Session Introduction
Challenges for the Old and New Players in the Secondary Lead Industry

Pb2023 Athens

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In the past ten years there has been a “resurgence” of Research & Development in the recycling and recovery of lead from ULAB’s

We have a lot of new methods proposed particularly in the recovery of lead from paste (PbO_2/$PbSO_4$)

This session we are going to hear from speakers presenting their latest work, along with equipment suppliers and updates on recent developments

But firstly, let’s see where we have come from…….

Laying the Foundations – Era I

The scientific foundations for the smelting, recovery and use of lead were well in place by the 1960's;

Gaston Planté 1859 - *"Lead-acid Battery"*

HO Hofman 1895 - *"The Metallurgy of Lead"*

AG Betts 1910 - *"Lead Refining by Electrolysis"*

W Hofmann 1935 - *"Lead and lead alloys"*

H Ellingham 1944 - *"Ellingham diagrams; Chem Soc"*

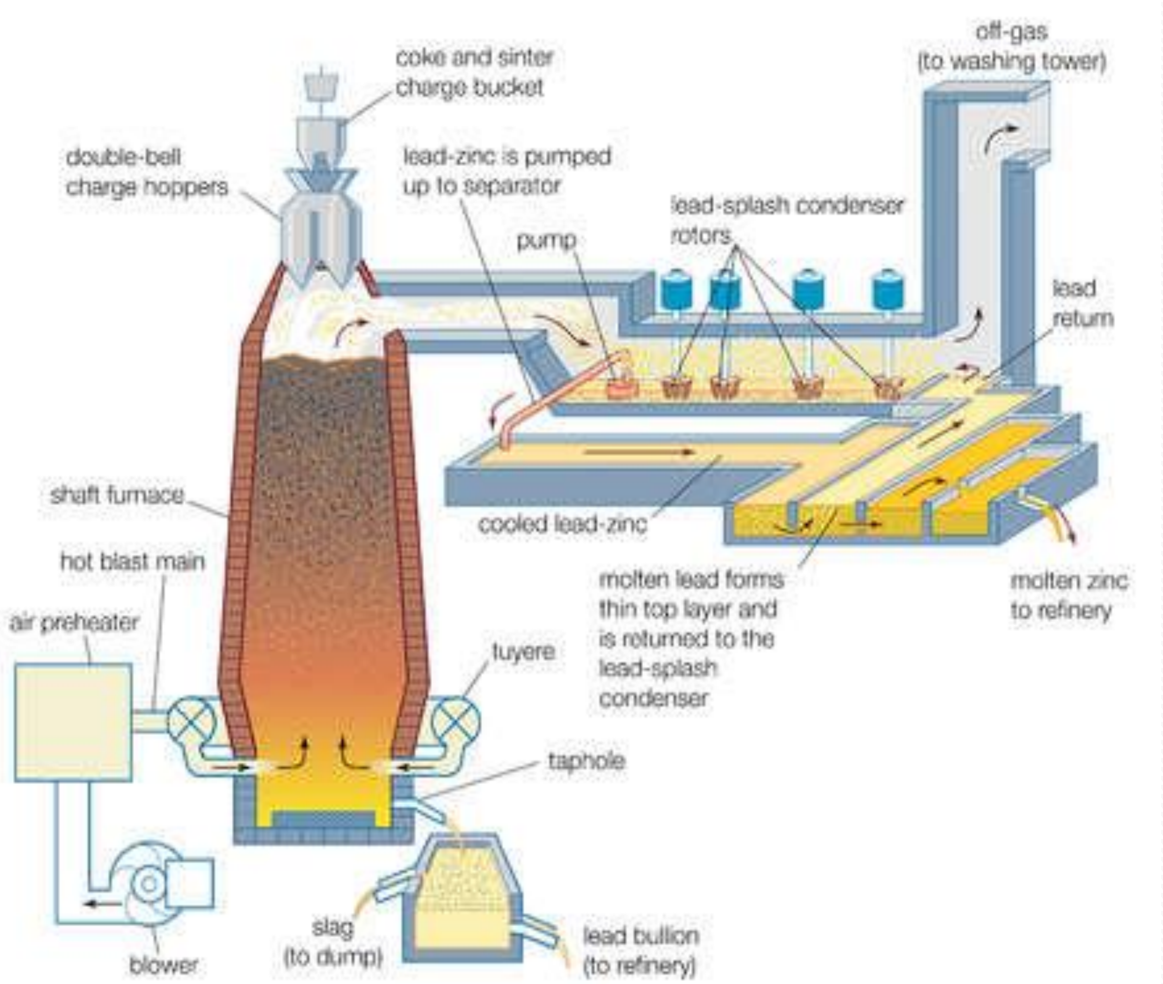
These "rules" apply today in the smelting and refining of lead at all operations around the world, however basic the plant

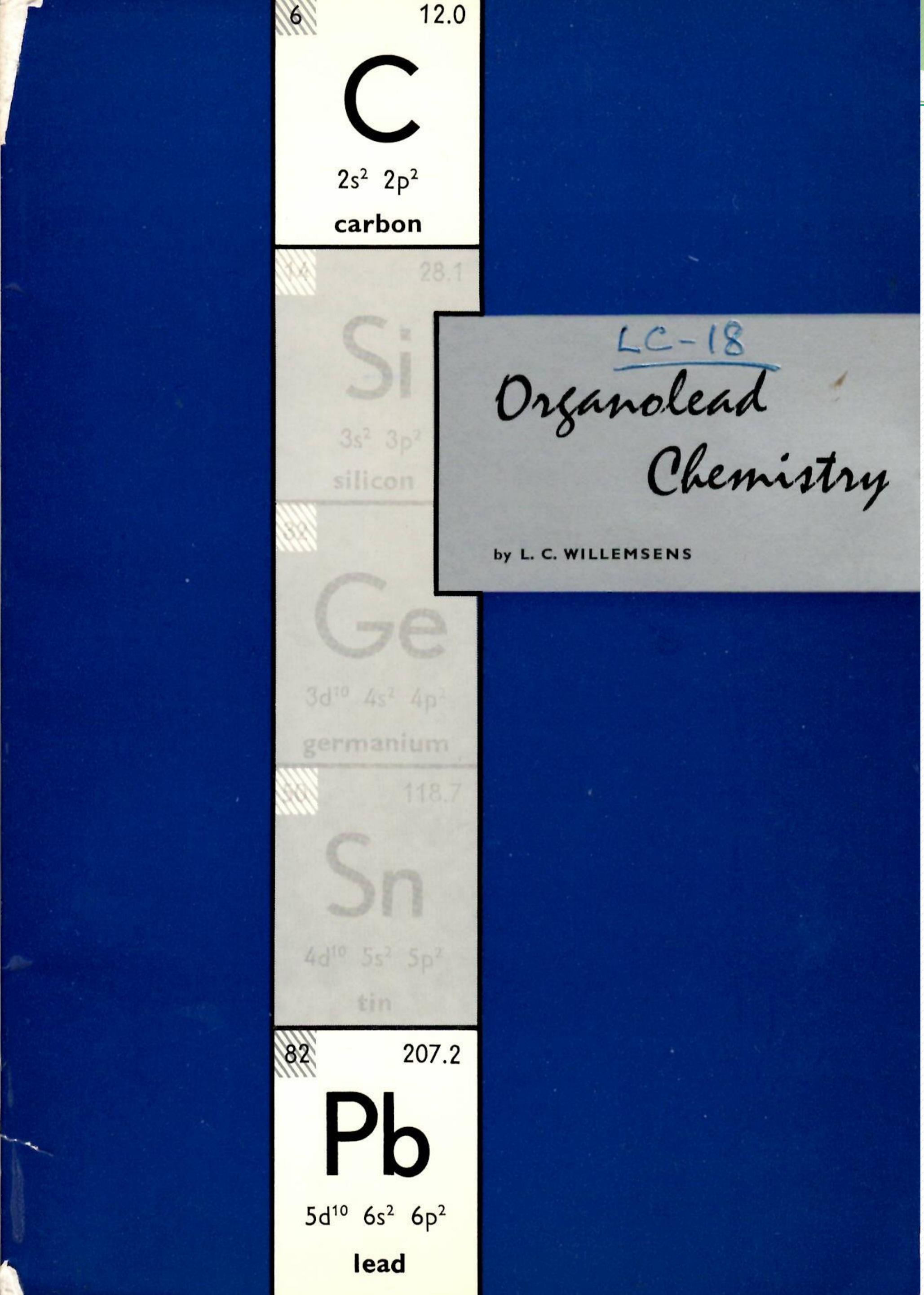
Halcyon Days of Lead Research – Era II

Once the “rule were established” there was a lot of research back in the 1950-60’s looking at better ways of recovery;

- Kivcet
- QSL
- ISF

But mostly focused around primary smelting and the treatment of ores/ concentrate.





ILZRO et al. …….. Era II

And there was a lot other research going on during this period;

- Organo-lead driven by tetraethyl Pb
- Nuclear uses
- Road additives
- Noise/acoustics dampening
- Earthquake research

And of course the “normal” subjects,

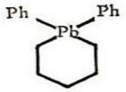
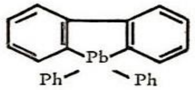
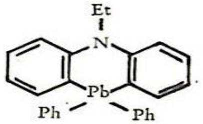
- Alloys
- Batteries

Table I *continued*

Compound	*Physical constants*	*References*
$R_3R'Pb$ *(continued)*		
$Ph_3(\frac{1}{2}Me_2SO_4.Et_2NCH_2CH_2CH_2)Pb$	m. 137-8°	2, 36, 293
$Ph_3PbCH_2CH_2CH_2PbPh_3$	m. 94-5°	2, 36
$Ph_3PbCH_2CH_2CH_2CH_2PbPh_3$	m. 134-6°	2, 36
$Ph_3PbC\equiv CPbPh_3$	m. 138.5°	132
$Ph_3PbC\equiv CC\equiv CPbPh_3$	m. 187°	134
$Ph_3(Br\text{-}p\text{-}C_6H_4)Pb$	m. 115°	2, 108
$Ph_3(Me\text{-}p\text{-}C_6H_4)Pb$	m. 125.5°	2, 36
$Ph_3(PhCH_2)Pb$	m. 95-6°	2, 36, 254, 255
$Ph_3(Br\text{-}p\text{-}C_6H_4CH_2)Pb$	m. 66-8°	2, 36
$Ph_3(CH_2{=}CH\text{-}p\text{-}C_6H_4)Pb$	m. 110-11°	124
	m. 107-9°	125
	m. 86-8°	126
	m. 88-90°	220
$Ph_3(CH_2{=}CHCH_2\text{-}p\text{-}C_6H_4)Pb$	m. 206°	131
$Ph_3(C_6H_{11}\text{-}p\text{-}C_6H_4)Pb$	m. 138°	138
$Ph_3(3\text{-}C_9H_7)Pb$*	m. 122°	143
$Ph_3(9\text{-}C_{13}H_9)Pb$*	m. 118-20°	143
$Ph_3[PhCH_2CH(COOH)]Pb$	m. 165-7°	65
$Ph_3(Ph_3SnCH_2CH_2\text{-}p\text{-}C_6H_4)Pb$	m. 177-9°	129
$(Ph_3PbC_6H_4\text{-}p\text{-}CH_2CH_2)_2Ph_2Sn$	m. ± 70°	129
$Ph_3(2\text{-}C_4H_3S)Pb$	m. 206-7°	2, 113
$(Me\text{-}o\text{-}C_6H_4)_3PbC\equiv CPb(C_6H_4\text{-}o\text{-}Me)_3$	m. 121°	133
$(Me\text{-}p\text{-}C_6H_4)_3PbC\equiv CPb(C_6H_4\text{-}p\text{-}Me)_3$	m. 130°	133
$(PhCH_2CH_2)_3\text{-}PbC\equiv CPb(CH_2CH_2Ph)_3$	m. 62°	133
$(2\text{-}C_4H_3S)_3EtPb$		113
$(2\text{-}C_4H_3S)_3PhPb$		113
$R_2R'_2Pb$		
$Et_2(CH_2Cl)_2Pb$	b_2 96°	2, 66
$(CH_2{=}CH)_2Et_2Pb$	b_1 30°	111, 113, 114
Ph_2Me_2Pb	b_2 151-2°; n_D^{20} 1.6263	2, 24
Ph_2Et_2Pb	b_8 176°; n_D^{18} 1.5939	2, 36

* C_9H_7 = indenyl; $C_{13}H_9$ = fluorenyl.

Table I *continued*

Compound	*Physical constants*	*References*
$R_2R'_2Pb$ *(continued)*		
$Ph_2(CH_2{=}CH)_2Pb$	$b_{0.05}$ 120-155°; $b_{0.002}$ 111-14°	109, 113, 119, 156
$[Ph_2(CH_2{=}CHCH_2)_2Pb]$		121, 156
$(CH_2{=}CHCH_2\text{-}p\text{-}C_6H_4)_2Ph_2Pb$	m. 96-7°	124
$(CH_2{=}CHCH_2\text{-}p\text{-}C_6H_4)_2Ph_2Pb$	m. 194-6°	131
$(C_6H_{11}\text{-}p\text{-}C_6H_4)_2Ph_2Pb$	m. 170°	138
$[(3\text{-}C_9H_7)_2Ph_2Pb]$*		143
$(9\text{-}C_{13}H_9)_2Ph_2Pb$*	m. 138-40°	143
$(Ph_3SnCH_2CH_2\text{-}p\text{-}C_6H_4)_2Ph_2Pb$	m. 180-2°	129
$[(\text{-}C_6H_4\text{-}p\text{-}CH_2CH_2SnPh_2CH_2CH_2\text{-}p\text{-}C_6H_4)Ph_2Pb\text{-}]_{18}$	softening at 70-5°	129
$(2\text{-}C_4H_3S)_2Et_2Pb$		113
$(2\text{-}C_4H_3S)_2Ph_2Pb$		113
		144
	m. 136-137.5°	145
	m. 121.5-123°	146
$R_2R'R''Pb$ and $RR'R''R'''Pb$		
$Ph_2(CH_2{=}CHCH_2\text{-}p\text{-}C_6H_4)\text{-}(CH_2BrCHBrCH_2\text{-}p\text{-}C_6H_4)Pb$		131
$Ph_2(CH_2OHCHOHCH_2\text{-}p\text{-}C_6H_4)\text{-}(CH_2{=}CHCH_2\text{-}p\text{-}C_6H_4)Pb$		131
$(C_6H_{13}CHMeO\text{-}p\text{-}C_6H_4)\text{-}(Me\text{-}p\text{-}C_6H_4)PhPrPb$		2, 18

* C_9H_7 = indenyl; $C_{13}H_9$ = fluorenyl.

Where Does Secondary Lead Fit In?

During Era's I and II all the research and work tended to focus on the smelting and recovery of lead et al., from concentrates.

- ULAB recycling was done, but under the auspices of "the scrap industry"
  - There were dedicated smelters in some countries but often copies of primary furnaces, i.e Blast Furnace.
  - Batteries were broken and "sorted" for supply to smelters

So a visit back to the archives……………….

LEAD 74

EDITED PROCEEDINGS
FIFTH INTERNATIONAL
CONFERENCE ON LEAD
PARIS

ORGANIZED BY THE EUROPEAN LEAD DEVELOPMENT COMMITTEE
SECRETARIAT:
LEAD DEVELOPMENT ASSOCIATION, 34 BERKELEY SQUARE, LONDON W1X 6AJ

Pb80

EDITED PROCEEDINGS
SEVENTH INTERNATIONAL
LEAD CONFERENCE
MADRID

ORGANIZED BY THE EUROPEAN LEAD DEVELOPMENT COMMITTEE
SECRETARIAT:
LEAD DEVELOPMENT ASSOCIATION, 34 BERKELEY SQUARE, LONDON W1X 6AJ

From the Archives.......... LEAD74

Major Issues

- Battery Breaking;
  - Just how to break the battery?
  - Or do we smelt the "whole lot"!
- Cases: We were still in the era of rubber, PP was just appearing
- Separators: Particularly the presence of PVC
- The new alloys coming through, particularly Ca alloys

"While we are today already dealing with the presence of plastic in battery scrap, the use of lead-calcium alloys may well be, at least in Europe, and with the exception of a few special cases, only a pipe-dream. The direction taken will probably be towards the use of alloys with a low antimony content."

From the Archives.......... LEAD74

Major Issues

- Direction was still being sort;
  - Tonolli Process
  - Varta Process
  - Stolberger Zinc, Oliforno, BBU processes!
- It was the thought between “melting v smelting”

“The metallic fraction could be melted down on the spot without endangering the environment; the paste could be sold to a smelting plant using ore (because of its high sulphur content) where it could be processed into soft lead.”

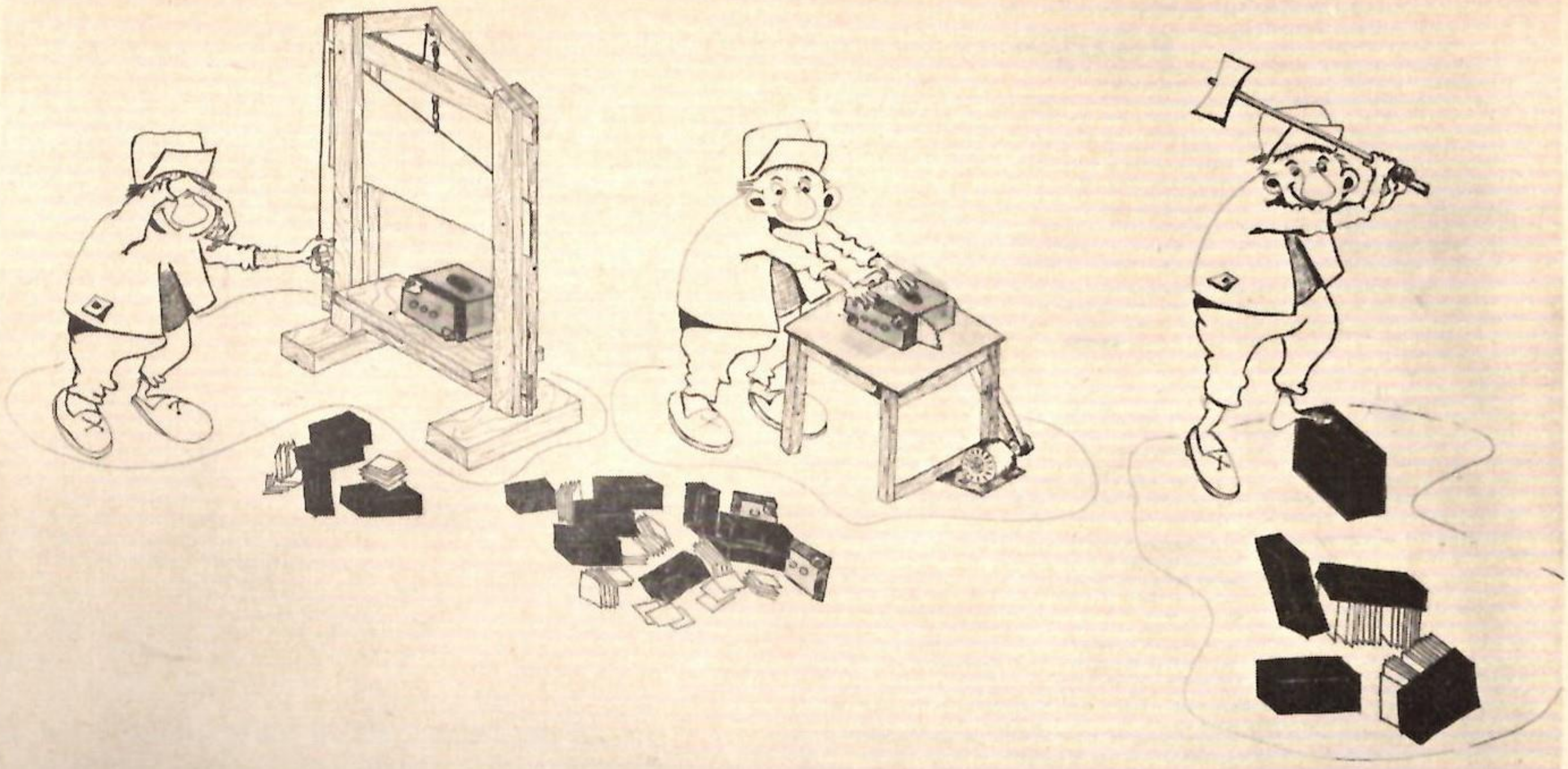


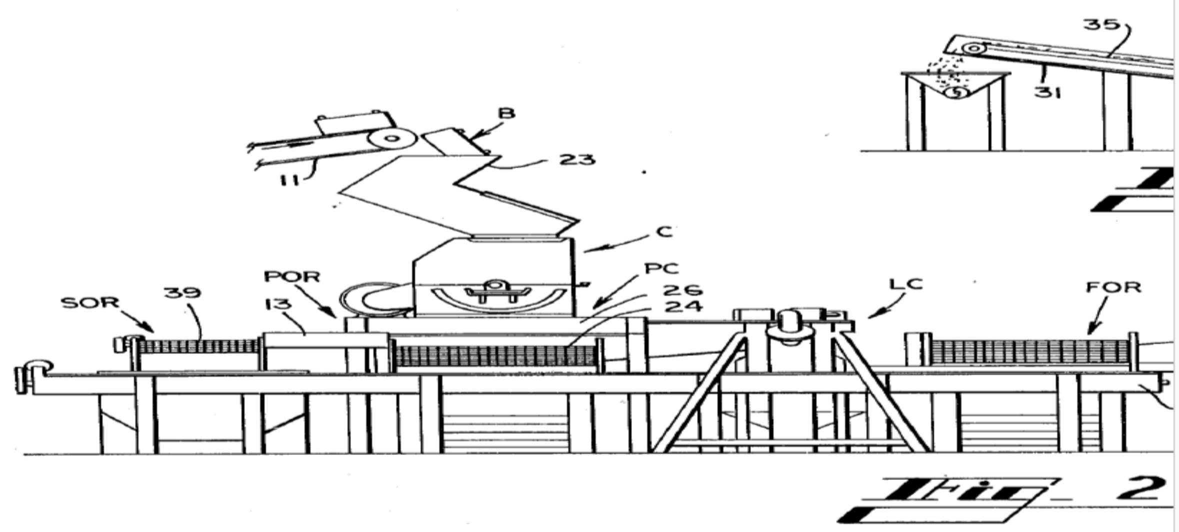
Fig. 3. Three methods of breaking old batteries.

From the Archives………. LEAD80

Major Issues

- The age of rubber cases was over, and PVC separators disappearing
- Battery breakers were becoming the norm
  - Tonolli (Engitec) Process
  - MA System (Wirtz)

Copy of figure 2 from MA Patent 4,397,424 of a partial drawing of a conveyor to the hammermill.



From the Archives………. LEAD80

Two Major Issues

- The first was the continued change in alloys, particularly Ca and new arrivals, Sr & Ba.
  - Could we make them
  - Could we refine the lead to the impurity levels required
  - What to do with the perceived “Sb Stockpile”
- The arrival of tighter OH&S and Environmental regulations
  - Air, water and solids regulations
    - TCLP tests
    - Soda-iron slags
  - LiB transfer levels

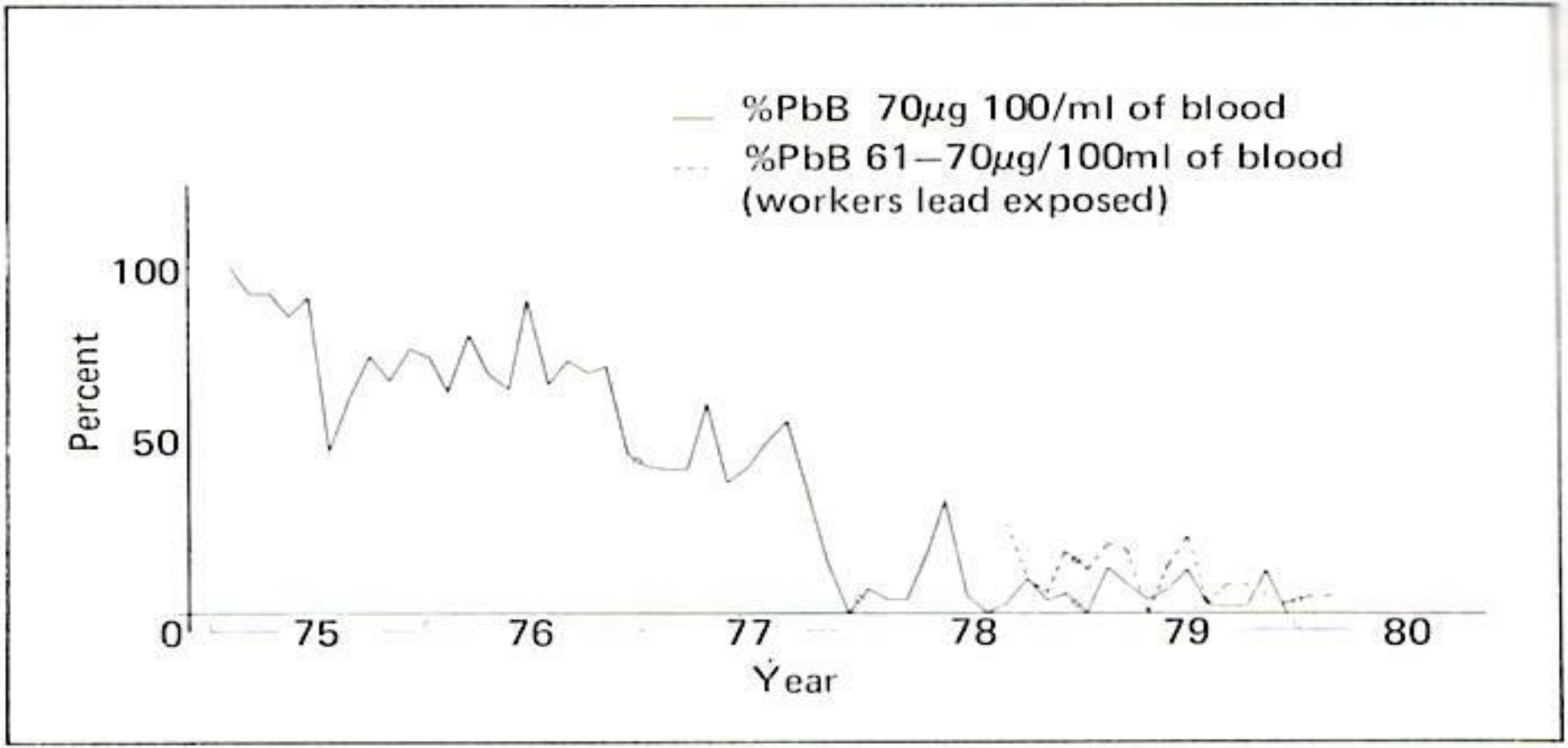


Figure 2. Blood lead levels of workers exposed to lead.

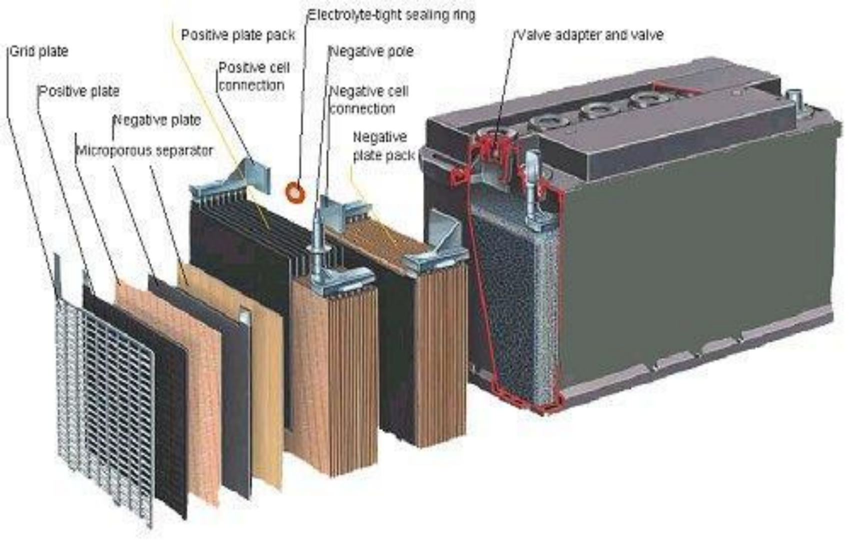
Era III – Study of Secondary Lead

So the timeline makes some sense.

- As the secondary sector has ramped up of the past 50 years it has solved many of its initial issues
  - Producing a consistent, quality feed
  - Recovery and sorting of the major components
  - Refining and alloy production
  - LiB transfer levels

So with a “steady state” of operation, we enter an era where improvements can be made, look at new recovery methods, and hopefully solve some of the problems we still face in the industry

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

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

“Foreign” Elements
- Nickel
- Cadmium
- Copper
- Cobalt
- Zinc
- Manganese
- Tellurium

Floc & Fibres
- Nylon/Polyesters
- PE/PP

Gums & Glues
- ethylene-vinyl acetate (EVA)

Era III Problems - The Four S's

Slag

Sulphates(Sulphur)

Separators

&

Simplicity

The Challenges in Era III

More lead paste is produced per annum than lead concentrate!

There a challenges for both the equipment suppliers and “process” researchers.

For equipment suppliers;

- Feed designed for the furnace
  - Including separators and plastic
- Better desulphurization of paste
- Plant design
  - Metal to bullion

The Challenges in Era III

- Plant design……..   cont
  - Increased energy recovery
    - Improved furnace design
    - Molten bullion to refinery
  - Refinery and casting
    - Design of kettles/pots
    - Reduction in dross on casting
      - Better casting techniques: Star wheels!!!!!

The Challenges in Era III

For the researchers;

- Understand and describe the part of the process being focused on i.e. paste
- Appreciate that hydrometallurgy has its own issues
  - A new species to handle - Pb^{2+}
  - Some of the “new” lead chemicals pose their own hazards i.e. some are suspected class 1 carcinogen
  - Residues – not only from the battery paste, but any process will produce their own waste
- Cost

The “Holy Grails”

“Sulphur is our enemy”

1. The removal of sulphur into a product that makes the process profitable.

2. The direct recovery of lead from lead sulphate

3. The recovery of alloying elements from the slag; Sn, Sb & As

Just Some Last Comments ……….

- During Era's I & II, there was a huge amount of work published and peer reviews took place.
  - PowerPoint presentation is the standard these days, with scant technical information and little peer review.
  - Many of the papers that are published come from the "waste perspective".
- Work with the industry – not against it…….
- Its not about "saving the world", but developing new, safe and cost effective processes.

"Achieve a process and the industry will beat a path to your door…."