 + CaO/Ca(OH)_2 \rightarrow CaSO_4 + H_2O \quad \text{----- 1}
\]

The general set-up of this type of acid treatment plant is quite basic, as being an aqueous process it generally involves a series of reaction and settling tanks. Thickener tank and filtering device such as a filter press, are then employed to remove the solid gypsum with reduced water content. Depending on the location of the plant there are cases where the gypsum is sold for a nominal price, although for the majority of the world's smelters, the gypsum is disposed of at a licenced waste facility as it is not a hazardous waste. The resultant liquid, once
meeting the required pH and TDS specifications are disposed of in effluent or trade waste systems under the prevailing license.

ii. Sodium Sulphate Production. In plants that utilize the battery paste desulphurization technique, such as in Engitec\(^3\) designed plants, the acid forms part of the sodium sulphate process being consumed in the reaction with sodium carbonate or hydroxide, (depending on which compound is employed) to produce sodium sulphate by the reactions:

\[
\begin{align*}
    \text{H}_2\text{SO}_4 & + \text{Na}_2\text{CO}_3 \rightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{O} \\
    \text{H}_2\text{SO}_4 & + 2\text{NaOH} \rightarrow \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O}
\end{align*}
\]

The resultant sodium sulphate is crystallized under vacuum and sold into the chemical industry. A significant portion of contained water is boiled off, so there is little or no liquid to be disposed of from the smelter. (In some countries there is no crystallization step, and the resultant liquid is disposed of in the effluent or trade waste systems. This is changing rapidly with Governments cracking down on this practice, such as in South Korea where smelters must now remove the sodium sulphate as they do not want this salt in the aqueous systems.)

iii. Reclamation of Spent Acid. There are a handful of companies across the world that recover spent acid that is then re-used in batteries and other purposes. The prime example of this process is at East Penn Batteries in the United States that recycle millions of litres a year by a process covered under a patent\(^4\) which was granted to the company. It is important to note that the smelter is located onsite at their large battery factory, and the majority of the acid is sourced from this plant because for the most part, it is uneconomical. Other battery producers have not adopted the process. There is another recently developed method of cleaning acid by the Brazilian company Antares\(^5\) although the acid produced by their approach is not returned for use in batteries.

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\(^3\) Engitec website  
\(^4\) US patent 4,971,780  
\(^5\) Antares website
6.1. **Hazelwood Proposal for Spent Acid Treatment**

The method initially proposed in the WAA, section 4.4.2., page 21, for the neutralization of the spent acid, was with the addition of zinc oxide sourced from galvanizers residues, although changed to agricultural grade zinc oxide in the subsequent AddWAA page ii. Whilst this is chemically feasible as this is one method of producing zinc sulphate, it is an uncommon process in the neutralization of battery acid, and no known smelter is operating this method.

Chunxing will now adopt the commonly used lime neutralization set as outlined above in point i, which poses a minimal risk in both operational and environmental aspects. The neutralization with zinc-based products will be reviewed as a Research & Development project to be work on at a later date.

Regarding points ii and iii from the above section:

- Chunxing would like to operate their furnace in the oxide slag matrix, so sodium compounds are an unwanted product in the furnace, so point ii would only cause problems with the slag matrix. (Although it should be noted that desulphurization techniques with sodium compounds, outlined in the following section, do produce a low sodium product through processes such as "back-washing" the paste whilst it is the press).

- Cleaning of the acid is not an option for this sized smelter, considering both volume and cost to clean. Further, for the amount of "clean acid" produced, there is no real outlet in Victoria for this type of material.
7. **The Importance of Sulphur**

One concept that is not well understood in the secondary lead industry (in fact most metallurgical sectors) is that processing and smelting operations are driven mainly by the need to remove sulphur. It is difficult to directly smelt many metals from a sulphide/sulphate compound, as oxides are preferred as they will easily reduce to the metal phase. The removal and capture of the element often dictate the equipment used at the smelter, and often operators are unaware of the role and effect it has on the overall process. The primary source of the sulphur in battery scrap is the lead sulphate (PbSO₄). This compound is present in the battery paste with levels of around 50 - 55%. Residual spent battery acid also plays a role in contributing sulphur to the system.

It is a stubborn element to remove in many metallurgical processes. For example, in primary copper, nickel, zinc and lead operations, the sulphur from the sulphide minerals is removed from the process via the formation of sulphuric acid. Unfortunately, this process is not relevant to the secondary industry as firstly; we are treating sulphate, not sulphides. Secondly, the set-up of the primary roasters/furnaces are designed to produce and collect a concentrated sulphur dioxide, the precursor to sulphuric acid.

For secondary lead smelting there are three paths for the removal of sulphur, being:

- **Pre-desulphurization:** Treatment of the lead paste feed before the smelting stage in order to reduce or remove the contained sulphur.

- **Furnace desulphurization:** Utilization of slag or matte to absorb the element.

- **Post desulphurization:** Treatment of the off-gases to capture the sulphur containing gasses.

In all smelters, there is at least one of these routes or methods used to remove most of the sulphur, but some smelters utilize all three processes to remove the element. Even to collect residual levels that remain the system after the smelting stage smelters are installing scrubbing units. The type of furnace selected also has a direct impact on the deportment of the sulphur as it can dictate whether a matte or oxide slag is to be formed. Most new smelters now incorporate a desulphurization step of some sort prior to the furnace, and importantly owners are much more cognizant of handling sulphur and its importance than previously.
7.1. **Desulphurization Methods**

7.1.1. **Pre-Desulphurization**

Treatment of the feed before smelting in the furnace is now considered a significant step at plants across the world, particularly those that operate rotary furnaces. This process is driven both by environmental regulations, and financial drivers with reduction of slag make and increased recovery performance, becoming standard features in many operations.

Generally, sulphur is around 5.3% in the paste mainly contained in the lead sulphate, although there can be a small amount of residual sulphuric acid present. The pre-desulphurization step generally forms part of the battery breaker operations and either integrated or in close vicinity.

The most common method employed throughout the world for this stage is the use of sodium compounds, albeit with several variants, and some newer processes using ammoniacal compounds as outlined below. One important note is that desulphurization methods are a cost to the smelter, and this is particularly the case for pre-desulphurization. For example, in the case of sodium, the cost of purchasing the sodium carbonate, converting it to sodium sulphate, then the crystallization step can cost the smelter upwards of USD100 per tonne equivalent of lead. Simply looking at the purchase price of sodium carbonate USD$350, the selling price of sodium sulphate USD$40, and adding in the molecular weight "factor" between the compounds, there is a substantial cost to the process.

i. **Sodium Compounds**

In most operations, lead paste from the battery breaker is screened/filtered from the metallic lead and plastic fractions once the battery has passed through the hammermill, and then pumped as a slurry into reaction tanks. Simplistically outlined, sodium carbonate is added to the reaction tanks and via reaction 4 allows the exchange of the sulphate present in the slurry to covert to lead carbonate:

\[
PbSO_4 + Na_2CO_3 \rightarrow PbCO_3 + Na_2SO_4
\]
Alternatively, the lead sulphate containing slurry may be treated with sodium hydroxide in place of sodium carbonate to produce lead oxide via the abridged reaction:

\[ \text{PbSO}_4 + 2\text{NaOH} \rightarrow \text{Pb(OH)}_2 + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O} \]

Each of the above processes has advantages over the other, in terms of sulphate conversion, the solubility of additives or formation of unwanted insoluble salts. The smelter will select the procedure most suitable, but as the cost of the reagents is the primary driver, sodium carbonate is often preferred as it is far cheaper than hydroxide.

The resultant desulphurized paste, which is de-watered via a filter press, will still contain some residual sulphur, generally between 0.5 and 1% depending upon the operations. The sodium sulphate produced is crystallized, often meeting food-grade specification and on-sold to the chemical market. Some equipment manufacturers produce a partially desulphurized product in their designs, with the final sulphur around 1.8 to 2.3% in the paste.

ii. **Ammoniacal Compounds**

The use of ammonium-based compounds is not widely used in the secondary lead industry (although research has shown it to be just as effective as sodium-based compounds) as the infrastructure is more complex.

Numerous paper and patents cover the subject including a patented method using ammonium carbonate/bicarbonate\(^6\) in a five-stage reaction which is termed the "amine" process. No known companies are operating this method, although the paper does quotes sulphur in the paste at around 0.5%.

Recently there has been an operation commissioned in Nigeria by STC Italy\(^7\) with urea being the precursor to the desulphurization of the paste by the reaction:

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

This plant has just commenced production, and it is the first plant to operate with urea. One significant difference between the other processes is that the reaction takes place between 140°C and 180°C and under high pressure, but the reported sulphur in the

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\(^6\) Comparative analysis of two processes for desulphurization of battery paste

\(^7\) http://lead.stcitaly.com/

\(^8\) New Innovative Route for the Desulphurization of Lead Paste, G Fusillo et al. LABAT 2020
paste is around 0.4 – 0.7%. Engitec had announced\(^9\) that Ecorusmetals in Russia were installing an ammoniacal system in 2014, but the company operates a system based on sodium.\(^10\)

### iii. Other Compounds

There is little other work done apart from with the above compounds, mainly due to chemistry, the solubility of the compounds, and the cost of the raw materials. Some work has been carried out by Morachevskii\(^11\) et al., with calcium hydroxide, but minimal results came from it. One of the main reasons again is the solubility of the compounds.

#### 7.1.1.1. Hazelwood Proposal for Pre-Desulphurization

Although paste desulphurization via sodium compounds is the most common process in secondary lead, it is understandable that Chunxing wants to avoid as much sodium compounds to the furnace as possible, thereby limiting the impact on the slag as the element tends to change the solubility of the slag. Whist there are simple methods to reduce sodium in the paste as mentioned above the other driver is cost.

Section 4.4.4., page 22, WAA, outlines the proposed method of desulphurization with either ammonium bicarbonate or lime. In correspondence with Chunxing and shown in Figure 19, page 61, WAA, the stated level of sulphur after desulphurization of the paste with ammonium bicarbonate is 3.44%. This could only be considered partial desulphurize compared the sodium processes with removal down to 0.5%. Further, due to the possible technical difficulty in using ammonium compounds in the reactions, Chunxing has decided not to use this method upon start-up. It will be reviewed under a future research and development project.

A lime (calcium hydroxide/oxide) solution will now be used in place of ammonium bicarbonate. The solution will be the "milk of lime", that is, the liquid from the lime/water solution containing minimum solids. Its first role will be to neutralize any remaining acid following the previously described reaction 1. Its second role will be to partly desulphurize the paste, as the compound has very low solubility in water at 0.12g/100g. In comparison, ammonium bicarbonate is 25g/100g and that of sodium

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\(^10\) [https://en.ecorusmetal.com/ecology](https://en.ecorusmetal.com/ecology)

carbonate of 29.4g/100g in water. Further hindering desulphurization is that the end product gypsum precipitates out of solution, unlike the very soluble sodium and ammonium sulphates.

Due to the formation of gypsum mixing with the paste during this partial desulphurization technique, the compound must be removed before it enters the furnace. The well-known method in mineralogy processing of Heavy Medium Separation (HMS) will be used by Chunxing to split the denser lead compounds from the lighter gypsum following defined Tromp curves. The separation will be done over three tanks to extract a clean gypsum fraction which will ultimately be mixed with the other gypsum streams onsite.

The final lead paste will still contain a high level of sulphur/sulphate and could only be considered as partly desulphurized.

7.1.2. **Furnace Desulphurization**

Generally, this involves the formation of a slag or matte with the ability to absorb sulphur into its matrix. One of the roles of slag is to capture impurities from the reactions occurring in the furnace. In all metallurgical systems, slags are the scavenges of many types of impurities and unwanted elements and are generally oxide based. But in the secondary lead industry, we have a slag that captures sulphur to become part of the slag matrix, to a level where it can be considered as a true matte, although we refer it as a slag. The two examples are outlined below.

i. **Soda Iron Slag System**

Known in the industry as the soda-iron system as the main constituents are soda ash and iron, it is well suited to the rotary furnace. Metallurgically, this slag regime is based around the sulphide reaction series, which means that the reactions are sulphur based, unlike that of primary lead and other smelters that are oxygen-based.

Sulphur-based reactions are an uncommon series, and there are very few applications in the metal recovery and smelting industry using it as described here. The recovery of antimony from antimony sulphide ores is the only other system that comes to mind.
For the lead sulphate compound in the paste, the system works in two stages. Firstly, the conversion of lead sulphate to lead sulphide by the addition of a reductant such as coke or coal. The lead sulphide formed in reaction 7 is then converted to metallic lead in the presence of iron, with the formation of iron sulphide via reaction 8. The metallic iron is generally in the form of waste turnings or cast iron borings.

\[
PbSO_4 + 2C \rightarrow PbS + 2CO_2 \quad ---- \quad 7
\]

\[
PbS + Fe \rightarrow Pb + FeS \quad ---- \quad 8
\]

\[
2PbSO_4 + Na_2CO_3 + Fe + 9C
\rightarrow 2Pb + FeS.Na_2S + 9CO + CO_2 \quad ---- \quad 9
\]

Sodium carbonate is added to completing the system, firstly as a fluxing agent, secondly as it has a significant role in combining with the iron sulphide to form the compound erdite, outlined above as FeS.Na_2S in reaction 9. (also written as NaFeS_2). In true metallurgical terms, is, in fact, a matte, due to the high sulphur content.

The two benefits of the soda-iron slag system are;

- The slags low melting point. It has a melting point of around 695°C. This temperature is much lower than for metallurgical reactions of any type. In other systems, such as silicate-type slags, temperatures range from 1,200°C to 1,700°C.

- Its ability to capture virtually all of the sulphur present in the battery scrap. The slag captures approximately 99% of the sulphur charged to the furnace in the battery scrap. The remaining 1% is usually found in the fume collected by a baghouse or other dust collection devices. (Previously, due to low levels in sulphur stack emission, no auxiliary equipment, such as acid plants or scrubbers, were required but operations are now installing scrubbers as insurance against sulphur dioxide emissions).

The negative aspect of the soda-iron slag is that secure landfills are required in most countries for its disposal. The amount slag produced from a plant varies depending upon the level of paste desulphurization; for a 15,000 tonne per annum plant the slag production would be around 5,000 tonnes for non-desulphurized paste whilst it is about 3,800 tonnes for a 0.7% sulphur containing paste. Interestingly, across the world, it has various classifications, from hazardous waste in Europe to places in South and
Central America where it is referred to as "green slag" and is classified as non-hazardous.

ii. **Iron-Calcia-Silicate Slags**

This type of slag is common for both primary and secondary lead smelter furnaces. In primary smelting, this is the mainstay of the industry with the various levels of its oxide constituents depending upon the furnace and feed. It is also used in secondary lead smelting.

It is not a slag often seen in rotaries due to the higher operating temperature required, but is common in reverberatory, blast, and cupola furnaces as they can operate well above 1000°C. Importantly, in a reverberatory, it is preferable that the sulphur-in-feed is relatively low as sulphide mattes and oxide slags possess an immiscibility between each phase, as displayed in figure 3 below:

![Diagram of phases in a reverberatory furnace](image)

**Figure 3. Schematic section of phases in a reverberatory furnace.**

It's not always possible to have a low sulphur feed and the furnaces with lancing/air injection operations (which includes blast furnaces and cupola's who use tuyeres to inject air), high sulphur can be treated and the element removed through a number of reactions forming sulphur dioxide. Including the reactions 7 and 8, many others do take place, such as:
FeS + O₂ → FeO + SO₂

2PbS + 3O₂ → 2PbO + 2SO₂

And the decomposition of lead sulphate at over 1000°C

PbSO₄ + Heat → PbO + SO₂/₃

The fundamental reactions in the furnace with sulphur-free material are:

PbO + 2C → Pb + 2CO₂

PbO + C → Pb + CO

It should be noted that the oxide reactions also take place in the soda-iron system as lead oxide is also present. (Lead dioxide PbO₂, which is the dominate oxide in battery paste decomposes at 290°C to PbO and plays no part in these reactions).

A significant feature between the two slags(/matte) is that reactions take place "inside" the soda-iron slag, changing the composition of the main ingredients, like iron to iron sulphide/erdite, whereas in the oxide slag properties are dictated by the level of the various oxides. For example, high silica (SiO₂) slag gives a sticky, thick flowing (viscous) slag that tends to entrap metal and results in an increased metallurgical loss. A high lime (CaO) slag has a higher melting temperature and makes opening the slag-tap hole more challenging. A slightly higher lime slag (20 to 22%) can help reduce tin and other element losses.

7.1.2.1. Comparison of the Two Slag Systems

Slag chemistry, with reactions and phases continually occurring at high temperature, is one of the most complex and unknown parts of the secondary lead industry.

Importantly for the smelter, once specific recipes and mixes are defined, consistency of each batch needs to be maintained to reduce variability. Understanding what is going into the furnace is critical, and a great effort goes into the sorting and separation of high and low sulphur feeds. This is particularly true for smelters who employ a paste desulphurization process to remove sulphur and, do not want to add high sulphur containing feed to it before it enters the furnace for smelting.
It has been shown at numerous sites that the higher the sulphur level in the feed, the higher the lead-in-slag. Previously with no desulphurization battery scrap, smelted lead in the slag was typically 3 to 4%, and levels below this were rarely seen. Critical to this was the level of iron and carbon added to the furnace.

With the change to a lower level of sulphur in feed, it has had an impact of not only the volume of slag produced but the lead-in-slag range. It is now standard practice for "paste smelts" that the lead-in-slag ranges between 0.8 and 1.5% in rotary furnace slags. Higher lead-in-slags tend to occur as the sulphur levels increase in feed.

For the oxide type slags, the matrix does not hold sulphur like the soda-iron slag as outlined above. Sulphur in soda slags can be upwards of 12% whilst the oxide type is around 1 to 2%. The oxide matrix can be quite complex, as displayed in figure 4., showing the CaO-FeO-SiO₂ ternary phase diagram, where the compositional elements of the slag are critical in producing good operating parameters for the furnace.

This slag system is widely used, not only in primary lead smelting but other non-ferrous metals smelting. An oxide system for secondary lead smelting similar to the Chunxing proposal was outlined by Jin W., Yang S., et al., discussing the Oxygen-Enriched Side-Blown Pool smelting technique developed in China. Along with information from the phase diagram, it can be seen that silica and calcia play a significant role in the formation of the slag.

The other major difference in the systems is the operating temperatures. The soda-iron slag operating range is around 900 to 1000°C whilst the oxide slag works at over 1100°C and depending on the ratio of the principal oxides can increase to over 1250°C as can be seen in figure 4. This elevated temperature results in a much higher intensity smelting operation compared to the dynamics of the rotary furnace.

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12 Reaction Mechanism on a Novel Enhanced Smelting Technique for Lead-Acid Battery Paste Recycling. TMS 2020 page 961-970
Figure 4. Ternary phase diagram of the CaO.FeO.SiO$_2$ matrix showing the complexities in the different ratios of the compounds (M Krickel).

7.1.2.2. **Hazelwood Proposal for Slag Formation**

As indicated by Chunxing, the slag is in the CaO.FeO.SiO$_2$ matrix and this is confirmed in a number of analyses subsequently received. This is a typical slag for the type of process outlined and lies within the normal range of the major elements.

i. **Lead.** Measured levels show the lead in the matrix to be around 0.8 to 1.2% which is the average level. The value is given in the WAA Table 37, page 126 of 0.2% is possibly from some other process, but the whole analysis given should be dismissed. (In the AddWAA, section WAA Erratum page iii, it mentions of the lead-in-slag change as a "minor numerical nature". I would consider the change a major one.)
ii. Sulphur. The level of sulphur in the slag is considered a standard range of between 1 and 2%. As outlined above, sulphur/sulphides are not compatible with the oxide matrix, so it will not be as high as the soda-iron slag. There is also another phenomenon that occurs with iron and sulphur; in the first instance iron will react with sulphur to produce iron sulphide, but after a prolonged time and heat, the iron sulphide will eject the sulphur ion and take up oxygen in its place.

iii. Other Elements. The other elements listed in the analyses supplied all fall within the typical "slag" range which includes the iron, silica and calcia values. One "marker" in secondary slag is barium which is an element not common in lead but is added by all battery manufactures into the negative plate of a battery as barium sulphate. It ends up in the slag and values in the analysis indicate it is from a secondary process.

The slag analyses for Chunxing is typical of smelting lead paste with an oxide slag matrix. Post-treatment generally has to take place in a high-intensity furnace to gain very low lead levels in slag. These furnaces operate in an oxidizing state, often termed a slag fumer where oxygen and high temperatures effectively oxidize elements such as lead, zinc, antimony and arsenic from the slag. Just to note, slag fuming cannot be done with the soda-iron slag due to the different matrix.

The proposal for the Hazelwood smelter is to quench the molten slag once it leaves the furnace, as shown in Figure 9, Page 26 of the AddWAA. This method is an advantage over casting to slag buckets as the slag is shattered and easy to handle on disposal as the material to slag buckets has to be physically broken. The breaking of slag by this method creates a potential dust problem for the smelter. It should be noted that this operation may increase the pH to the quench water, as shown in the TCLP leach results supplied by Chunxing in the initial pH data upon contact with water.
7.1.3. **Post Desulphurization**

Post-desulphurization describes the method of capture of sulphur dioxide that has been emitted from the furnace generally via an alkaline scrubbing system. For plants that operate an oxide-based slag, such as blast furnaces, cupola's, old-type reverberatories, a scrubbing system is a standard feature of these plants. Flue gas desulphurization (FGD) technologies have focussed on scrubbers to be the primary treatment of sulphur dioxide emissions from the furnace.

Scrubbers are also a common feature at secondary smelters who utilize rotary furnaces and the soda-iron system, generally as a safety backup and to meet the ever-tightening emission limits across the world. A well-managed scrubbing tower can remove 98% of any residual sulphur dioxide contained in the off-gas after pre-sulfurization or desulphurization during smelting.

7.1.3.1. **Hazelwood Proposal for Post Desulphurization**

The Hazelwood proposal has been outlined in section 4.4.7.1., page 27 of the WAA, with the use of two wet tower scrubbers in series, using lime to precipitate the incoming sulphur dioxide. There will also be another set of redundant scrubbers to aid the plant in continuous operations, cleaning and maintenance.

This set-up is standard for this type of furnace and operation, and this technology has been in use for many years in well maintained secondary smelting operations. The redundant set that has been designed is also good insurance to maintain plant operation.
7.2. **Overview of the Department of Sulphur and its Removal**

As indicated previously, the soda-iron system was the predominant choice for slag formation, and effectively, the desulphurization process for rotary furnaces for many years. This has now changed, and the standard western secondary lead plant now has pre-desulphurization steps installed, for example, the new plant in Nigeria with STC novel technology and TNC’s Thailand plant using Dross Engineering’s "in-situ" desulphurisation technique.

Importantly, as outlined in the pre-desulphurization processes, not all sulphur is removed from the paste, and the soda-iron reactions are still called upon in the rotary furnaces to capture the last of the sulphur. The benefit of this is that there are fewer reagents, (iron and soda ash), added to the furnace and slagmake is significantly smaller than previous operations without pre-treatment. Often these smelters also have a scrubbing system as a final backup to capture over 98% of the initially contained sulphur. Smelters have also become much smarter in the handling of feed, particularly categorizing feed into high sulphur and low sulphur.

All of this impacts the overall system and operating parameters, in particular, lead-in slag and slagmake. We can see this in the deportment of the sulphur across the different operations in the following graphs.
Figure 5. Deporment of sulphur in the soda-iron system

As expected, figure 5 shows the extent the older type soda-iron slag systems were reliant on the slag capturing all the sulphur. There was rarely a backup scrubber in those systems due to low sulphur dioxide emissions. Slagmake was high at around 300 kilograms per tonne of bullion.

With the installation of a pre-desulphurization process, most sulphur is deported to the sulphated by-product and removed before the furnace. The low sulphur load to the furnace results in lower slag to metal ratio of around 150 - 180 kilograms per tonne of bullion depending on the operator. Figure 6 shows the effect of desulphurization on the sulphur deportment, which is the system used by the Enirgi Wagga Wagga plant often compared to in both reports. Modern smelters also operate scrubbing systems to remove any lingering sulphur in the gas stream.

Figure 6. Deporment of sulphur in a rotary furnace with desulphurized paste.

For an oxide slag system, figure 7 displays the sulphur deportment from a current cupola operation which was taken from a smelter in Thailand that operates the FeO.CaO.SiO₂ system. There are no pre-desulphurization steps, and the feed is untreated. The capacity of the furnace is around 15,000 tpa.

Whilst some small portion of sulphur reports to the slag as a matte in a FeS-CaS complex, the majority of the sulphur reports to the scrubbers, which are the packed-
bed type. These large units remove the sulphur dioxide as gypsum. This is a typical chart for the old blast furnace/cupola systems, of which many have been closed but would also mimic the old Chinese coal-fired reverberatories.

Figure 7. Deposition of sulphur in a cupola system with no pre-desulphurization stages.

Figure 8. Deposition of sulphur in a U.S. reverberatory system with pre-desulphurization. (Note. This is for a two-stage system)
Some Reverberatory type furnace operators in the United States have now added a pre-desulphurization step to remove the sulphur before entering the furnace, and this is shown in figure 8. It must be remembered that this is for a two-stage process as this type of furnace produces a slag that must be treated in a second furnace.

The last chart, figure 9, displays the sulphur distribution from the proposed Hazelwood operation. The chart uses data supplied, including the pre-desulphurized paste figure of 3.55% which was using ammonium sulphate and the corrected slag/sulphur from the AddWAA Figure 19, Page 61, which reads "S - 3.0t" should read "S - 0.45t".

![Proposed Hazelwood](image)

**Figure 9. Deportment of sulphur in the proposed Hazelwood system.**

This deportment ratio is also not surprising as previously referred to, Page 27 of the WAA:

“..........*through close control of the O₂ lance, to oxidise the FeS-bound sulfur back to SO₂ (FeS + O₂ → Fe + SO₂ and 4Fe + 3O₂ → 2Fe₂O₃).*”

The operating parameters of the furnace dictate that sulphur levels in the slag are continually driven to sulphur dioxide and therefore to the scrubber system. The proposed Hazelwood process, as outlined in the documents, is very much dependent on the efficiently and capture of sulphur dioxide in the scrubber system.
8. **Furnace**

The furnace is often considered the heart of the operation, with the major metallurgical reactions occurring inside these vessels, producing the bullion lead. Over the years, the type of furnace and their designs have undergone significant change and development across the world. Blast and cupola type furnaces were very common right up into the 1980’s. Subsequently, new developments were introduced, such as the European Bergsoe process where whole batteries were charged to the furnace utilizing the plastic case as a fuel and a reducing agent. Others also included the top-blown Kaldo process and long-barrelled rotary kilns.

Many of these processes have closed, although some furnace variants like the Bergsoe process operate at a single site. Newer developments are replacing them, such as the proposed Chunxing furnace and Hubei Lusheng's "side-blown pool smelting" process. Current and new operations can be classified as one of the following groups:

i. Small plants (10,000 to 25,000 tpa). The rotary furnace and its variants are the most common furnace now being installed in the secondary lead industry. Simple design, cost-effectiveness, operating in batch mode and ease of operation make it the furnace of choice for many small operators. Variants include tilting rotary and rotary reverberatory, but improvements in areas such as burner technology have made it an efficient system. There are still several small cupola type and blast furnaces operating around the world, but they are being phased out due to tighter regulations and the pollution problems associated with them.

ii. Larger plants - USA (> 40,000 tpa.) In the 1980's and 90's the United States phased out many of the older style blast furnaces, closing many of the smelters and developing a two-stage smelting process with the first part using a single reverberatory furnace coupled with a slag/dross treatment furnace. A soft bullion is producing in the reverberatory, and the dross/slag contains the other elements such as antimony and tin.

The second furnace can be any type including, rotary, electric arc and conventional blast furnace. These are still operating and are generally larger units of around 80,000 to 100,000 tpa.

iii. Larger plants - Rest of World. (> 40,000 tpa.) Although there have been
several companies adopting the US-style reverberatory furnace set-up, such as Ecobat's H.J. Enthoven\(^\text{13}\) operation, many of the older companies have upgraded their facilities. For example, Weser Metall\(^\text{14}\) of Germany with Ausmelt's Top Submerged Lance (TSL) technology\(^\text{15}\). Newer smelting technologies for larger plants have come out of China. The most notable is the SKS (Shuikoushan)\(^\text{16}\) furnace which has been widely adopted for primary smelting. In secondary smelting, new developments range from the side-blown furnace as outlined by Chen\(^\text{17}\) et al., to work by done by Chunxing. This process is partly described in the WAA document.

iv. Larger scaled plants are using a multiple number of rotary furnaces to increase the tonnage of the plant, such as the Clarios (formerly JCI) operations in South Carolina and their Mexican operation in Villa de Garcia where each site is rated at 130,000 tpa.

Each system has its "pro's and con's" and idiosyncratic nature of the operation, but each result in the production of bullion lead and slag of some type/matrix. The bullion passes onto the refinery for further treatment, whilst the slag can be disposed of or further treated.

Rotaries generally use the soda-iron system as outlined in section 7.1.2.1, but they can also operate with oxide matrices, including the FeO.CaO.SiO\(_2\) system. There are some exceptions, but the general slag type from the other furnaces mentioned is oxide based. (Exceptions would involve the formation of a matte for further treatment). Furnace systems across the world are continually undergoing improvement in both environmental and performance aspects. Under normal production parameters, the type of furnace does not generally dictate the reactions of the furnace, the metal output or the slag composition. They are mainly dependant on the slag system chosen and the feed being smelted.

There have been attempts by the sellers of new or novel smelting technology to scale down their systems to suit a smaller smelter such as Ausmelt (which has a joint venture with Gravita India\(^\text{18}\) to promote TSL technology). One major hurdle is the capital cost

\(^{14}\) https://recylex.eu/en/weser-metall/
\(^{16}\) https://www.researchgate.net/figure/Schematic-diagram-of-an-SKS-Shuikoushan-smelting-furnace_fig1_320436066
\(^{17}\) https://link.springer.com/chapter/10.1007/978-3-319-48093-0_16
\(^{18}\) https://www.researchgate.net/publication/270338739_Small-Scale_Secondary_Lead_Processing_using_Ausmelt_TSL_Technology
of this type of set-up compared to a rotary system. There have been two Isasmelt smelters (which also utilize the TSL technology) built for secondary lead and both were shuttered over ten years ago. The first one in Britannia, Northfleet U.K. (at the time a subsidiary of MIM the owner of Isasmelt) shut down in 2004 and MRI in Malaysia closed several years later.

8.1. **Hazelwood Proposal for the Installed Furnaces**

The Chunxing proposal is for two 5 metre diameter side-blown furnaces to smelt battery paste and drosses under an oxide slag matrix. The output of the two furnaces is 9,100 tpa each giving a smelting capacity of 18,200 tpa, which in equivalent is the yield from a five cubic metre tilting rotary furnace (TRF).

It has been documented numerous times in the WAA (Section 4.5.5. page 41) and AddWAA (page 117) that the Chunxing’s secondary lead smelting technology is from "modified ISASMELT process". Based on the limited technical information supplied, it is not based on a modified ISASMELT, but the proposed Chunxing furnaces have more in common with a reverberatory smelting system. The Isasmelt furnace is a high-intensity operation utilizing top submerged lance (TSL) technology which is also used for concentrates to produce litharge along with reduction. This cannot be done in a reverberatory or the proposed Chunxing furnaces.

Figure 10 below shows a schematic of a typical reverberatory furnace common in the United States, whilst figure 11 shows the view of the proposed Chunxing smelter. In comparison with the new furnace techniques being developed figure 12 shows the cut-away of the Hubei Lusheng Environmental Engineering Co.‘s oxygen-enriched side blowing furnace. All three furnace variants drive the sulphur off in the charge to sulphur dioxide (SO₂). The significant difference between the three shown is the use of lances and burners to the furnace, and the traditional reverberatory is a rectangular design rather than circular like the Chinese designs.

(Note: Small coal-fired reverberatory furnaces of around 8,000 tpa capacity were very common in China before being phased out due to pollution problems amongst other issues, so the local industry has a good understanding of the dynamics of this furnace. The coal-fired rotaries were rarely found outside of China.)
Figure 10. The cut-away view of a typical reverberatory furnace.

Figure 11. A detailed outline of the proposed Chunxing furnace set-up for Hazelwood.
From the information given regarding the Chunxing furnace:

i. It is a novel "twin" furnace utilizing heat from each furnace, whether to heat the incoming feed or to smelt. Effectively the "filling side" or empty furnace is acting as a storage for the product from the battery breaker. Waste heat is an area underutilized by many furnace operations, and it good to see being used here in this set-up.

ii. The proposed smelter has several advantages over the reverberatory, particularly the ability to mix periodically with the air lances (although oxygen lances are also mentioned). This is aided by the circular structure of the furnace, assisting the movement of the smelting products and slag. It is expected lancing rates are controlled so as not to start the re-oxidization of the lead, as done in cupellation. This is outlined on page 27 of the WAA:

"The furnace conditions are switched from reductive (to maximize Pb recovery) to oxidative later in the smelting cycle, through close control of the
O₂ lance, to oxidize the FeS-bound sulphur back to SO₂ \( (\text{FeS} + \text{O}_2 > \text{Fe} + \text{SO}_2 \text{ and } 4\text{Fe} + 3\text{O}_2 > 2\text{Fe}_2\text{O}_3) \)."

The other advantage with the air injection is that slag can be formed, unlike that of the U.S. reverberatories where the slag has to re-treated in another furnace.

iii. Fume from the furnace seems to be well controlled as everything appears to be enclosed, although this will have to be confirmed.

As new smelting concepts across the world develop engineering and control dynamics continually evolve. Smelters are designed with consideration of all aspects, including fume capture, operating parameters of workers, etc. I believe this will continue with the design of the proposed furnace.

What does not change is the reactions in, and the outputs out, of the furnace. The matrix of the slag will depend upon the raw materials added to the furnace.
9. Melting and Processing of Metallics

One of the "holy grails" of secondary lead smelting is the ability to process lead-bearing material by simply melting rather than smelting. The relatively low melting point of the element at a mere, 327°C, allows some material to bypass the furnace, thereby having distinct advantages over smelting, namely:

- Melting is a much simpler, cheaper and cleaner process than smelting.
- There are cost savings between melting and smelting the product.
- Better recovery of product overall. Although the dross recovered from the melting operation has to be re-smelted, the overall recovery is much higher.
- It also saves elements like antimony and arsenic from being lost to the slag.

One of the major problems is that although the product from a battery breaker is termed "metallic", the material still actually contains a lot of oxidized and sulphated material. One of the functions occurring in the lead-acid battery is that with continuous cycling and use of the battery, the positive plate decomposes. This is the primary failure mechanism of the battery, as in the electrochemical reaction of the battery, as outlined in Appendix A, causes the metallic grid to corrode and convert to lead dioxide eventually. The negative plate, on the other hand, does not undergo corrosion and retains its metallic integrity and as such, can be remelted with some ease. Tests at numerous smelters around the world have shown that direct melting of the metallic fraction direct from a battery breaker is extremely difficult at best, although the melting of the larger fraction. Internal work at a European smelter shows that as the size of the metallic fraction decreases, the amount of dross increases to a point where there is no metal recovered.

9.1. Hazelwood Proposal for Metallic Melting

From figures 20 and 21, on pages 63 and 64 respectively, AddWAA, the data shows that between 37 to 41% of the metal production from the Hazelwood plant will be derived from the direct melting of the metallic fractions produced from the battery
breaker. I believe this figure/range to be reclaimed from melting this fraction is very high, as in a spent lead-acid battery there is rarely this level of metal present, as indicated in table 1, section 5.

Chunxing is proposing the use of a mineralogical process to clean the metallic fraction. This novel process will remove the oxide, and sulphated corrosion layer on the fraction and the simple process of melting in a pot at 500°C will yield metal and dross which will be returned to the furnace. By directly melting the metallic fraction and recovering the metal in bullion form is an overall benefit to the operation and profitability.

The final product would be a hard lead bullion containing a number of general alloying elements such as antimony, arsenic, tin and copper. It will require further refining if an alloy is to be produced, of which there are many thousands in the battery manufacturing world.
10. Refining and Casting

As outlined in section 5, with the design of battery breakers, there is also no world standard design for the layout of a lead refinery. Even in turn-key plants, there are options for the buyer to select from several differing designs. The layout of a refinery is dependent on the plant/furnace set-up, logical molten metal flow and the final products required. Some of the key attributes to a well-designed and functioning refinery are:

- Have the ability to keep bullion metal molten rather than casting it to block. There are energy and manufacturing savings by having the metal delivered from the furnace in liquid form.

- Design the refinery from an operator’s perspective so that material handling is minimized and drossing, casting and access to the kettles is not hindered.

- Refining Kettles adequately designed and at a height that can be easily "worked" by the operator. This also includes the volume, which should be matched to the required pure/alloyed lead.

- Have the ability to pump the finished molten lead product efficiently to the casting machine.

- Correct positioning of the casting machine adjacent to the refining kettles will aid in less dross and ease of casting.

10.1. Refining Methods

Once bullion lead has been tapped from the furnace to the refinery, it must undergo processing to remove impurities. Bullion lead, as such, cannot be used for any part of the lead-acid battery or other end products due to the high level of contaminants present, such as nickel, antimony, arsenic, sulphur, in secondary and further levels of silver and bismuth in primary material.

There are two methods of lead refining in the world: the electrolytic Betts process and the pyrometallurgical method employing the Harris and Parkes processes. These methods are well established across the globe. The Betts methodology will not be
discussed here as it is only used in Primary lead circuits.

10.1.1. Pyrometallurgical Refining

Also referred to “Fire Refining”, this process is the most common technique used in the refining of both primary and secondary lead throughout the world. The overall method involves five major stages for the refining of primary lead, of which secondary smelters utilize only three of the steps due to the much lower level of impurities, namely silver and bismuth.

In primary refining, because of these higher elemental levels, the Parkes process is used to remove the silver and gold if bismuth is elevated, it must be removed by the Kroll-Betterton method. Each of the processes is quite complex and carried out in their own refining kettle or section of the plant, and the metallurgy will not be discussed here. The Harris process is adopted in conjunction with oxygen softening to remove the other impurities, along with copper which is extracted with simple sulphur addition. Because of these various refining steps, a primary refinery involves the "pumping" of lead from one section to the next before final casting.

Unlike Primary, secondary producers can operate the refinery in a true batch mode by using one pot to refine and if needed, alloy the lead to the required specification. Refining of secondary lead is not as complicated as refining of primary lead as the low levels of bismuth and silver are generally below the specification limits required for most lead alloys and therefore do not require removal. With simple drossing operations to "clean" the lead by lowering the level of impurities, lead bullion is available for softening/alloying almost immediately. The major removal steps for the elements is given below:

i. Copper. This element is often first to be removed with the addition of sulphur (or a mix of iron pyrite (FeS) and sulphur) to the bullion lead, with the removal by the formation of a copper sulphide dross.

ii. Antimony, arsenic and tin. The Harris process was first patented in 1919\(^\text{19}\) in involves the adding of sodium hydroxide or sodium nitrate to molten lead at around 500°C to remove these elements under the following reactions:

\[
5\text{Sn} + 4\text{NaNO}_3 + 6\text{NaOH} \rightarrow 5\text{Na}_2\text{SnO}_3 + 2\text{NO}_2 + 3\text{H}_2\text{O} \]

---

\(^{19}\) US Patent 1,582,037
2As + 2NaNO₃ + 4NaOH > 2Na₃AsO₄ + NO₂ + 2H₂O ----- 16

2Sb + 2NaNO₃ + 4NaOH > 2Na₃SbO₄ + NO₂ + 2H₂O ----- 17

In many cases, one compound is often added to remove the elements, particularly sodium nitrate due to its oxidizing properties. If the elements are too high, particularly antimony and tin over 0.5%, pure oxygen is often lanced into the molten metal to oxidize these elements from the batch. Once the level has been reduced to an acceptable level, the Harris process is then used.

iii. Nickel. This element has been the recent focus by battery companies due to the problems associated with gassing in the battery. Specifications have written with tighter limits at to meet these limits the process of adding red phosphorous to the pot is now becoming common, via the reaction:

\[ 8\text{Ni} + P₄ \rightarrow 4\text{Ni}_2P \]  ----- 18

The final product from a secondary refinery will often meet many lead specifications other than those with tight silver and bismuth levels. The physical quality will also be on-par with the Primary product.

10.2. **Hazelwood Proposal for the Refinery**

The design and operation of the proposed refinery at the Hazelwood plant are typical of many other plants around the world. Whilst the proposed size of six refining kettles, (five will be used in the refining process), each holding 120 tonnes of lead is quite large for a 28,000-tonne operation, it is a benefit to have excess capacity in this part of the process. It aids in better scheduling of the operation, better refining time and in future expansion plans of the company as this arrangement could easily cope with the doubling of furnace capacity. The company may want to consider if they were going to produce lead-calcium alloys a pot size of around 50 tonnes would be more preferential to produce alloys.

Figure 14, Page 42, AddWAA, shows the kettles opposite to the furnaces, which is a logical set-up as it can take advantage of the molten metal flow directly from the
furnaces. As indicated, this method saves the company both energy and time in processing the metal and that a solid lead bullion product is not cast separately and requires storage.

Lastly, the employment of the Harris process in refining the lead bullion is standard in the lead industry and poses no process risk. Although stated in WAA and corrected in the AddWAA, this refinery cannot produce 99.994% lead but will yield a product around 99.97% to 99.985% purity.
11. Pollution Control

Pollution and accompanying environmental parameters and performances are major considerations in the safe and responsible operations of a lead smelter. Over the years, there has not only been a considerable improvement in environmental performance but a greater awareness of employee welfare, the need to be environmentally sound and provide safe working conditions. An example of this is the steps taken by the industry, as its initiative, to install equipment to continually drive emission levels down such as the Wet Electrostatic Precipitator as outlined below.

As with the other components of a smelter, the baghouse has become an essential and normal part of operations. For scrubbers, and regarding section 6.2. and sulphur deportment, many rotary set-ups did not need this system as the sulphur was removed during the other treatment stages. They are now being installed to these plants to reduce the risk of sulphur dioxide emission further and thereby improve environmental performance. The major items of equipment in pollution control are listed below:

i. Baghouse. The baghouse is a standard feature of all secondary lead smelters across the world and designed not only for fume and dust capture but being designed for improved drafting right across the plant. The primary driver, of course, is the removal of particulates from the gas stream and preventing particulate emissions into the environment, It also captures the lead-bearing dust which is returned back to the furnace for smelting and recovery. Continuous improvement is always a feature of filter cloth design and construction along with better cleaning techniques in the latest baghouses,

ii. HEPA Baghouse Filters. High-efficiency particulate air (HEPA) filters are now becoming quite common in smaller secondary smelters around the world. They generally have a smaller footprint than the traditional cloth baghouse.

iii. Scrubbers. As indicated earlier in section 6.1.3., scrubbing systems have been around for many years for the collection of sulphur dioxide. They are a standard installation even for those smelters operating rotary furnaces and soda-iron slags.

iv. Wet Electrostatic Precipitators (WESP). Sections of the secondary lead industry have been continually lowering their particulate emissions, and in the United States, one significant improvement was the installation of
WESP’s. This technology has been used for many years in the Power Generation area, particularly for coal-fired power stations. The first one for the secondary lead industry was installed in California in 2012, and the process has been rolled out at other smelters across the world. The technology facilitates the capture of particulates down to 0.1 micron and reduction levels in lead and arsenic of greater than 95% are achieved\(^{20}\), with emissions less than 50kg per year for 100,000 tpa operations.

v. Regenerative Thermal Oxidizers (RTO’s). Along with WESP’s, smelters are also installing RTO’s in operations to oxidize any volatile organic compounds that may be in the gas stream.

Other items in plant operations also should be included in pollution control, such as the latest burner technology of Oxygen/low NO\(_X\) units. These are commonly used across the industry now, not only to minimize the formation of NO\(_X\) gases but to increase production.

11.1. **Hazelwood Proposal for Pollution Control**

The proposal for the Hazelwood plant is to install a baghouse/wet scrubber set-up which would be considered the basic requirement for the system described. The WAA and AddWAA documents state there is excess capacity in the system, including the redundant dual scrubbing tower, with the size of the scrubbers, but reflects the level of sulphur dioxide reporting to the system.

It should be noted that WESP’s and RTO’s are becoming more common, but currently, they are being installed in the larger capacity plants in the USA and Europe due to their initial installation cost. Figure 8, page 33, WAA, is most likely a representation of Chinese reverberatory operations, not reverberatory plants in the West.

12. Future Developments in Lead Smelting

Novel methods proposed for recycling of lead-acid batteries without the need of smelting have been promoted for over 50 years. The majority of these ideas stem from the fact that people consider the material as "waste" and look for a better way to recycle ethically. Often mentioned is the elimination of poor practices of battery recycling in third world countries. These projects look at bypassing the furnace and focus on novel hydrometallurgical or wet chemistry routes, but all have the same fundamental flaws:

i. The primary focus of these ideas is the treatment of the paste only, and there is no recovery of any of the other elements present in the battery such as antimony, arsenic, tin, barium, etc.

ii. The remaining "residues" from the battery and process are required to be treated in the furnace.

iii. Most new processes require the dismantling of the battery by a breaker system, and the paste must be desulphurized. Other than the shelved Engitec FAST method none of the newer processes can recover lead directly from lead sulphide/sulphate.

iv. Some of the processes do not produce lead metal but a lead oxide. Whilst lead oxide is a key component in the production of a battery; it is quite different from the product derived from these processes.

v. No full-scale plant has been built and operated, with most only making it to the pilot stage. No system has been adopted for large scale commercial operations.

Theoretical models or pilot plants can’t accurately predict outputs of full-scale plants due to the complexity of systems, the wastes they generate and the form of the final product. Many of these new processes are based on hydrometallurgical or electrochemical concepts. They often fail to account for the complexity of control inherent in a production scenario, rather than the lab or bench testing environment.

For example, the plants for the recovery of zinc and nickel are very complex operations, having their own waste problems to solve. Primary lead is also refined by
electrochemical methods, utilizing the Betts Process\textsuperscript{21} developed in 1908. Lead to the purity 99.994\% is recovered; however, the process requires bullion metal from a furnace. This method produces a higher purity lead than that recovered by pyrometallurgical refining.

Some of these shelved processes are listed below:

i. Engitec process. This process uses a leach solution of fluoroboric acid and lead fluoroborate where the desulphurized battery paste is added to a reactor with the leaching solution. Lead carbonate and lead oxide convert into soluble lead fluoroborate, whilst lead dioxide is converted to lead oxide in the presence of metallic lead and addition of hydrogen peroxide. The solution is heated and stirred, aiding the conversion of the lead dioxide. Metal is recovered via an electrolytic cell.

ii. RSR EW process.\textsuperscript{22} This process uses fluorosilicic acid as the leaching solution. To convert the desulphurized paste to a form accessible by the solution the paste is dried and then heated to convert the lead carbonate and lead dioxide to lead oxide. The lead is electrowon from the solution using lead-dioxide-coated graphite anodes.

iii. PLACID/PLINT process.\textsuperscript{23,24} The PLACID process was based on the electrowinning of lead from a chloride solution in a cell. A semipermeable membrane separates the cathode and anode. Lead oxide and dioxide are converted to soluble lead chloride, whilst lead sulphate is converted in a hot brine circuit. The sulphate ion is removed as gypsum after the addition of lime. The PLINT process is an advanced adaptation of the PLACID process operating in parallel with a pyrometallurgical route smelting the metallic lead fractions from the battery.

\textsuperscript{21} Betts. A. Lead Refining by Electrolysis. 1\textsuperscript{st} Ed. J. Wiley 1908.
Current Processes that are under development include:

iv. Aqua Metals. The company developed a process of recovery of lead by the dissolution of lead oxides in methane sulphonic acid (MSA) and plating the pure lead onto rotating anodes. The paste must be desulphurized before treatment with MSA. A full plant was built but did not operate to capacity and since a fire, has been pulled back to pilot plant stage. The company has indicated that the process is a "bolt-on" to current smelters, as the residues from the process need processing in the furnace.

v. Aurelius. This company uses research developed at Cambridge University looking into a method involving the dissolution of lead oxides into citric acid to produce lead oxide suitable for batteries. No metal is produced, and a small pilot plant has been constructed.

vi. There are other research programmes such as Veerden in India with a process based on sodium hydroxide and at London College looking at eutectic lixiviants for a novel hydrometallurgical method. Each is still at "benchtop" stage.

Currently, there is no "new" process operating that can replace the current recycling methods for lead-acid batteries.

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25 https://aquametals.com/
26 http://aureliustechnology.com/
Reactions in the Lead-Acid Battery

In the operation of the lead-acid battery, electrochemical reactions that take place once the device is connected, thereby creating a circuit and producing a current. On the positive plate, the contained lead dioxide (PbO$_2$) starts to convert to lead sulphate (PbSO$_4$) on discharge. Electrochemically this can be written as:

$$\text{PbO}_2 + \text{HSO}_4^- + 3\text{H}^+ + 2\text{e}^- \rightarrow \text{PbSO}_4 + \text{H}_2\text{O} \quad ----- \quad 19$$

While on the negative plate, the metallic lead (Pb) on the plate again converts to lead sulphate (PbSO$_4$) on discharge and can be written as:

$$\text{Pb} + \text{HSO}_4^- \rightarrow \text{PbSO}_4 + 3\text{H}^+ + 2\text{e}^- \quad ----- \quad 20$$

These reactions do not work individually, so in combination, the total reaction of the battery system is the lead dioxide, lead and sulphuric acid convert to lead sulphate to produce an electrical current. The overall reaction in a battery is, therefore:

$$\text{Pb} + \text{PbO}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{PbSO}_4 + \text{H}_2\text{O} \quad ----- \quad 21$$

Once all the products have converted to lead sulphate the battery is discharged or "flat". Upon recharging the battery, these reactions are reversed, and the lead sulphate (PbSO$_4$) converts back to lead dioxide (PbO$_2$) and lead (Pb) on the respective plates. One problem is that this "cycling" gradually takes its toll on the battery dynamics, such as lead sulphate not totally reconverting back to lead and lead dioxide, to a point where the battery does not function as required and therefore becomes a "spent" or now commonly termed as a used lead-acid battery, ULAB.
## Glossary of Terms

<table>
<thead>
<tr>
<th>Term</th>
<th>Definition</th>
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<tbody>
<tr>
<td>AddWAA</td>
<td>Abbreviation of the Addendum to the Works Application Approval document dated 29th June 2020</td>
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<tr>
<td>Cell</td>
<td>In a battery, it refers to a group of negative and positive plates, along with the separators that are assembled in the battery.</td>
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<tr>
<td>Cupola</td>
<td>A vertical furnace similar in operation to a blast furnace. Often used previously to remelt cast iron.</td>
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<tr>
<td>Deportment</td>
<td>A metallurgical term to describe the distribution of elements throughout a system or process.</td>
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<tr>
<td>Desulphurization</td>
<td>A chemical process where the sulphur or its compounds are removed from a product.</td>
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<tr>
<td>Gangue</td>
<td>Waste material.</td>
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<tr>
<td>HEPA filter</td>
<td>High-efficiency particulate air filter for fine dust particles. Also known as high-efficiency particulate absorbing and high-efficiency particulate arrestance.</td>
</tr>
<tr>
<td>Partitions</td>
<td>The word has been used throughout the WAA and AddWAA documents with reference to separators. A partition is part of the battery container that divides each cell. They are effectively the fixed wall of the battery case.</td>
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<tr>
<td>Phase Diagram</td>
<td>Graphical representation of the temperature/compositional relationships of a set of elements or compounds.</td>
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<tr>
<td>Primary Lead</td>
<td>Finished lead metal associated with the production from a Primary smelter sourced from ore.</td>
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<tr>
<td>RTO</td>
<td>Regenerative Thermal Oxidizer which are used in industrial processes to treat volatile organic compounds.</td>
</tr>
<tr>
<td>Secondary Lead</td>
<td>Finished lead metal that is produced from secondary or scrap source like lead-acid batteries.</td>
</tr>
<tr>
<td>TCLP test</td>
<td>Toxicity Characteristic Leaching Procedure is a procedure used on wastes to determine whether there are hazardous elements present in a leachate.</td>
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<tr>
<td>Abbreviation</td>
<td>Description</td>
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</tr>
<tr>
<td>tpa</td>
<td>Tonnes per annum.</td>
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<tr>
<td>ULAB's</td>
<td>Used lead-acid batteries.</td>
</tr>
<tr>
<td>WESP</td>
<td>Wet Electrostatic Precipitators which are pollution control devices to remove ultrafine particulate matter.</td>
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</tbody>
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