The Dilemma of Antimony

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Element 51 – Always the Sideshow

The supposed demise of antimony alloys has been rumoured for many years, particularly with the development of Ca alloys. Still, the element plays a critical role in battery alloys.

However, once the price of the element increases, focus goes into how it can be recovered better in the smelting system or how alloys can be changed to save money.

But changing specification is not as simple as it seems!

TYPEMETALS AND PRINTERS ALLOYS

Moreland Specification No.	DESCRIPTION	COMPOSITION													
		Sn		Sb		Cu	As	Bi	Zn	Cd	Al	Fe	Ni	Te	S
		Min.	Max.	Min.	Max.	Max.	Max.	Max.	Max.	Max.	Max.	Max.	Max.	Max.	Max.
MM 301	2-3 Electro backing	1.8	2.2	2.8	3.2	0.075	Not to exceed 90% of copper content	0.05	0.001	0.001	0.001	0.001	0.001	0.001	Between 0.5 and 1.5 parts per million
MM 302	3-3 Electro backing	2.8	3.2	2.8	3.2	0.075		0.05	0.001	0.001	0.001	0.001	0.001	0.001	
MM 303	3½-3½ Electro backing	3.25	3.75	3.25	3.75	0.075		0.05	0.001	0.001	0.001	0.001	0.001	0.001	
MM 304	3-11 Intertype	2.8	3.2	10.75	11.25	0.05		0.05	0.001	0.001	0.001	0.001	0.001	0.001	
MM 305	4-11 Intertype, Linotype	3.8	4.2	10.75	11.25	0.05		0.05	0.001	0.001	0.001	0.001	0.001	0.001	
MM 306	4-12 Linotype, Ludlow	3.8	4.2	11.75	12.25	0.05		0.05	0.001	0.001	0.001	0.001	0.001	0.001	
MM 307	5-12 Linotype	4.8	5.2	11.75	12.25	0.05		0.05	0.001	0.001	0.001	0.001	0.001	0.001	
MM 308	6-12 Linotype	5.8	6.2	11.75	12.25	0.05		0.05	0.001	0.001	0.001	0.001	0.001	0.001	
MM 309	6-14 Stereotype	5.8	6.2	13.75	14.25	0.025		0.05	0.001	0.001	0.001	0.001	0.001	0.001	
MM 310	6-15 Stereotype	5.8	6.2	14.75	15.25	0.025		0.05	0.001	0.001	0.001	0.001	0.001	0.001	
MM 311	6-16 Stereotype	5.8	6.2	15.75	16.25	0.025		0.05	0.001	0.001	0.001	0.001	0.001	0.001	
MM 312	7-14 Stereotype	6.8	7.2	13.75	14.25	0.025		0.05	0.001	0.001	0.001	0.001	0.001	0.001	
MM 313	8-15 Stereotype	7.8	8.2	14.75	15.25	0.025		0.05	0.001	0.001	0.001	0.001	0.001	0.001	
MM 314	8-16 Stereotype	7.8	8.2	15.75	16.25	0.025		0.05	0.001	0.001	0.001	0.001	0.001	0.001	
MM 315	8-16 Monotype	7.8	8.2	15.75	16.25	0.075		0.05	0.001	0.001	0.001	0.001	0.001	0.001	
MM 316	9-16 Monotype	8.8	9.2	15.75	16.25	0.10		0.05	0.001	0.001	0.001	0.001	0.001	0.001	
MM 317	9-19 Monotype	8.8	9.2	18.5	19.5	0.15		0.05	0.001	0.001	0.001	0.001	0.001	0.001	
MM 318	10-15 Monotype	9.8	10.2	14.75	15.25	0.10		0.05	0.001	0.001	0.001	0.001	0.001	0.001	
MM 319	10-16 Monotype	9.8	10.2	15.75	16.25	0.15		0.05	0.001	0.001	0.001	0.001	0.001	0.001	
MM 320	12-25 Display Monotype	11.8	12.2	24.5	25.5	0.15		0.05	0.001	0.001	0.001	0.001	0.001	0.001	
MM 321	12-25 Founders	11.8	12.2	24.0	26.0	0.50		0.05	0.001	0.001	0.001	0.001	0.001	0.001	

TYPEMETALS AND PRINTERS ALLOYS

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MM 304	3-11 Intertype	2.8	3.2	10.75	11.25	0.05		0.05	0.001	0.001	0.001	0.001	0.001	0.001	
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MM 316	9-16 Monotype	8.8	9.2	15.75	16.25	0.10		0.05	0.001	0.001	0.001	0.001	0.001	0.001	
MM 317	9-19 Monotype	8.8	9.2	18.5	19.5	0.15		0.05	0.001	0.001	0.001	0.001	0.001	0.001	
MM 318	10-15 Monotype	9.8	10.2	14.75	15.25	0.10		0.05	0.001	0.001	0.001	0.001	0.001	0.001	
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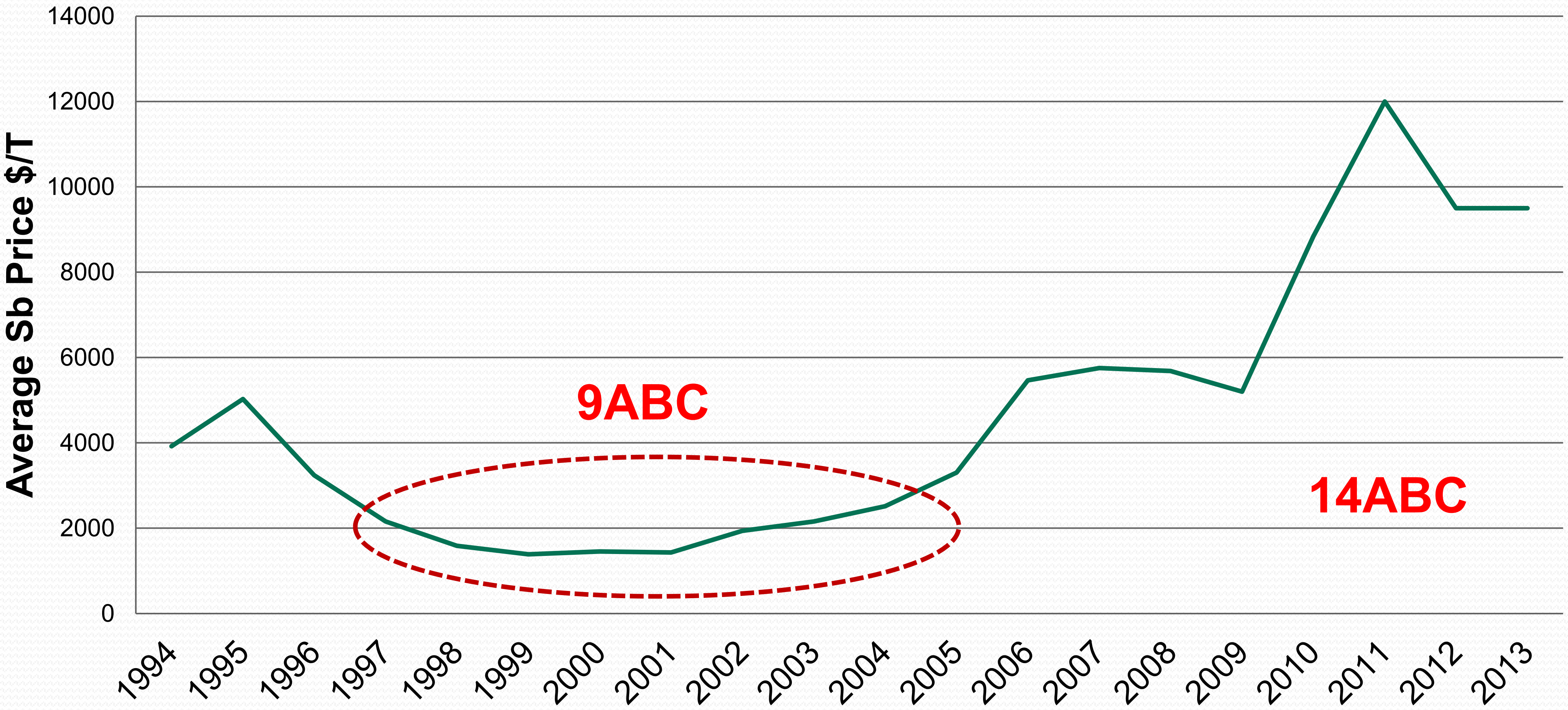
MM 320	12-25 Display Monotype	11.8	12.2	24.5	25.5	0.15		0.05	0.001	0.001	0.001	0.001	0.001	0.001	
MM 321	12-25 Founders	11.8	12.2	24.0	26.0	0.50		0.05	0.001	0.001	0.001	0.001	0.001	0.001	

Antimony – Always the Sideshow

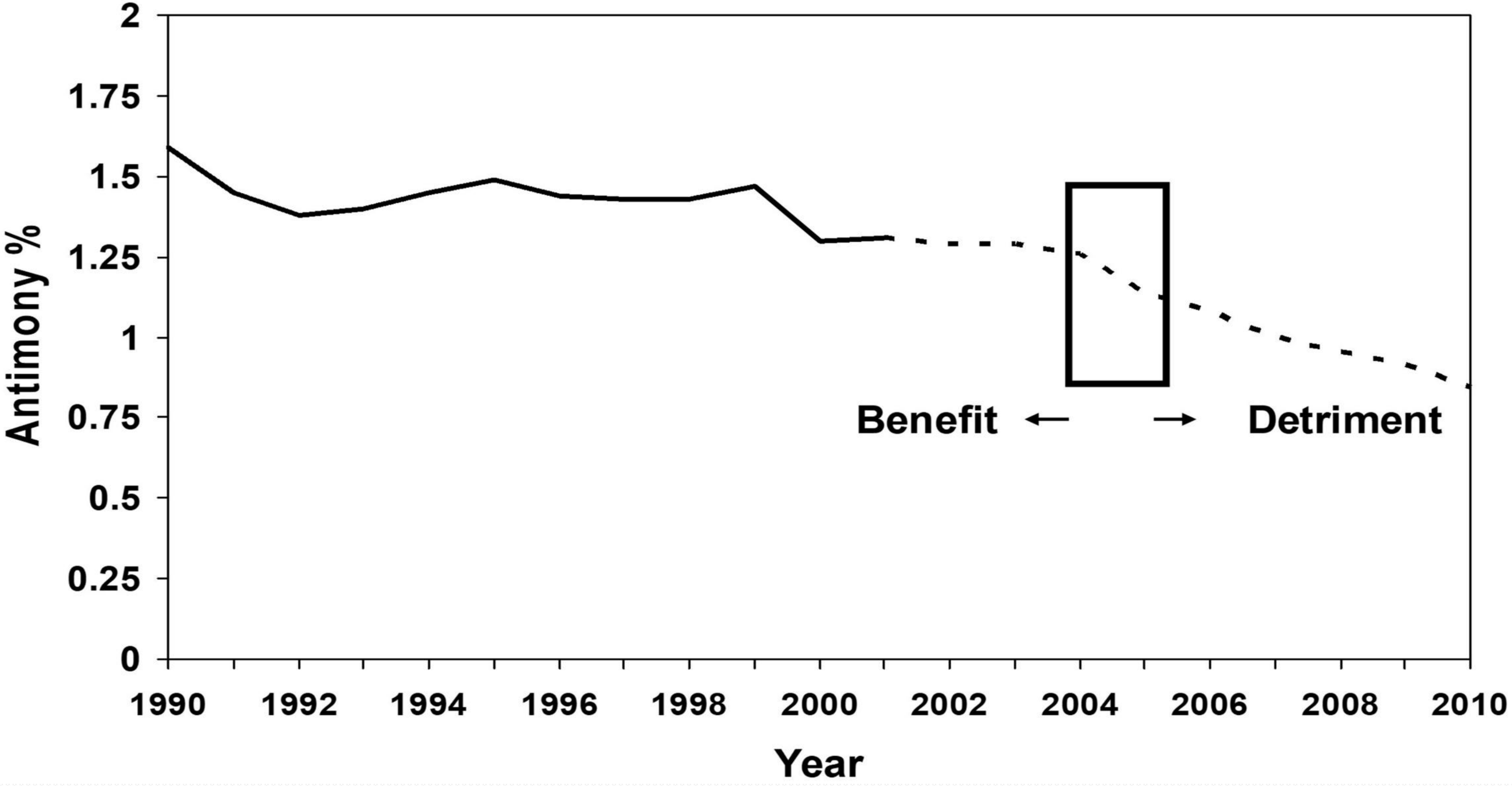
We have looked at the element for over 25 years at the ABC/ISLC from many different angles;

- Excess antimony	(9ABC, 3ISLC, 7ISLC)
- Stockpiling product	(9ABC, 14ABC)
- Shortages/overcapacity	(12ABC, 3ISLC, 7ISLC)
- Phasing out	(6ABC, 3ISLC)

Antimony Prices – 1994 to 2013



9ABC Projections – A Warehoused Product!



Antimony Prices – 2006 to 2025

Focus Back to Element 51 – Better Recovery

Smelters start to refocus on better recovery of the element from battery scrap.

We know where it is!

Metallic Fraction Breakdown

Metallic Fraction Analysis

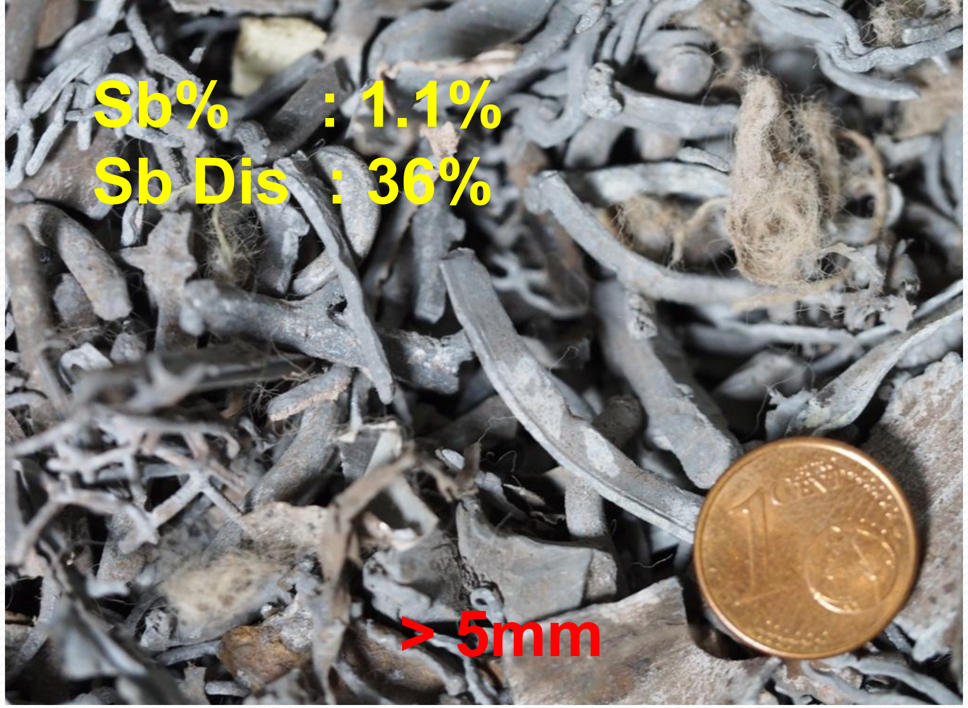
Sample	Sb	As	Sn	Cu
Terminals	2.5	0.13	0.28	0.02
> 5 mm	1.1	0.008	0.32	0.008
3 to 5mm	0.6	0.004	0.28	0.004
1 to 3mm	0.3	0.002	0.24	0.005
Paste	0.1	0.001	0.18	0.002

Metallic Fraction Analysis

Sample	Sb	As	Sn	Cu	% Fraction	% Sb Dis
Terminals	2.5	0.13	0.28	0.02	10	33
> 5 mm	1.1	0.008	0.32	0.008	25	36
3 to 5mm	0.6	0.004	0.28	0.004	22	17
1 to 3mm	0.3	0.002	0.24	0.005	30	12
Paste	0.1	0.001	0.18	0.002	10	2

Whilst the "Terminal" fraction has the higher Sb content, there is more of the element in the "> 5mm" fraction.

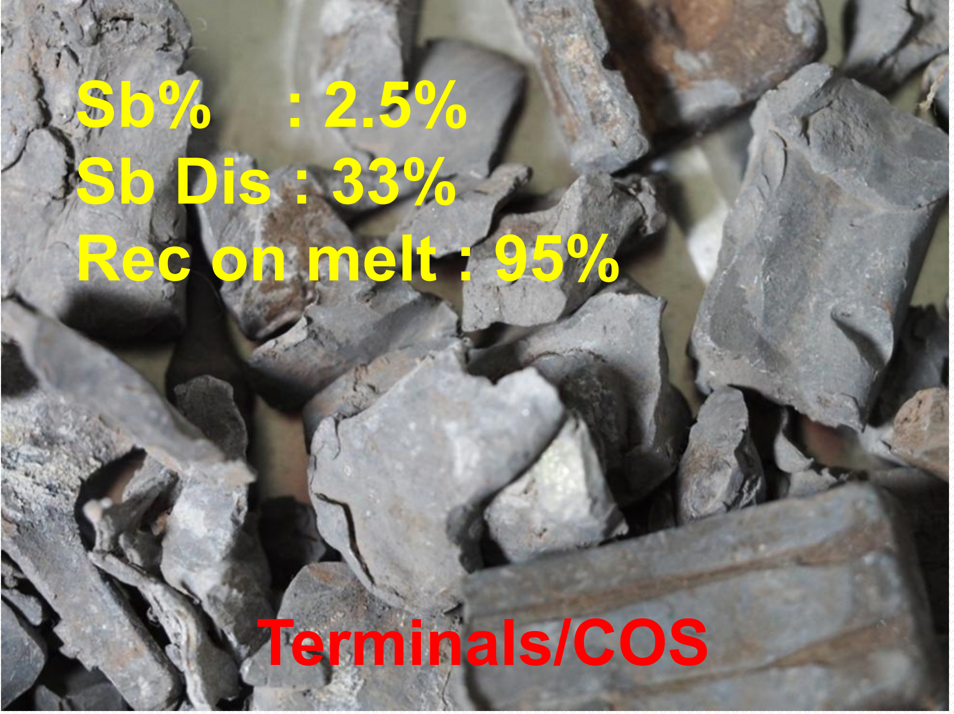
Metallic Fraction Breakdown

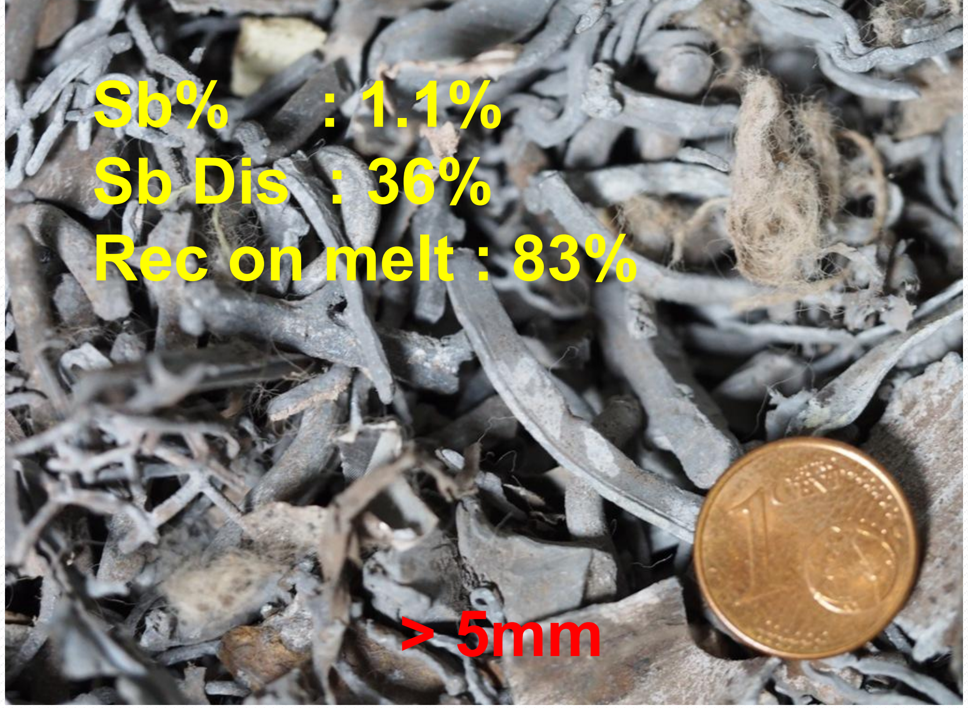


Metallic Fraction Analysis

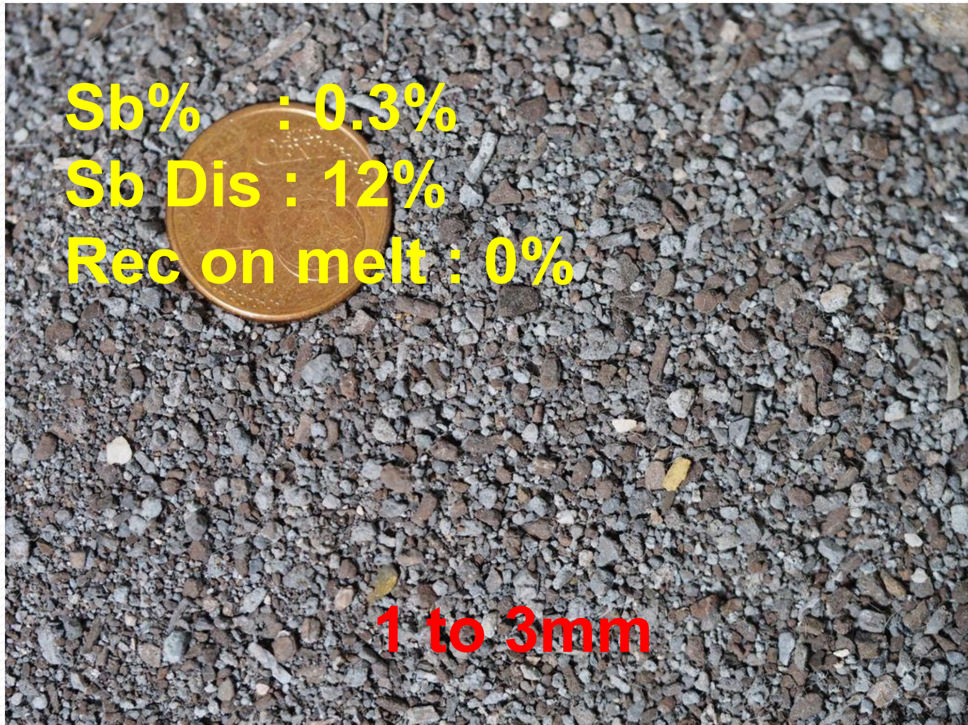
Sample	Sb%	% Frac	% Sb Dis	Recovery%	
				Metal	Dross
Terminals	2.5	10	33	95	5
> 5 mm	1.1	25	36	83	17
3 to 5mm	0.6	22	17	39	61
1 to 3mm	0.3	30	12	0	100
Paste	0.1	10	2	0	100

Whilst the "Terminal" fraction has the higher Sb content, there is more of the element in the "> 5mm" fraction. But on melting, "> 5mm" has a higher drossmake and more Sb is lost to the dross





Metallic Fraction Breakdown



Off to the Furnace……

- The key to better Sb recovery is to bypass the furnace with “>5mm” fraction, but easier said than done!
- Older battery breakers produce a poor-quality metallic feed with a high paste loading.
- This material is “all but impossible” to direct melt in the refinery
- The vast majority of Sb travels through the furnace.

Off to the Furnace……….

Pb and Sb sit close to each other on the Ellingham Diagramme.

Sn sits lower.

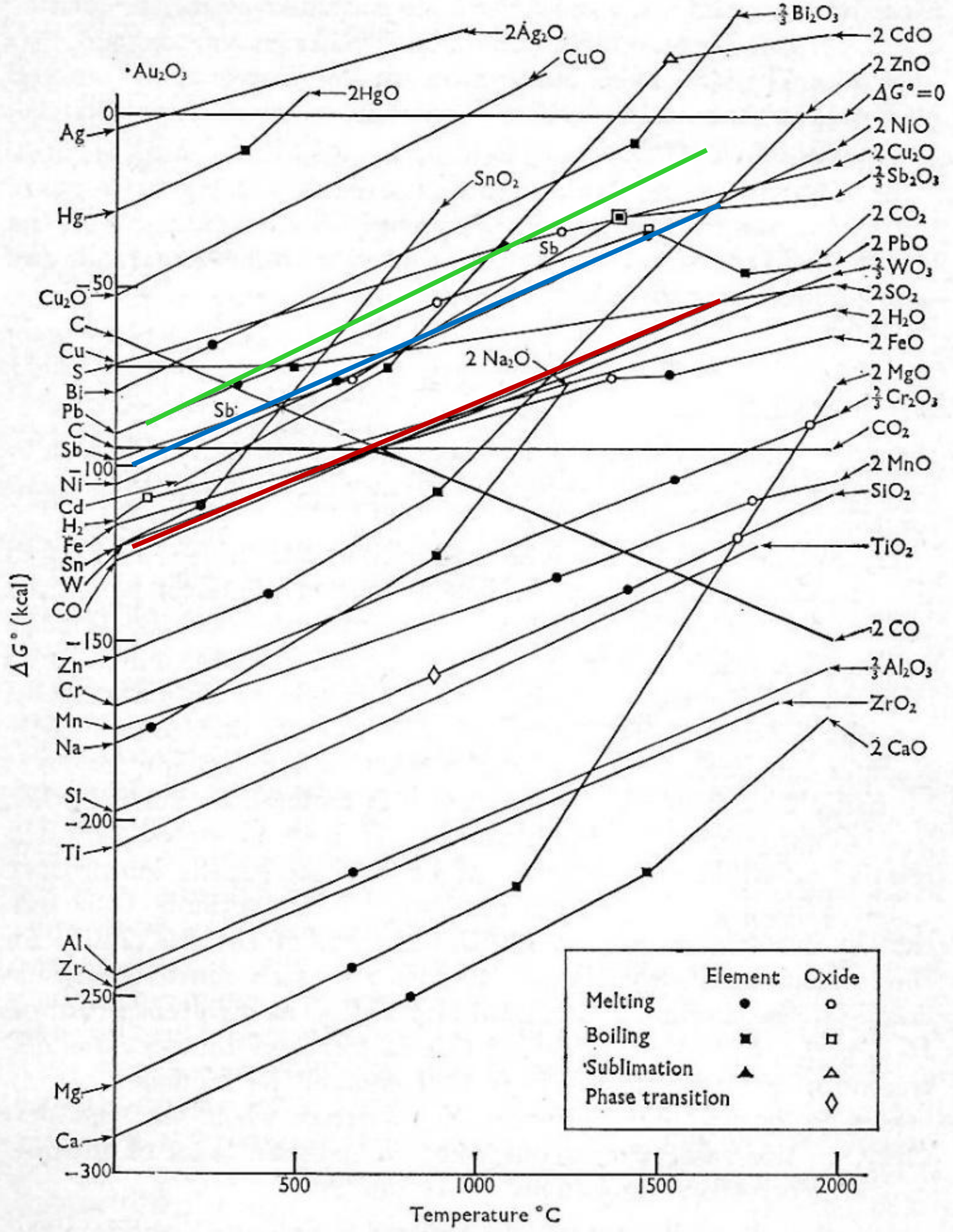


FIG. 2. $\Delta G^\circ, T$ diagram for oxide formation

Off to the Furnace……

The recovery of Sb is now up to the type of furnace.

"High Intensity Reduction" - Blast, Side-blown, Cupola.

"Low Intensity Reduction" - Rotary

In HIR, a higher portion of Sb (& Sn) is recovered in bullion. For the reverb/blast setup, this can be clearly seen in the second stage smelting operations.

For LIR, the Sb (& Sn) deportment is variable, with a higher percentage going to slag.

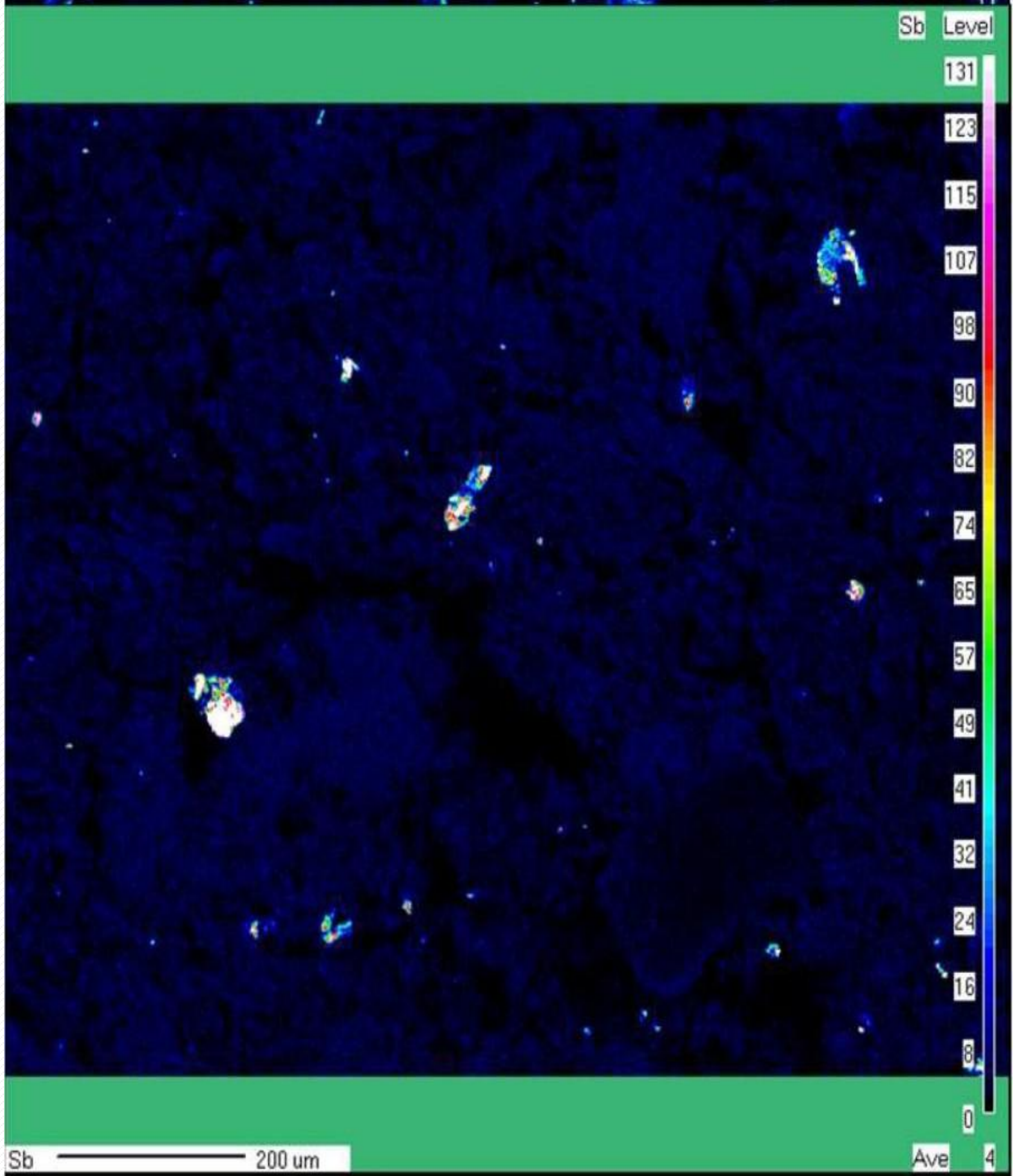
Deportment of Elements (Rotary)

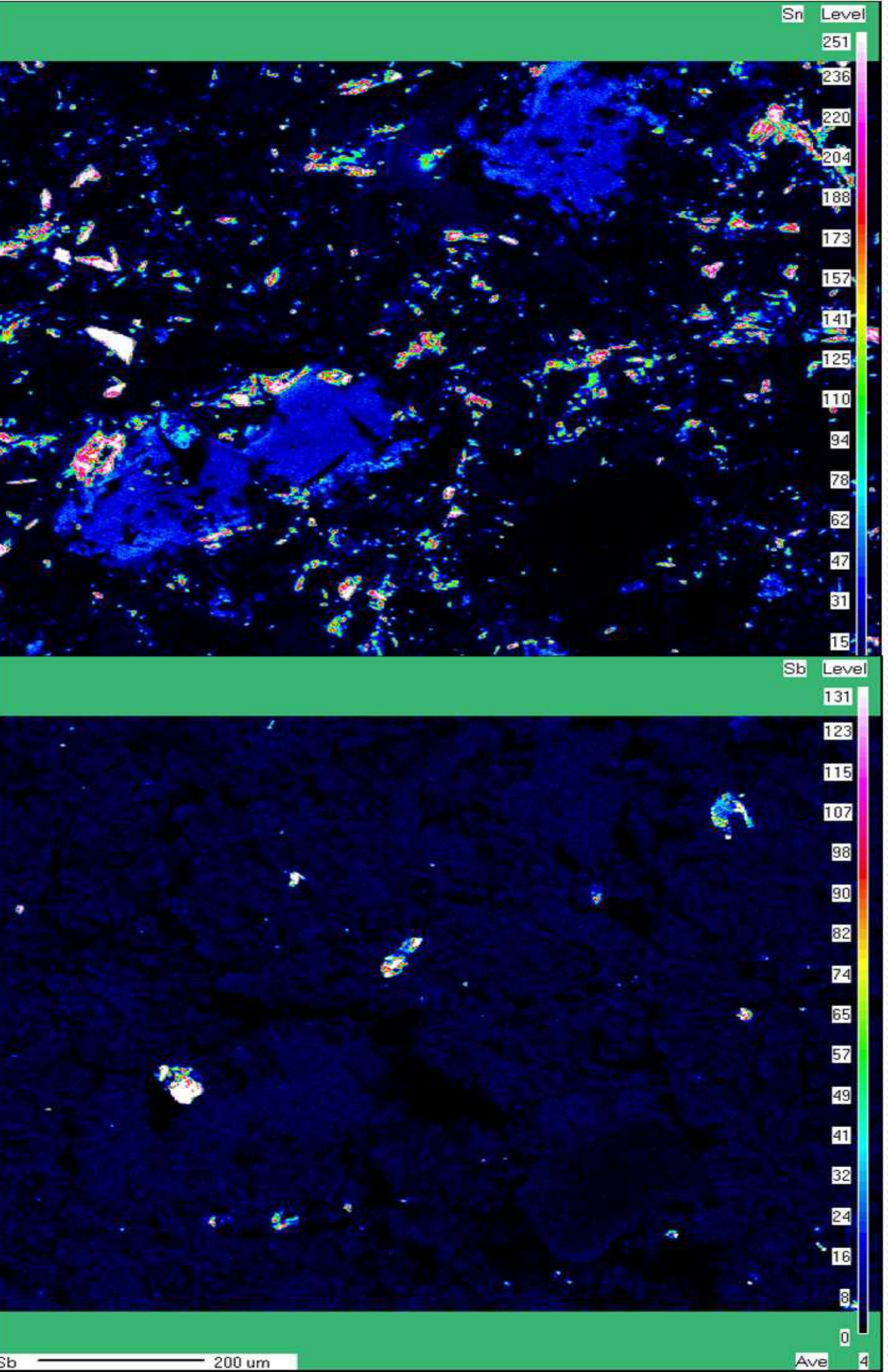
Element	Source	Level in the battery	Deportment (%)			
			Furnace			
			Slag	Metal	Fume	Gas
Ag	Impurity and an alloying element	In USA; 0.005% in PAM/NAM	2	98	0	0
Al	Alloying element in Calcium alloys	0.01% in Ca alloys	100	0	0	0
As	Alloying element in antimony alloys	0.1 - 0.2 in Sb alloys	60	25	15	0
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

Recover from Slag?

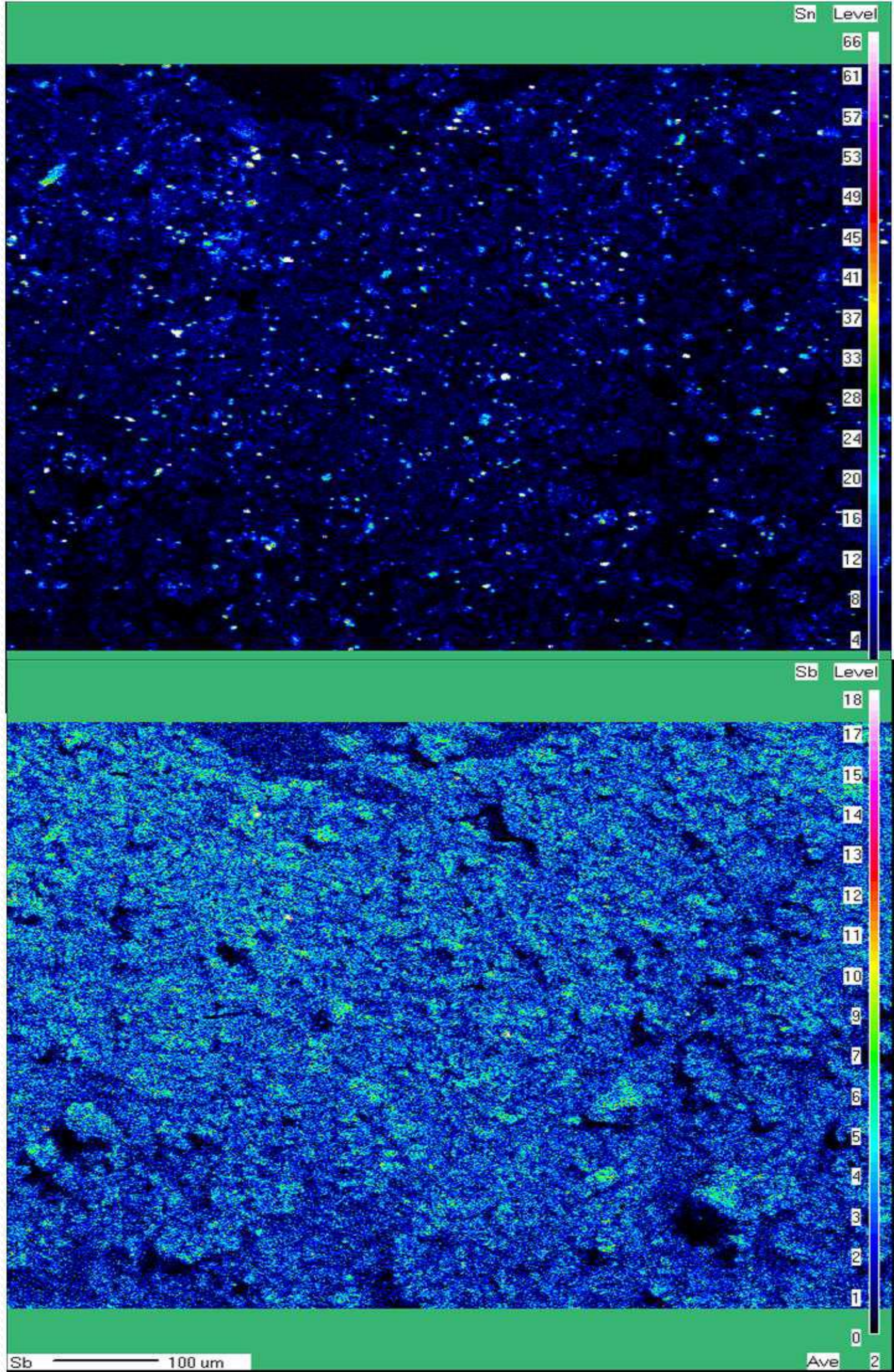
At the moment there is no solution to the recovery of any metal from slags, particularly soda-iron.

Once lost to slag, lost forever…..





We now add Sb recovery to the "Holy Grail"



Changes Afoot

With the increase in the cost of alloys, battery makers are looking at savings from all angles, two include;

- Changing alloys from Sb to Ca. OK in some applications, but not possible in parts and deep discharge alloys.

- Reducing the level of Sb in the alloy. There are reasons, both physical and electrochemical for certain levels of Sb in alloys, back by years of research.

Ever-changing Battery Technology

Battery Type	**Conventional**	**Low Maintenance**	**Very Low Maintenance**	**Maintenance Free**	**Valve Regulated**
Purpose	"Old" batteries Very few made	Most common SLI battery made in Asia	Most companies moving to hybrid	Common in US and Europe but growing in Asia	Increasing in production for Auto's. Will be used in hybrids
Grid Alloys	3 to 6% Sb + & -	1.6 to 3% Sb + & -	1.6% Sb + Ca/Sn -	Ca/Sn + & -	Ca/Sn + & -
Oxide	Oxide lead of little relevance (generally secondary lead)	Oxide lead purity of increasing importance	Oxide lead purity of increasing importance	Oxide lead purity very important	Oxide lead purity critical (1 ppm order)
Performance/Properties	Battery performance dominated by high Sb • gassing • self discharge • but good cycling	Performance still dominated by Sb but: • gassing lower • self dis lower • cycling conservation	Gassing and self discharge still occur but at low levels • Positive Sb used for cycling	Very low gassing and and self discharge. Lower resistance and CCA's. cycling much lower due to Sb-free effect	No gassing permitted on the -ve (H). Gas from +ve recombined (O). Self discharge very low. Cycling possible

Antimony in the Battery

The element seems to have been present in lead alloys “from the start”; terminals, COS, alloys, etc. And the indications to smelters is that it’s there for the physical properties.

- Gives the alloy hardness
- Helps in creep resistance
- Lowers the melting point of the alloy to ~ 280^{o}C
- But is susceptible to cracking

Antimony in the Battery

But the element does more than that!

We learnt the hard way in the 1990's that if Sb is removed from the alloy, the battery would not recharge once discharged, particularly in Ca alloys. It was termed Premature Capacity Loss (PCL).

Through work lead by the ALABC, the addition of high levels of Sn in the +ve, overcame PCL. (This is why +ve & -ve alloys have different Sn levels)

The Risks of Changing Sb Levels

It seems to be a simple solution – reduce the Sb levels, money saved!

The potential problems are both electrochemical and physical;

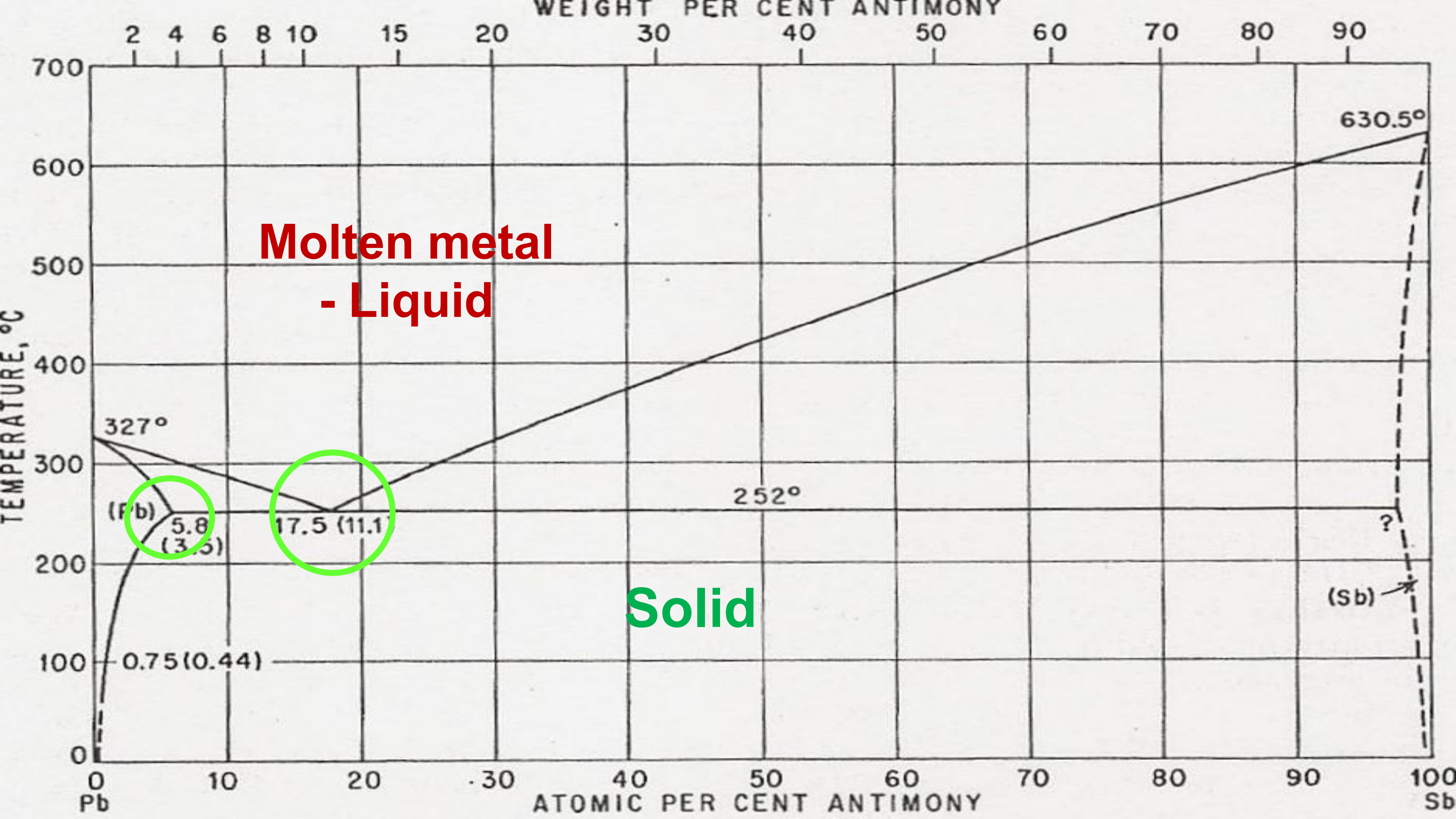
- E. Lower Sb levels affect the recovery from discharge. Little is known on levels of <1%, and only way to gauge is conduct test-work, often taking months/years to obtain results.
- E. Life expectancy is an unknown.

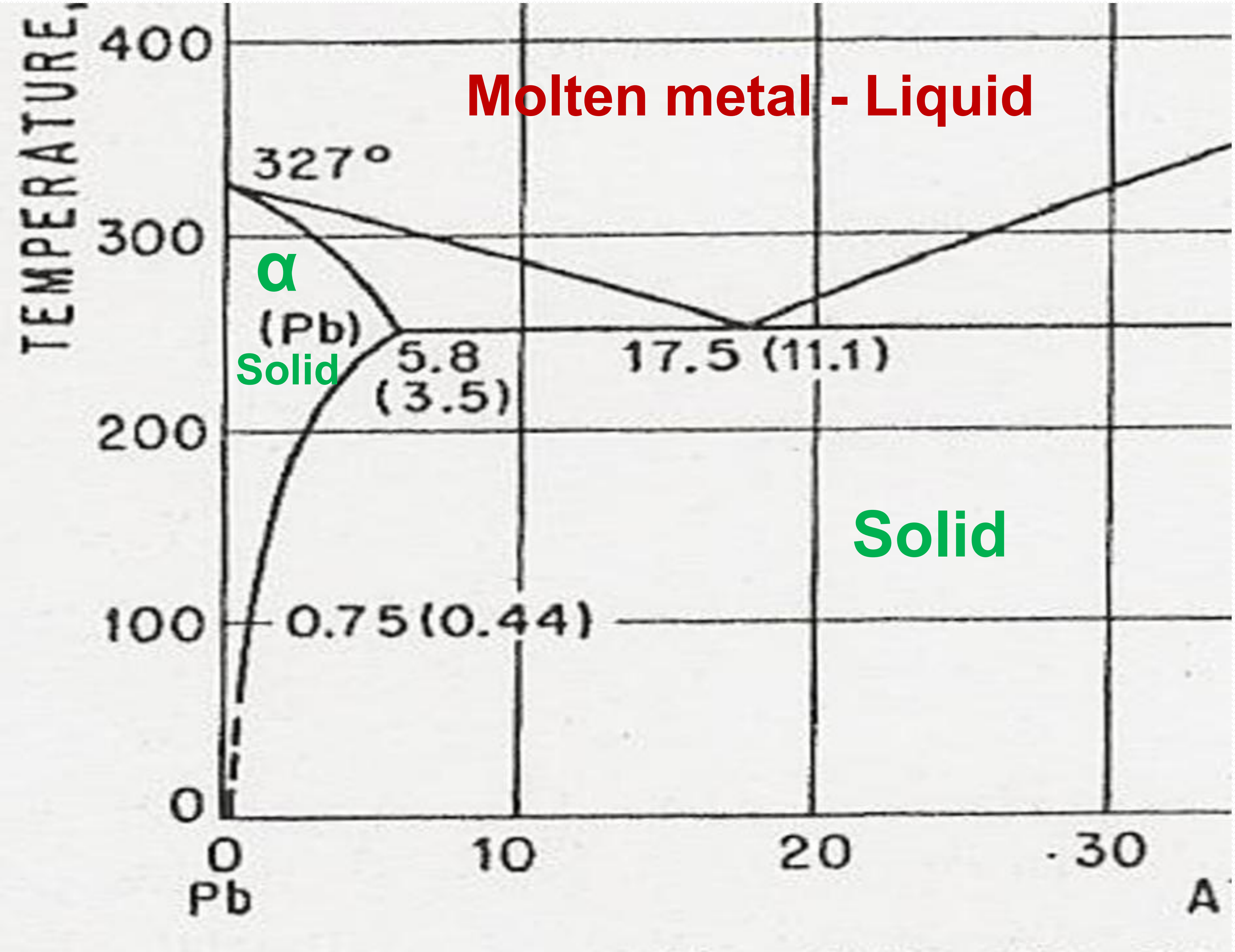
The Risks of Changing Sb Levels

It seems to be a simple solution – reduce the Sb levels, money saved!

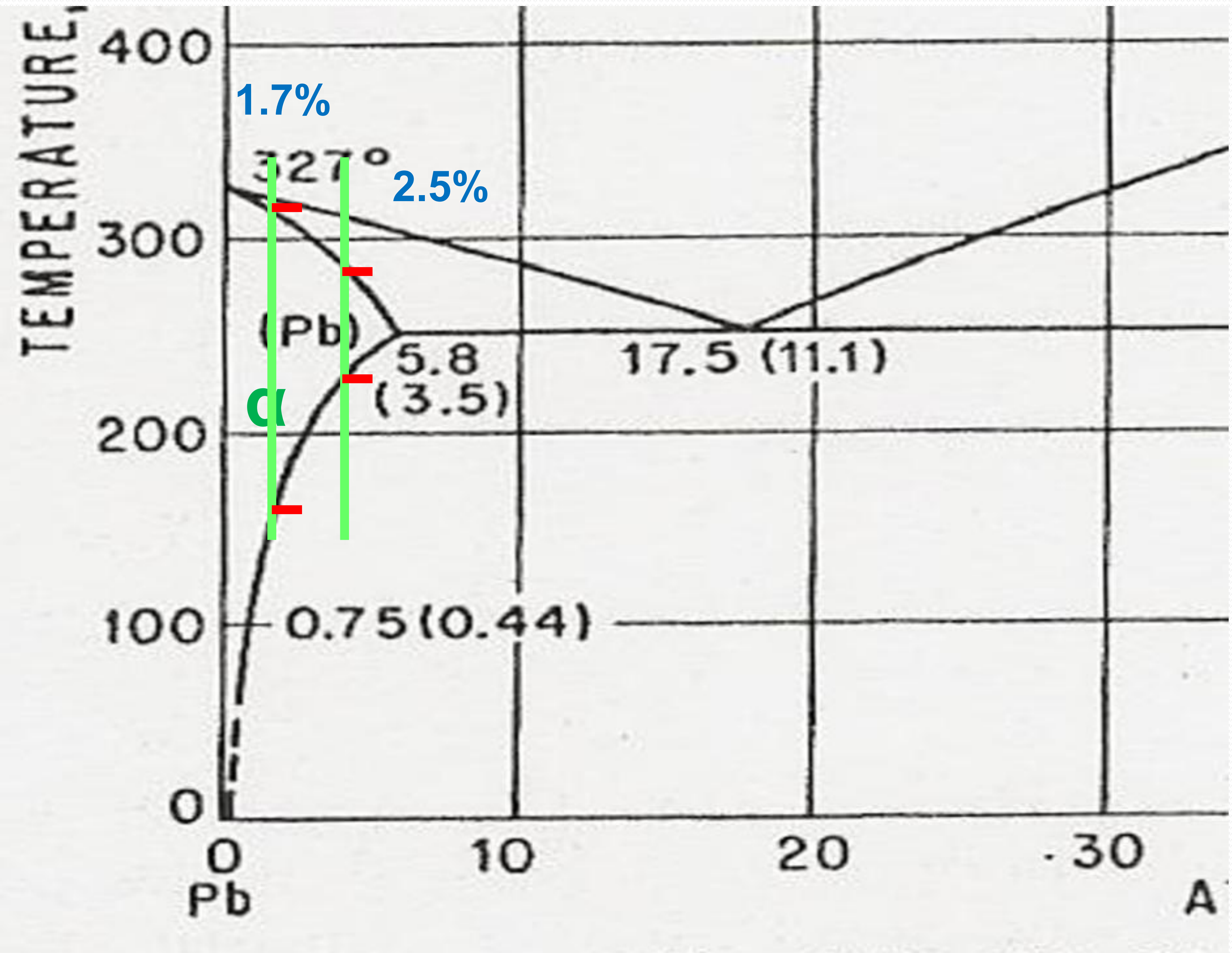
- P. Cracking, Cracking, Cracking!
- P. Once Sb levels go below 3% grain refiners have to be added. And the lower the Sb, more refiners are needed.

Battery companies must be aware of these, and other risks involved in altering specifications. A consider decision!

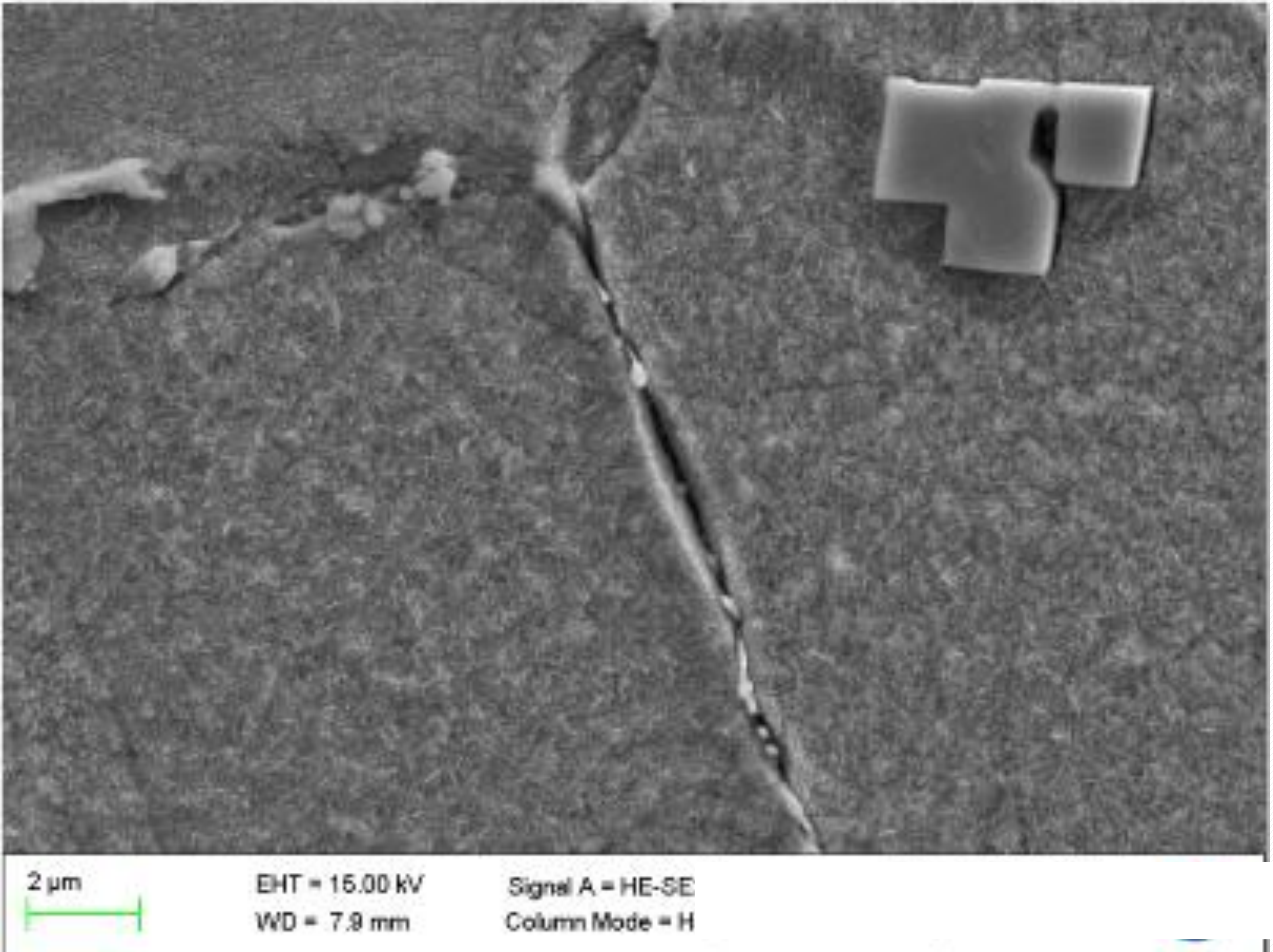

WEIGHT PER CENT ANTIMONY
2
4
6
8
10
15
20
30
40
50
60
70
80
90
700
600
500
400
300
200
100
0
TEMPERATURE, °C
630.5°
Molten metal
- Liquid
327°
252°
(Pb)
5.8
(3.5)
17.5 (11.1)
?
Solid
(Sb)
0.75 (0.44)
0
Pb
10
20
30
40
50
60
70
80
90
100
Sb
ATOMIC PER CENT ANTIMONY



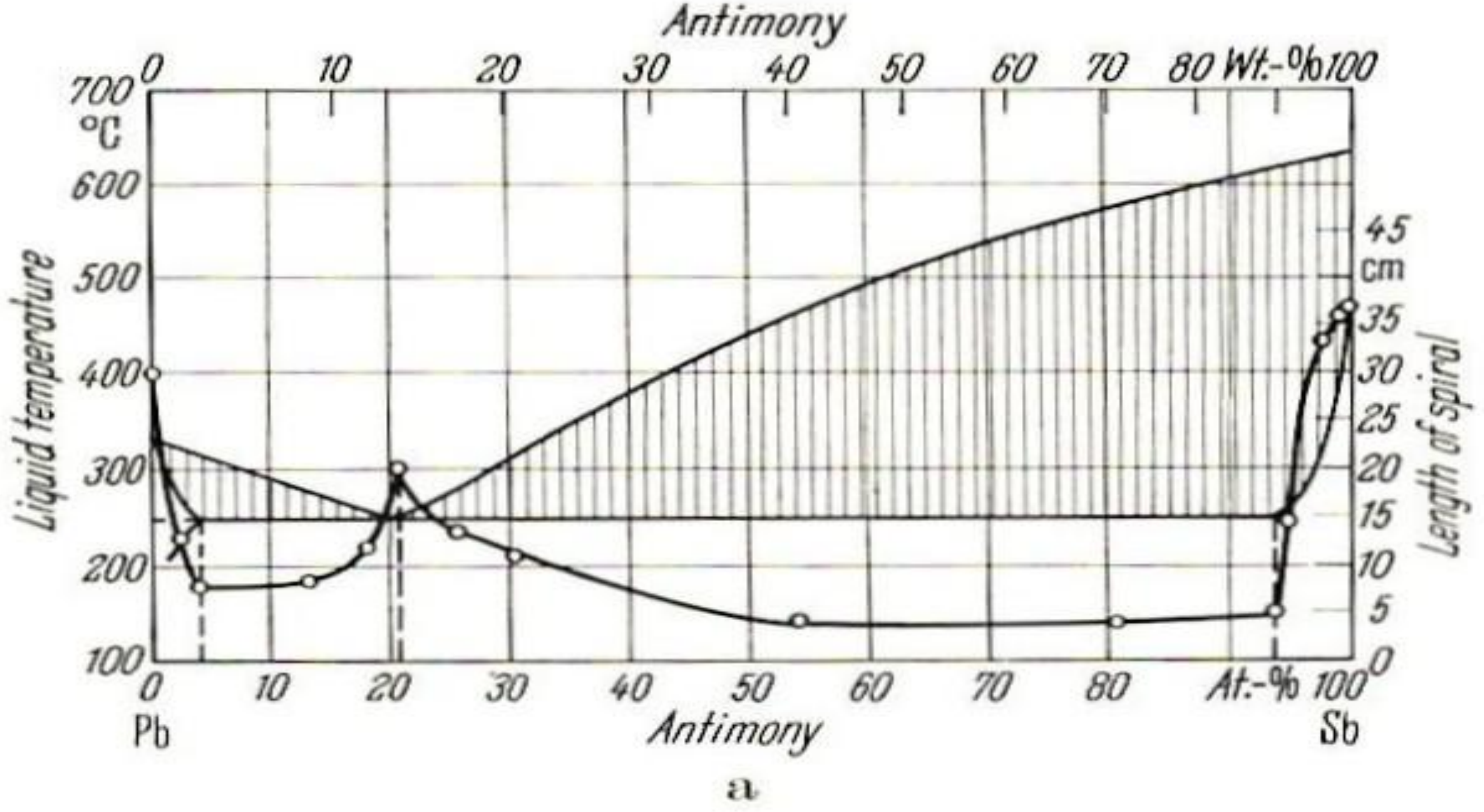
TEMPERATURE,
400
300
200
100
0
Molten metal - Liquid
327°
α
(Pb)
Solid
5.8
(3.5)
17.5 (11.1)
Solid
0.75(0.44)
0
Pb
10
20
30
A


TEMPERATURE,
400
300
200
100
0
1.7%
327°
2.5%
(Pb)
α
5.8
(3.5)
17.5 (11.1)
0.75(0.44)
0
Pb
10
20
30
A

PbSe Cubic Structure



Another Effect - Castability



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- P. Cracking, Cracking, Cracking!
- P. Once Sb levels go below 3% grain refiners have to be added. And the lower the Sb, more refiners are needed.

The onus is on the battery producer to understand the possible problems and consequences modifying alloys!

Our 2011 comment on the 2001 Prediction

So how Far off the Mark?

2. Antimony would be in excess, and due to the cost of removing a pure product, be tied up in a Pb/Sb bullion

The **opposite** has occurred!

Antimony is now a valued alloying element with its price in recent years outstripping lead and other common commodities.

In fact antimony has been listed as a strategic element by a number of countries