Latest Developments in the Secondary Lead World

International Lead Zinc Study Group
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The recycling of batteries is now a “hot topic”, particularly around Lithium-ion. While this sector is in its infancy, driven by their use in EV’s, recycling lead-acid is a well-established industry.

Many of the processes and methods for lead production and refining are over 100 years old; the Harris process was first patented in 1919 and is still used today. The Betts electrolytic process was proposed in 1908.

The halcyon days of research into other methods of recovering the element were in the 1950’s and 60’s.

In the past five years we have seen a “renaissance” of R&D in treating lead compounds sourced from spent batteries.

Methods are now being explored, examining hydrometallurgical and novel chemistry routes to recover the element rather than undergoing smelting.

However, any new process should consider the “whole” picture of recycling the battery, understanding that other elements and compounds can influence or affect processes.

But are we in a “Renaissance of Research”?

There has been a lot of talk about new processes and plans, but we have seen little action at the plant level.

- Little “real” data is being published
- PowerPoint seems to be the main line of communication
- Looking into the hydrometallurgical routes
- Some are novel, others have been tried before
- Only addressing the lead paste

Secondary lead producers are keenly interested on any new method or improvements to their operations

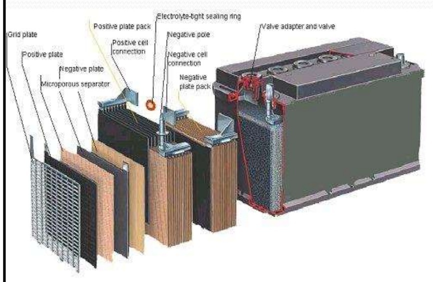
Lead-Acid Battery – An Urban Mineral Resource

A lot is written about the ULAB and recycling, but effectively it is a valuable "Urban Mineral" product, a key part of a "Circular Economy". In mining/mineral terms, once the product has been dismantled it is;

- High lead metallic fraction > 95%
- A compound of lead sulphate/dioxide with Pb > 70%
- Very little payables (i.e. Silver)
- Minor organic contamination
- Recoverable plastic payable

So what makes up this Urban Mineral Source………

Lead-Acid Battery – Not Just Lead



Additives (Expanders)
- Barium sulphate
- Carbon black
- Carbon/Graphite
- Lignosulfonates

Sulphates
- Hydrogen (Acid)
- Sodium
- *Cadmium*

Lead
- Lead sulphate
- Lead dioxide (no oxide)
- Lead

Plastics
- Polypropylene
- Polyethylene
- PVC
- Polystyrene
- ABS/SAN

Separators
- Polyethylene
- Polyvinyl Chloride
- Glass Mat
- Polyesters

"Foreign" Elements
- Nickel
- Cadmium
- Copper
- Cobalt
- Zinc
- Manganese
- Tellurium

Floc & Fibres
- Nylon/Polyesters
- PE/PP

Gums & Glues
- ethylene-vinyl acetate (EVA)

Alloying Elements
- Tin
- Antimony
- Arsenic
- Copper
- Bismuth
- Silver
- Calcium
- Barium
- Aluminium
- Selenium

Treatment of Battery Products

For any process, whether hydro or pyro, consideration must be made on the treatment, recovery and disposal of **all** elements and compounds contained in a battery.

- In current operations, internal circuits and processes are used to handle the elements, some of which are often unknown to the operator
- The "new" processes designed to treat only one portion of the battery, such as lead paste, must consider the residues and by-products remaining from their method.

But the most significant element to consider in any process is sulphur.

Sulphur is the Driver

The raw materials we use in the lead industry are associated with sulphur:

- Lead Sulphide (PbS - Galena). The major compound of the world's ore bodies.
- Lead Sulphate ($PbSO_4$ - Anglesite). The decomposition product of the lead-acid battery.

These two lead forms are very different, even to the point where they distinguish primary and secondary smelting. (Globally, more lead paste is produced than lead concs per annum).

Sulphur – the Hidden Driver

In non-ferrous metallurgical operations, the element that drives much of the technology and methodology we utilize is sulphur. Importantly:

- There are very few processes that directly convert a metal sulphide to metal.
- Even rarer is the direct conversion of metal sulphate to metal.

Whether taking a hydro- or pyrometallurgical route, intermediate processes must convert sulphur compounds into forms that can "access" the metal.

The First Hurdle……

This "accessing" the metal is critical in formulating a new process and depends on the leachate or method used. Reactions are limited to the solubility of the metal compounds, and lead is no different.

Whilst many of lead's inorganic compounds are either slightly soluble or insoluble, they are much more amenable to organic acids such as acetic and citric.

But, the conversion from a sulphate/sulphide still has to take place to allow the element to be open to the lixiviant.

In most processes, oxides and carbonates are the preferred species, although in some cases, PbO2 has to be converted to PbO.

The First Hurdle…… Simplistically

No currently proposed process converts lead sulphate to lead metal!

and in some cases,

Cannot convert the lead dioxide (PbO_2) to oxide either!

Methods currently used in smelters must be employed to convert these products - desulphurization.

For decomposition of lead dioxide, complex chemical steps have been suggested. In smelting, the dioxide is converted to oxide by simply heating above 300^{o}C.

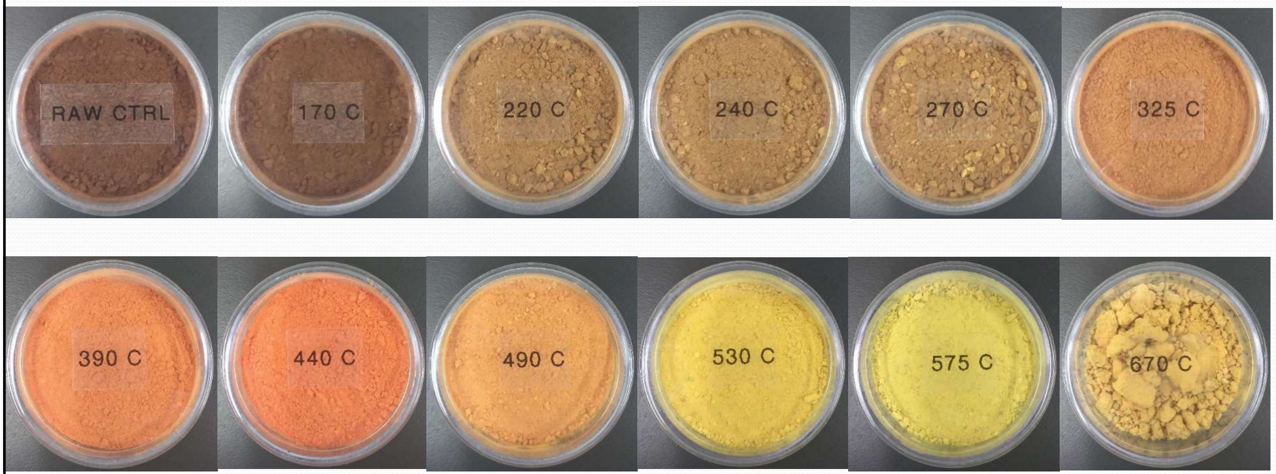
Desulphurization

The most common method to desulphurize lead paste is using sodium carbonate, via the aqueous reaction;

$$PbSO_4 + Na_2CO_3 \rightarrow PbCO_3 + Na_2SO_4$$

Other compounds, such as NaOH and ammoniacal based products, can be used, but it is important to note that they are all equilibrium reactions. Therefore, some levels of sulphur-bearing compounds remain in a residue. The actual level depends on the process and methods used, but up to 20% of sulphur compounds can still be unconverted.

Dynamic Nature of Paste



The Second Hurdle…… Residues

As mentioned, there are numerous other compounds in a battery that have to be handled. A residue is left when treating the paste in many of these processes.

- Sulphates. Part of the lead sulphate does not undergo desul conversion and reports to the residue
- Carbon. This element is added to all batteries, mainly as carbon black. It is used to enhance cycle life and help the battery recover from deep discharge
- Carbonaceous products. Lignosulphonates and other expanders are added to the battery paste to improve performance.

The Second Hurdle…… Residues

- Barium. This element is added as sulphate and plays an important role on the negative plate to prevent compaction. All auto batteries contain this element.
- Flocs & Fibres.

The suggestion for the solution to this problem is to return this residue back to a smelter. Problem is this residue has a higher portion of unwanted elements for a smelter and may invoke a TC!

However, some elements, like carbon, can be helpful in the furnace.

Flocs and Fibres

Flocs and fibres are added to the paste as mechanical reinforcement, holding the paste to the grid and thereby reduce shedding.

They are resistant to acids, alkalis and heat in a battery.

When charged to the furnace mixed with paste, they form part of the “carbon group” that aids in reduction.

For any leaching, techniques the material will remain in the residue.

The Other Hurdles……

So far only the issues of handling the lead paste have been outlined, but there are other “hurdles” facing the researchers;

- Trace Elements There are at least 15 minor and trace elements found in the lead components of a battery.
  - Tin. Is a major alloying element in nearly all batteries ranging up to 2%.
  - Antimony & Arsenic. These alloys are still in wide use. Upon plate decomposition they enter the paste streams.
  - Se, Cu, Ni, Ag, Bi, et al.

Deportment of Elements

Element	Source	Level in the battery	Deportment (%)			
			Furnace			
			Slag	Metal	Fume	Gas
Ag	Impurity and an alloying element	In USA; 0.005% in PAM/NAM	2	98	0	0
Al	Alloying element in Calcium alloys	0.01% in Ca alloys	100	0	0	0
As	Alloying element in antimony alloys	0.1 - 0.2 in Sb alloys	60	25	15	0
Ba	BaSO4 is added to the negative plate	0.4% as BaSO4 on the negative	100	0	0	0
Bi	Impurity in lead and alloys	0.01 in most lead alloys and soft	5	95	0	0
C	Additive to the Neg plate	up to 2% in neg plate	10	0	0	90
Cd	Impurity but was an alloying element	formly 1.5% in Absolute positive	50	0	50	0
Cu	Impurity and an alloying element	0.03% in Sb alloys	2	98	0	0
Ni	Impurity from deleterious sources	Mainly from Stainless Steel	60	40	0	0
Sb	Alloying element in antimony alloys	Sb ave in bullion around 0.7%	25	70	5	0
Se	A grain refining element in Antimonial alloys	0.02% in low Sb alloys	50	0	50	0
Si	From Separators	Insoluble in lead	100	0	0	0
Sn	Alloying element in nearly all alloys	1.2% in pos Ca; 0.2 in neg ca/Sb alloys	75	25	0	0
Te	Impurity in battery	0.002 in some Euro/US lead	20	80	0	0
Tl	Impurity in battery	0.002 in some Euro/US lead	?	?	?	?
Na	Additive in battery/In dross from NaOH/NaNO3	Mainly from dross	80	0	20	0

The Other Hurdles……

- Leaching Medium or Lixiviant.
  - Excess requirements
  - Solubility
  - Reuse/Recyclability
  - Toxic/Carcinogenic Characteristics.
  - Volume
- Waste Streams
  - Volume
  - Toxicity/Solubility
  - Solids disposal


Mag x40


Mag x40

Summary

New entrants in the market should take time to understand these dynamics and see where processes and procedures can "fit in" to improve the performance and operations of lead-acid battery recycling.

Their most likely success will be treating the residues and by-products from primary and secondary operations, such as flue dusts and drosses.

We still have a long way to go……….

The Current Situation

Over the past 50 years, we have made tremendous gains in OH&S, and some great work and programmes continue in that area.

However, the secondary industry still faces many technical and environmental challenges globally. Each operation has its priorities, often dictated by the country and region they operate in, and although they vary smelter-to-smelter, the problems are common.

Lead's Challenge - The Four S's

Slag

Sulphates(Sulphur)

Separators
&
Simplicity

The First "S"

Slag

The Importance of Slag

Rarely in smelting operations do we consider the “value” of the slag, metallurgically speaking. Little focus is often given to the product, due to:

- Environmental issues
- No monetary value
- Seemingly quite complex

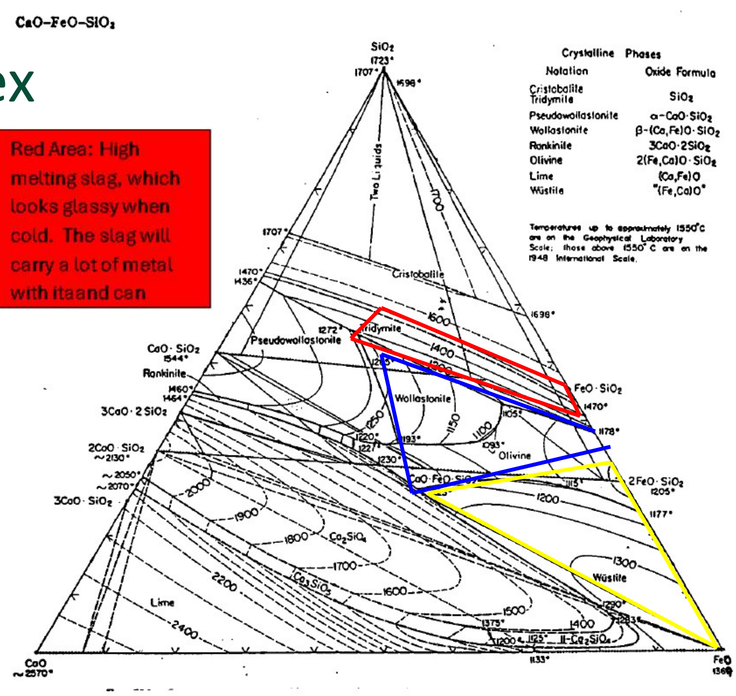
But it should be considered the first stage of refining as it gathers the major impurities in the smelt cycle

Matrix’s are Complex

Blue Area: Low melting slag, which carries a low amount of metals. This slag is the most likely to pass hazardous waste testing. It does not freeze quickly and allows a fast smelting furnace.

Red Area: High melting slag, which looks glassy when cold. The slag will carry a lot of metal with itaand can

Yellow Area: High iron and low melting slag; fast smelting, but carries a lot of metal with it. This generally fails hazardous waste testing and causes iron sows and crusts to form in the furnace.



Secondary Slags

But the problem for smaller secondary lead plants the operating parameters for an oxide slag is harder to achieve;

- Type of furnaces utilized/operated
- Rotaries of varying size
- Operating temperature achieved
- Consistency of charge material

And Sulphur…….

The Soda-Iron system

The name “Soda-Iron” refers to the slag produced upon smelting. On the surface, the system seems quite basic, with several simple additives;

- Lead-bearing scrap
- Soda Ash (sodium carbonate)
- Iron
- Carbon (Coke, coal, anthracite, etc)

And carried out in basic rotary furnaces….

Element Capture

There are a whole host of other elements and compounds in typical battery scrap:

- From plates
  - Sb, As, Sn, Ca, Cd, Al, Cu, Ba
- From separators/plastics
  - SiO_2, Al_2O_3, Cl, Br
- From refractories and other sources
  - Cr, Mn, NiCad's

The slag easily absorbs these elements into the matrix and encapsulating them into various compounds

Soda-Iron has Its Problems

However, Soda-iron slag breaks down due to its sodium content.

- It continues to react after cooling
- Can spontaneously combust
- Varying lead content, from 1% up to 10%
- Leachable
- Limited use in some countries, banned in others
- Dumping costs

Whilst the reactions are metallurgically complex, this slag is easy to produce and is the most common slag type worldwide.

The Second "S"

Sulphur (Sulphates)

Sulphur – the Hidden Driver

In non-ferrous metallurgical operations across the world, the element that drives the technology and methodology we utilize is sulphur.

This is not recognized in many areas of smelting which means that the operator never really understands the system they operate.

And it is not easy element to handle in the smelting system, either producing a product of little value or is a waste

It dominates 3 of the 4 S's!

Secondary Lead - Desulphurization

There are three areas in secondary smelting where sulphur can be removed:

1. Pre-Desul - The removal of sulphur from the feed before it enters the furnace i.e. treatment of feed.

2. In Situ Desul - The capture of sulphur in a slag or matte matrix.

3. Post Desul - The capture of sulphurous-rich fume (sulphur dioxide), which is released from the furnace.

1. Pre-Desulphurization

The most common Pre-Desul method is the addition of sodium carbonate (Na_2CO_3) to a slurry of battery paste from the breaker.

$$PbSO_4 + Na_2CO_3 \leftrightarrow \mathbf{PbCO_3} + Na_2SO_4$$

- A basic exchange reaction, but importantly, not always to completion, as a portion of lead sulphate remains in the paste.
- The solid lead carbonate/paste is filtered out, and the aqueous sodium sulphate is removed for either recovery or disposal

Battery Paste

De-Sul

- Higher Running Cost
- More complex
- "Technical" Operation
- Good quality scrap
- Lower slag make
- Environmentally better
- What to do with Na_2SO_4

No De-Sul

- Cheaper
- Less complex
- Basic Operation
- OK quality scrap
- Higher slag make
- Environmentally difficult

2. In Situ or Furnace Desulphurization

This method is where a slag or matte is formed in the furnace to capture the sulphur in its matrix.

PbSO4 + C > PbS + CO2

then

PbS + Fe > Pb + FeS

3. Post-Desulphurization

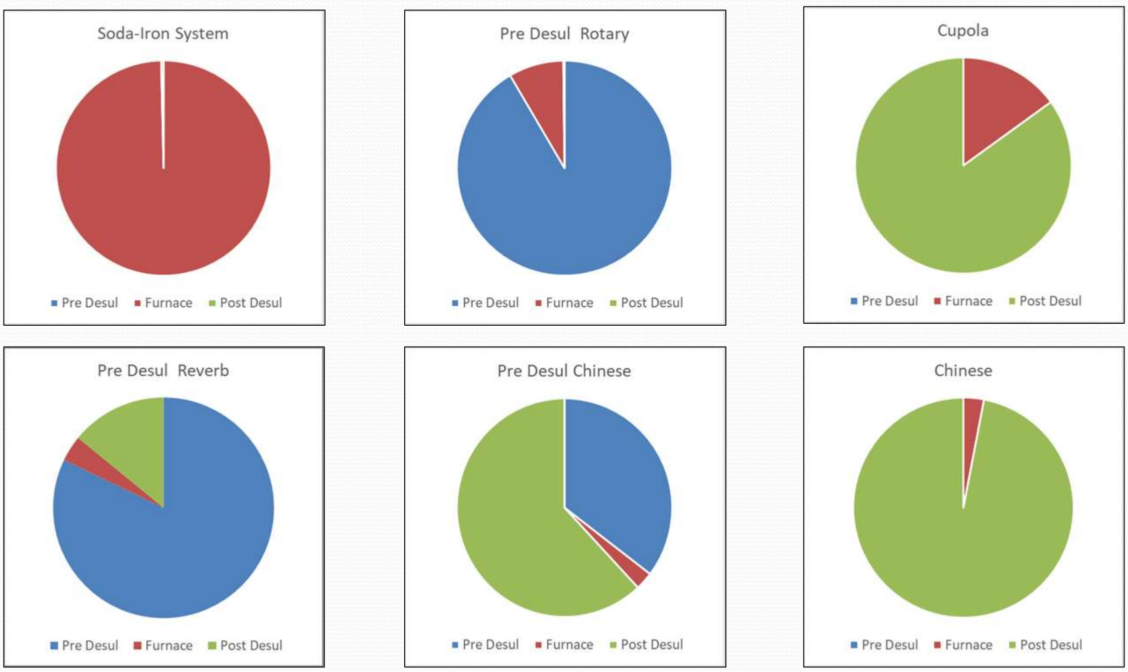
One problem with older type furnaces, particularly blast and cupola, they do not use a sulphur capturing slag.

The sulphur dioxide is emitted into the gas stream and must be removed by complex scrubber systems, or in primaries, acid plants.

$$SO_{2(gas)} + Ca(OH)_2 > CaSO_4 \text{ (Gypsum)}$$

or

$$SO_{2(gas)} + \{H_2O\} > H_2SO_4$$



The Third "S"

Separators

Separators – A Dilemma

The only major section of a used battery that is not recyclable is the separator.

To many smelters they don't see the problem as whole cells are smelted, but with the "newer" battery breakers, they are extracted as a separate stream/product.

Some regions demand they be disposed, in others customers just don't know what to do with them.

But more problems loom with the growth of the AGM separator

Separators – The Problem

The "problem" varies across the world;

- Many countries classify the material has hazardous and they must be disposed correctly, costing up to €750 per tonne!
- Others are forcing smelters to "recycle" them, as they consider them as polyethylene (PE)
- Some companies try to burn them with little success.
- Other countries have no restrictions on disposal and are done a cheap as possible.

Separators – The Problem

Although we often classify them as PE, there are a number of reasons why they cannot be recycled like the PP battery cases;

- One of the major issues is that they are not only PE but contain up to 60% silica
- They still contain lead and as many tests have shown, it is very hard to remove the element
- Each company has its own "sep" formula
- Contamination with other separators such as AGM and gauntlets

Tests have been carried out to examine recyclability

Separators – A "Temp" Solution

The general composition of a separator is quite simple, Silica, PE and mineral oil. This material can find a home in the furnace as;

- Reducing agent. The PE effectively replaces part of the carbon in the furnace.
- Recovery of lead. The contained lead in the separators can be recovered.
- Slag Former. Silica is a slag forming agent in the smelting process. We don't want too much though!

The Final "S"

Simplicity

Simplicity ….. What Does it Mean ?

Lead compounds are simple to smelt!

- There is no other common metal that is so easy to smelt and recover that metal
- Aluminium and other metals are “recycled/reused” by melting not smelting
- The feedstock is easily available

This is why smelting methods range from 44-gallon drums to 120,000 tpy reverb furnaces, which of course results in poor smelting practices and environmental & health concerns.

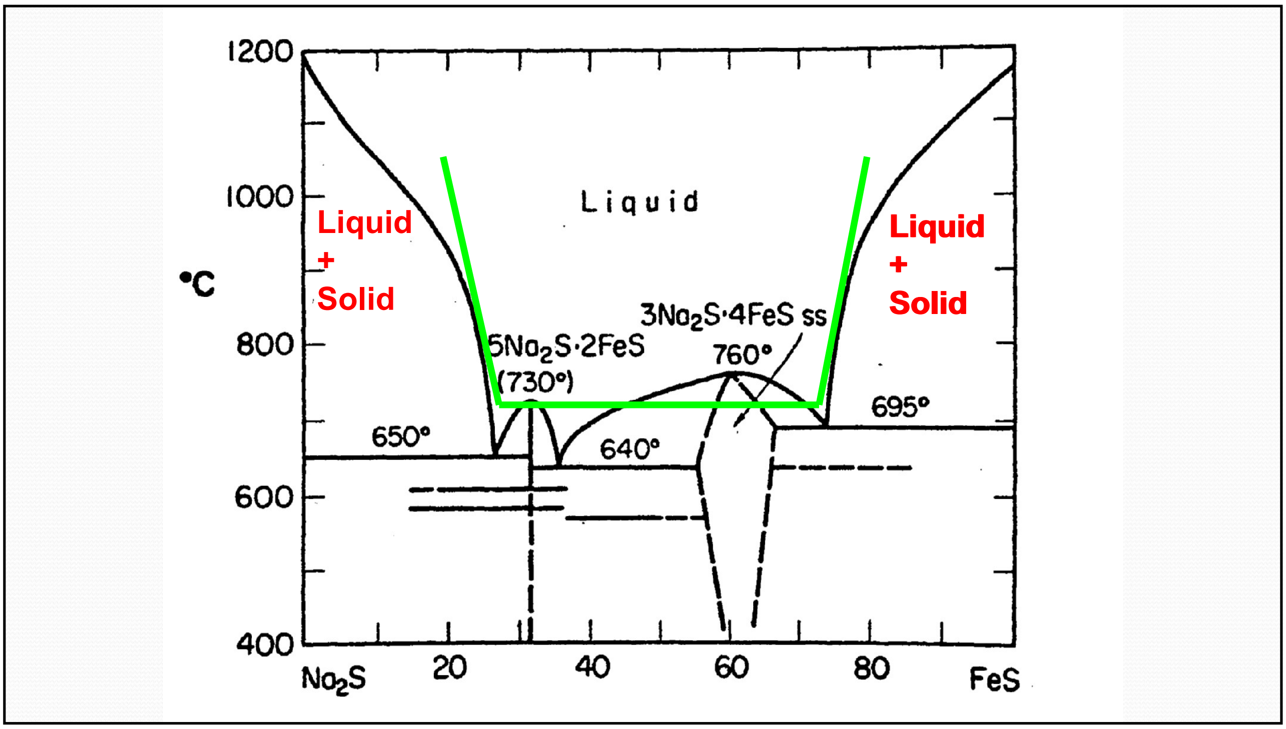
This is Part of the Problem!

All these reactions outlined, although complex, take place quiet easily.

- They occur at low”ish” temperatures
- They generally go to completion
- Very little activation is needed

Aiding this is the “window of operation” for the slag.

In the metallurgical world this is massive! In oxide slag matrixes we talk of +/- a few percent, for the soda-iron we talk in “10’s of percent”!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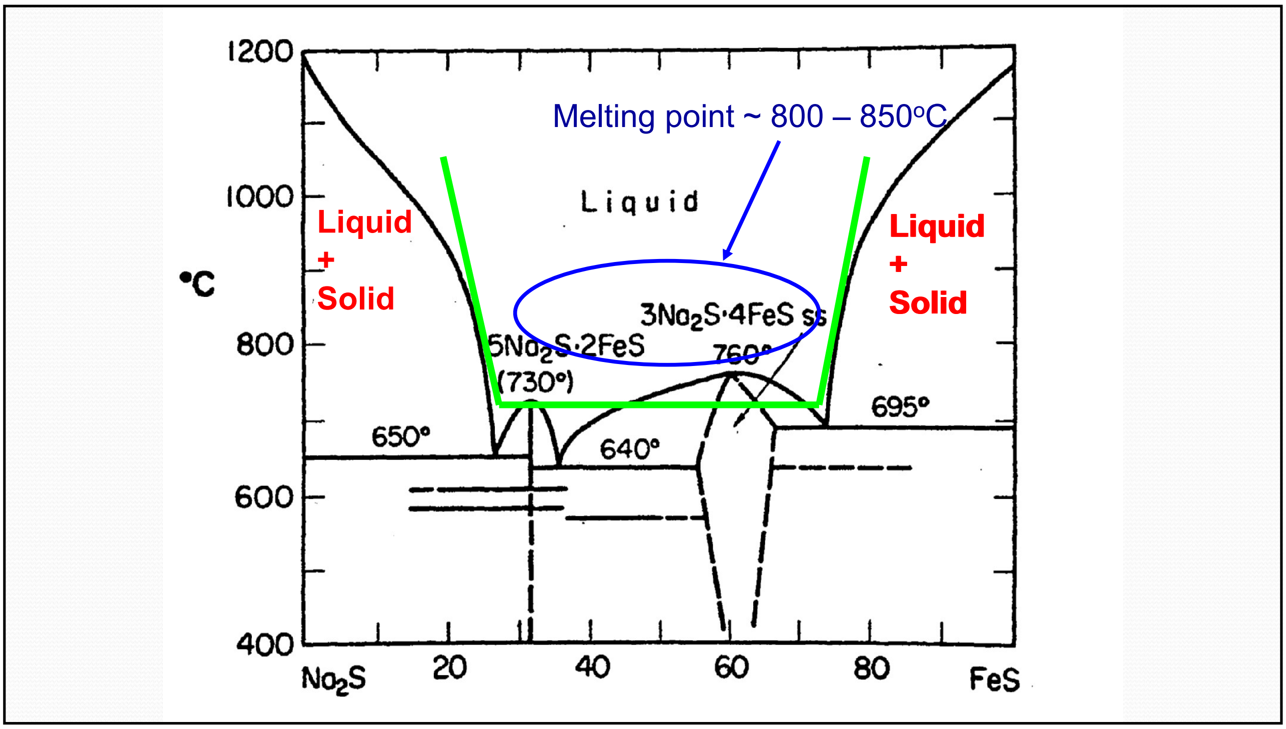
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The Current Situation

Other global challenges in recycling ULAB's also exist, varying from country to country and region to region. Informal backyard recycling is a significant problem and undermines all the excellent work undertaken by the responsible players in the industry.

Issues such as the dumping of the electrolyte from the battery before transport to a smelter is a major environmental issue

This problem alone should be the driver for new methods of processing and recovery of products.

Global Environmental Problem

ULAB's are a traded scrap commodity. ISRI categorize them as;

Rains *SCRAP DRAINED/DRY WHOLE INTACT LEAD*

To be free of any liquid. Cases to be either plastic or rubber and be complete including caps. Non-lead (nicad, ni-fe, carbonaire, etc.) not acceptable. Industrial, steel cased, aircraft (aluminum cased) and partial, cracked or broken batteries and batteries without caps subject to special agreement. Review packaging specifications and regulatory status pertaining to shipping with buyer prior to sale.

Summary

Research is vital to maintain the growth of an industry, and the secondary lead sector is no different. New ideas and processes should always be supported to improve the operation of the industry.

But it is also worth remembering that the current operations deal with just more than lead, recovering, treating and capturing the numerous components, compounds and elements that make up the battery. The whole battery is treated, not just selected sections.