Cu-Pb-Me-S-balances during lead refining

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1 Introduction

Crude lead bullion produced from different reduction processes typically contains copper, tin, arsenic, antimony and silver besides other minor elements. The first refining step is a double-stage decopperization followed by the well known oxidation and precipitation steps. This paper looks in detail into the processes with the aim of clarifying the major principles of copper removal.

Copper has to be removed completely because even small amounts interfere the following refining procedure through forming of intermetallic alloys/compounds. On the other hand it is well known, that third elements can also assist or hinder the decopperization step. A broad review on published data, experimental tests at IME Process Metallurgy and Metal Recycling, Technical University Aachen as well as a extended analytical investigations at the refinery plant of VARTA Recycling GmbH, Krautscheid was the basis to develop a mechanism theory and based and this recommendations for a improved production process.

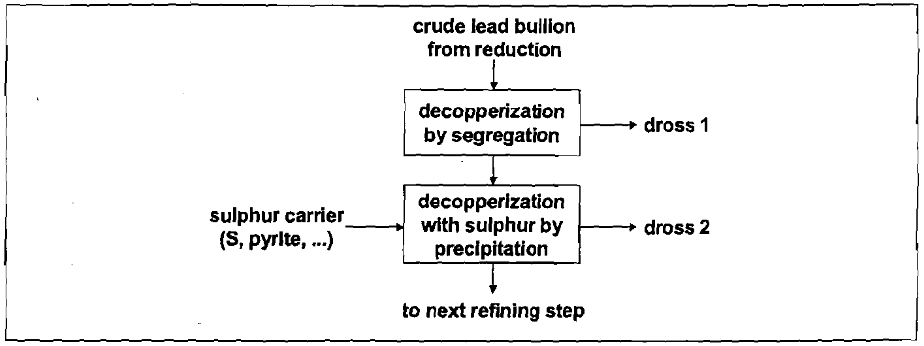

Figure 1: Scheme of the first refining step for crude lead

2 Copper removal by segregation (first step)

2.1 Equilibrium Pb-Cu

Figure 2 presents the binary-phase-diagram Pb-Cu. It is obvious that there are very good conditions to separate Cu by segregation. The progression of the liquidus line on the one hand and the eutectic near 100 % Pb on the other hand improve to cool down the crude lead to separate most of the dissolved copper as pure metallic crystals. At the eutectic temperature the residual melt contains 0,06 % to 0,07 % copper [4,5].

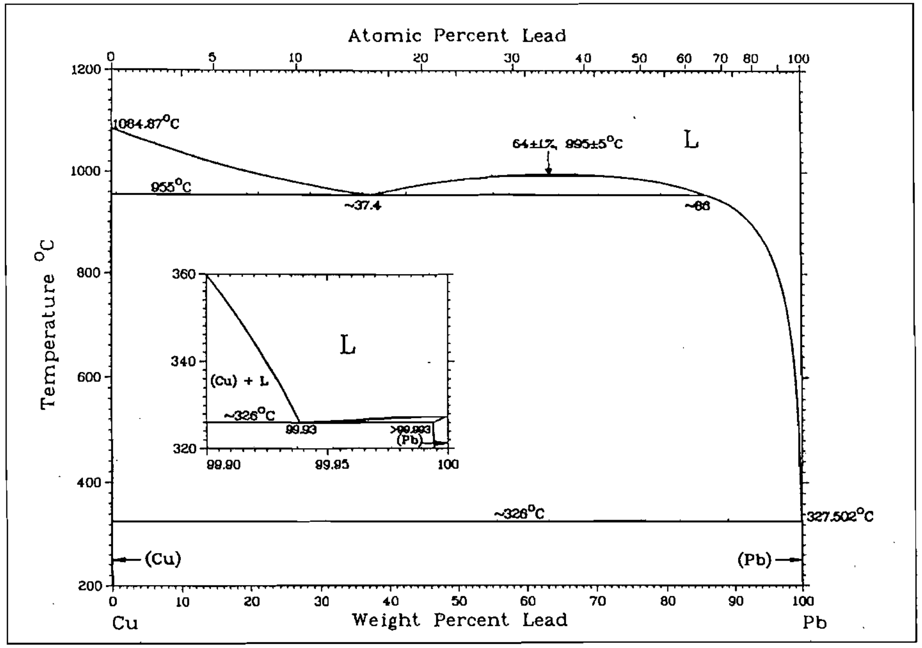

Figure 2: Binary-system Pb-Cu

2.2 Influence of third-elements on copper-solubility in lead

Crude lead consists on the following alloying elements, their binary solubility's are shown in Table 1.

Table 1: Concentration of alloying elements in crude lead and thin solubility in lead [3]

	Amount of alloying elements (Me)	Solubility of Me in Pb at 350 °C	Eutektika (see figure 2)	
Cu	0,5-3,0 %	0,1 %	0,06 – 0,07 %	327 °C
As	1,0-2,0 %	7,0 %	2,8 %	288 °C
Sb	1,0-3,0 %	25,0 %	11,1 %	252 °C
Sn	1,0-3,0 %	completely	61,9 %	183 °C

Figure 3 shows that all alloying elements with exception of copper have even at eutectic conditions a larger solubility than concentration in crude lead.

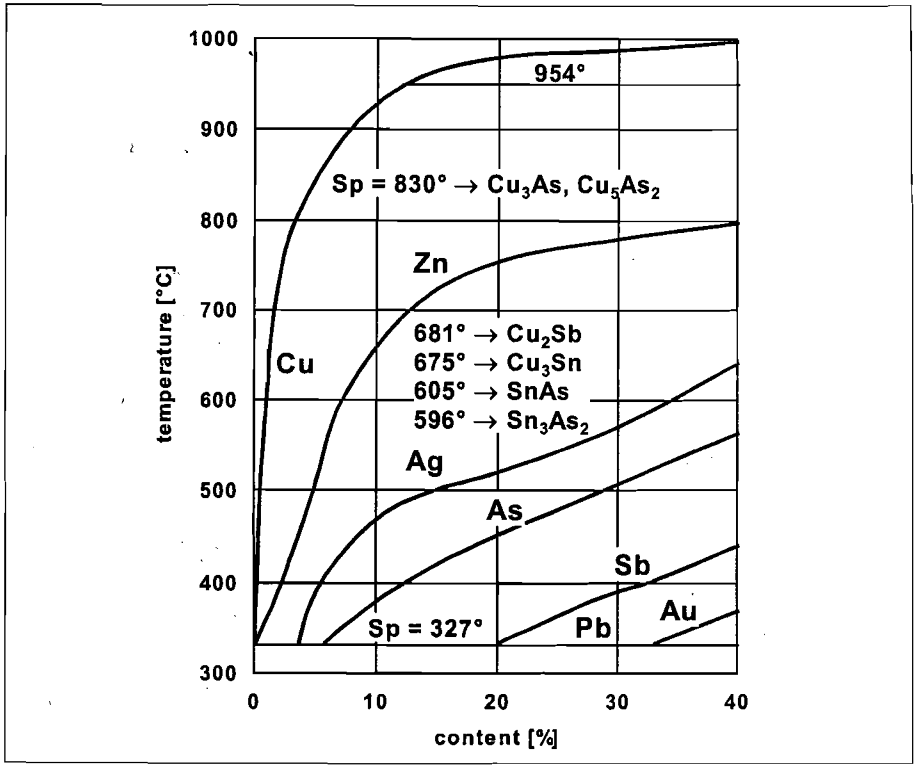

Figure 3: Equilibrium solubility of alloying elements in lead and melting points of relevant intermetallic phases [3]

By cooling of the lead-bullion the solubility of Cu in lead is reduced, the copper separates from the melt. Because of the lower density of the copper it moves to the surface like contained or formed intermetallic phases. Copper and the intermetallic phases form together with incorporated lead the so called copper-dross.

Small amounts of third elements strongly influence the separation of copper. For example through addition of 0,3 %. As the solubility of Cu in Pb decrease from 0,06 % to 0,02 % and 1,5 % Sn leads to a solubility reduction for copper to 0,02 %. The reason for these effect is the formation of intermetallic phases like Cu_6As, Cu_5As_2, Cu_2Sb, Cu_3Sn [7]. A summary of the effects of third elements on copper-solubility is shown in figure 4 [6].

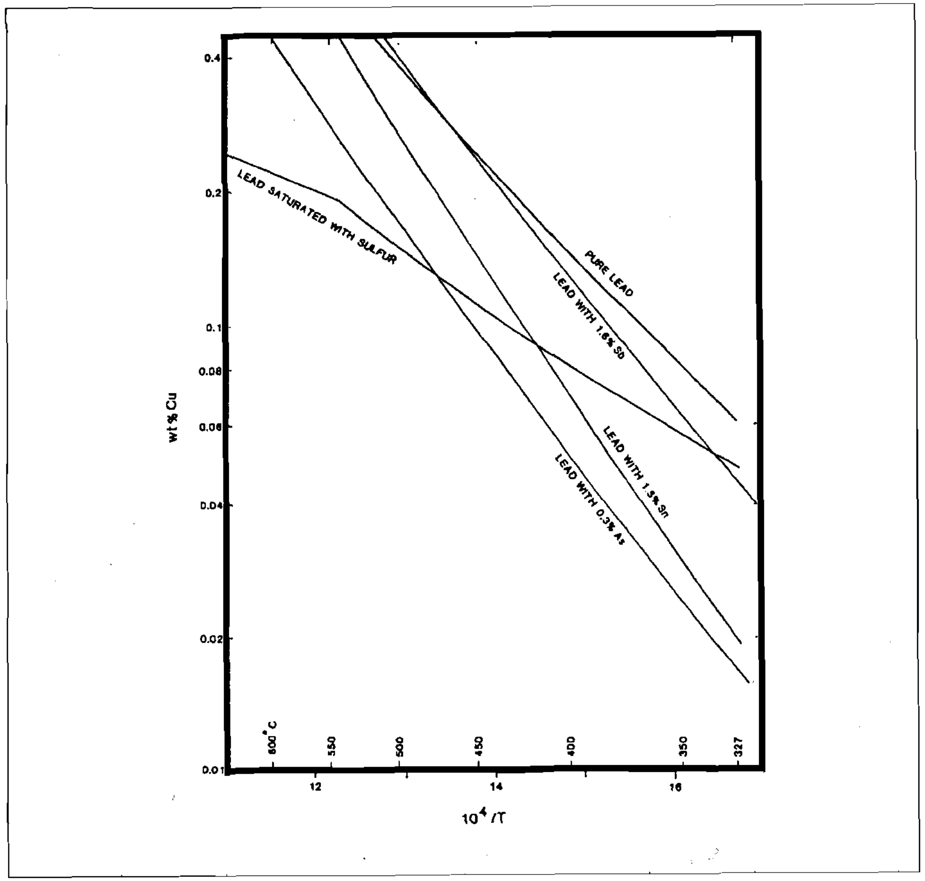

Figure 4: Solubility of copper in lead as a function of temperature in presence of third elements

The removal of copper as a first refining step has found fully acceptance as

- tin and arsenic seem to assist the decopperization [1,2], antimony on the other hand is suspected of inhibiting the reaction
- copper disturbs a selective removal of other alloying elements in subsequent refining steps

The phase diagram Pb-Cu-Sn shows, that by primary crystallisation of Cu-solid solution crystals or the intermetallic phase Cu_3Sn the Cu-content of the lead bullion in the ternary system Pb-Cu-Sn decreases. The Cu-value reaches at a temperature of 319 °C and a tin-concentration between 0,6 and 2,0 % its minimum (approx. 0,02 %). Above 2 % Sn in the melt the Cu-content rises again (figure 5). The process of Cu-solubility in presence of tin was verified also by [9] investigations.

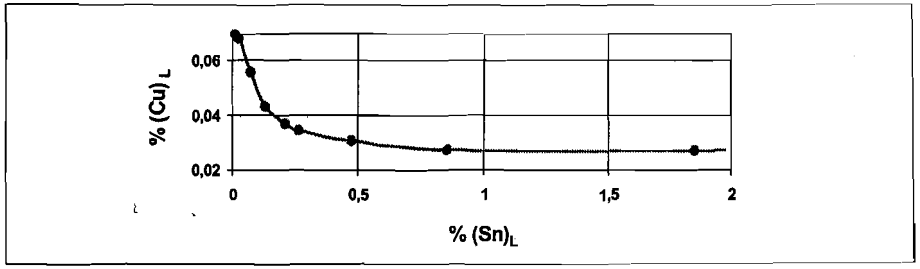

Figure 5: Pb-Cu-Sn-system; isotherm of Cu-solubility at 337 °C

Arsenic

The reducing influence of As to the solubility of Cu in Pb starts at a concentration of 0,003 % As. This is combined with the formation of the intermetallic phase Cu_3As [8]. The Cu solubility in the Pb-Cu-As-system (figure 6) shows up to 0,25 % a similar trend of the isothermal Cu-solubility-line as the PbCu-Sn-system, above these concentration the Cu solubility increases [10].

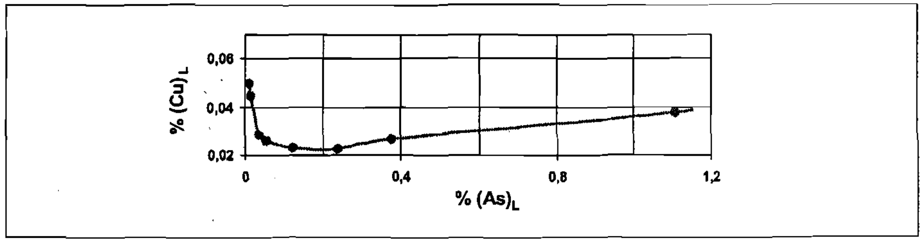

Figure 6: Pb-Cu-As-system; isotherm of Cu-solubility at 337 °C

At similar concentrations the influence of As is higher than that of Sn. A copper concentration of 0,05 % is in equilibrium with 0,01 % As, compared to 0,06 % Sn.

Antimony

The solubility of Cu in the Pb-Cu-Sb-system shows an irregular course as seen in figure 7 [10]. For low Sb-concentrations this zone is enlarged in figure 6b. After a slow rise at low Sb-concentrations the Cu-concentration decrease to a minimum at 1,5 % Sb and than increase again. In equilibrium with the melt is the intermetallic phase Cu_2Sb. Its constitution is independent from the Sb-content of the melt [10].

In the ternary systems Pb-Cu-Sn and Pb-Cu-As the copper-solubility decreasing effect of the ternary component starts early. In the system Pb-Cu-Sb the effect is connected with the Cu_2Sb formation and starts at a much higher Sb-concentration (0,03 %) at 337 °C. This Sb-concentration is in equilibrium with the saturated Cu-solution in the binary system Pb-Cu (0,07 % Cu).

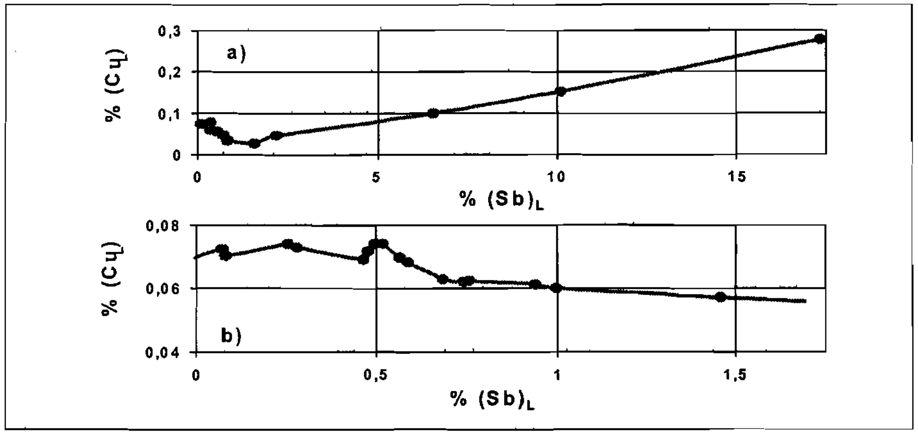

Figure 7: System Pb-Cu-Sb isothermal solubility of copper at 337 °C

The phase diagramme of the system Pb-Cu-Sb (figure 8) [11] demonstrates the existence of three two-phase and three three-phase equilibria in the lead corner.

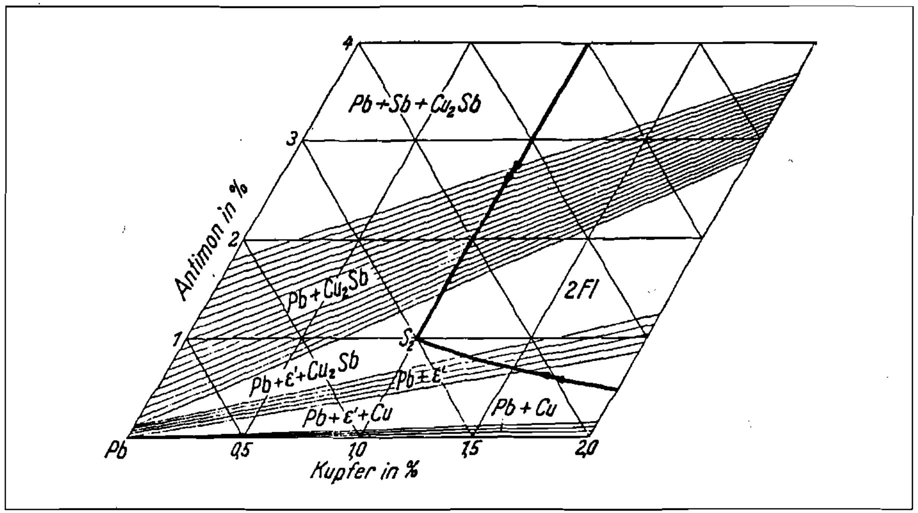

Figure 8: Lead corner at the Pb-Cu-Sb phase diagram after homogenisation at 20 - 30 °C below solidification temperature [11]

The single-phase Pb area and the two-phase Pb-Sb area are remarkable slim due to very low solubility of copper in a Pb-Sb-alloy. The system derived from [11] makes evident that the irregular curve of the copper solubility is caused by precipitation of phases in the melt because the slim two-phase Pb-Cu area is easily left. In the three-phase area Pb-ε-Cu the copper solubility increases with increasing Sb-content. In the two-phase area Pb-ε the copper solubility decreases rapidly with increasing Sb-content. In the three-phase area Pb-ε-Cu_2Sb the copper solubility decreases more slowly with increasing Sb-content and in the two-phase ares Pb-Cu_2Sb the solubility of copper in lead increases intensively. In [8] the difference between the phases Cu_2Sb and ε' was not taken into consideration and both were identified by examination as Cu_2Sb due to their almost identical composition. Starting with a ternary crude lead alloy the described course at the decopperization seems to be most probable.

For the respective quaternary phase systems (Pb-Cu-Sn-As/Pb-Cu-Sb-Sn) the copper solubility can be estimated by the solubility of the components Cu_3As and Cu_3Sn respectively Cu_2Sb and Cu_3Sn in the lead.

In the same manner the quinternary phase system Pb-Cu-Sb-Sn-As can be described by the single solubilities of Cu_2Sb and Cu_3Sn and Cu_3As. For instance starting with an 1 – 2 %-Sb-content it is evident that

- Sn will have no influence on the Cu_2Sb-solubility due the high practical existing concentration (> 1 % Sb)
- As has an effect on the copper solubility beginning with 0,015 % As (at 1 % Sb level) and with 0,042 % As (at 2 % Sb level)

Crude lead has to be called a multiple component system considering all existing accompanying elements. The latest publications discussing lead systems describe the formation of a compound with the formula Cu_6AsSb ($Cu_3As \cdot Cu_3Sb$) [13] in the system Pb-Cu-As-Sb and compounds like $Cu_{12}Sb_3Sn_7$ and $Cu_{10}SbSn_9$ [14] in the system Pb-Cu-Sb-Sn. These multiple component compounds participate to the copper removal depending on their solubility in lead. Therefore the above presented transfer to quarternary and quinternary systems have to be considered as a first approximation.

2.3 Characterization of the relevant multicomponent system

The knowledge of the potential compounds and reactions in the lead melt is very important for the evaluation of the efficiency of the removal of copper and type and volume of the formed dross. Multicomponent systems are up to now unidentified to draw the principles of copper removal from crude lead. In order to give a prediction for the reactions and end-products in a ternary system, a technique can be used which is described in numerous publications on ternary and quarternary systems [15, 17-20].

The main principle of this method consists on a triangulation of the ternary subsystems and a following partitioning of them, using quasi-binary cuts. The isolated secondary tetraeders can be reduced to manageable equilibrium systems with simple components. Before developing a metallurgical process, whose exact constitutional diagram of the components is not known, it is recommended that previous to a experimental work a triangulation and tetraedration of the system is carried out. Data of the quinternary system Pb-Cu-As-Sb-Sn are not published. From the proper binary and ternary systems of lead is known that these alloying elements don't form intermetallic compounds with lead. Therefore it is possible to estimate the phase structure of copper and the other alloying elements by the leadfree quarternary system Cu-As-Sb-Sn.

The triangulation, shown in figure 9 is carried out on the basis of published data, on experimentally proven quasi-binary cuts [24, 26-27], on the already accomplished triangulation of the system Cu-Sb-Sn [6, 24, 26, 27], on own thermodynamic calculations [28-31], and finally on own experimental kinetic studies of copper removal from lead copper solubility and dross composition from.

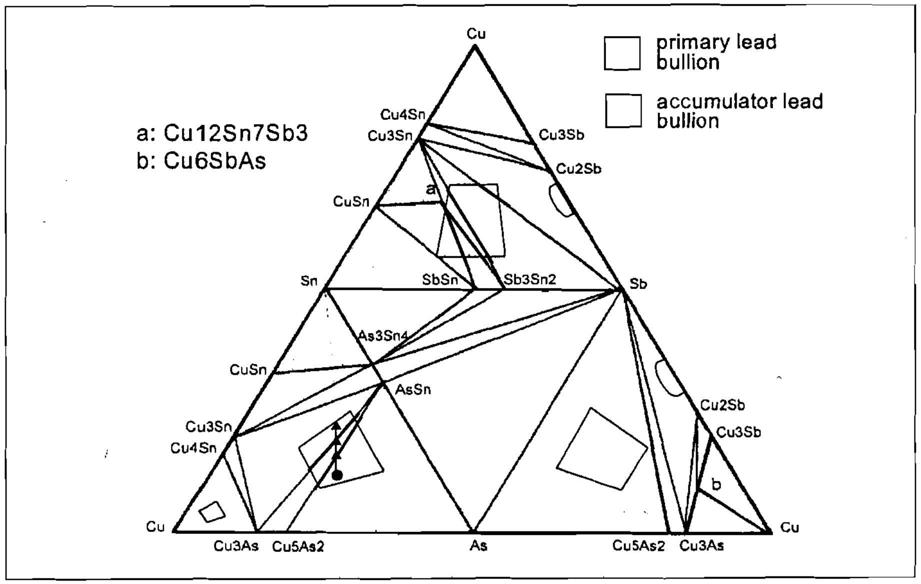

Figure 9: Triangulation of the system Cu-As-Sb-Sn

The triangulation of ternary corner systems of the Cu-As-Sn-Sb-system show that several subsystems exist:

- $Cu-Cu_4Sn-Cu_3Sb$
- $Cu_4Sn-Cu_3Sb-Cu_2Sb$
- $Cu_4Sn-Cu_2Sb-Cu_3Sn$
- $Cu_3Sn-CuSn-Cu_{12}Sn_7Sb_3$
- $CuSn-SbSn-Cu_{12}Sn_7Sb_3$
- $SbSn-Sb_3Sn_2-Cu_{12}Sn_7Sb_3$
- $Cu_3Sn-Sb_3Sn_2-Cu_{12}Sn_7Sb_3$
- $Sn-CuSn-SbSn$
- $Cu_3Sn-Sb_3Sn_2-Sb$
- Cu_3Sn-Cu_2Sb-Sb

From this partitioning it can be followed that the copper solubility in conventional crude lead can be defined by the solubility of 7 intermetallic compounds and 3 metals. 10 combinations with the connected eutectic channels explain the complexity of the segregation process. In figure 9 the dashed areas (horizontal: accumulator crude lead , vertical: primary crude lead) represent practical concentration ranges of copper and other alloying elements when standardized to 100 %. The arrows in the system Cu-As-Sn point out the influence of Sn on the copper compound structure. From the investigation of the systems $Cu-Me_1-Me_2$ (Me = Sn, As, Sb) the copper-phase in the lead melt can be determines the copper solubility. The composition of the bullion from battery recycling is typically on the line As - Sb/Cu ≈ 9,5 and is in the Sb-corner. It crosses three secondary systems with binary copper compounds, which points out a complicated dependency of the copper solubility on the arsenic content in a lead antimony melt. This causes the unsteady run of the copper solubility during copper removal (e.g. figure 6).

The tetrahedration (figure 10) of the system Cu-Sb-As-Sn was accomplished on basis of the previous shown triangulation of the three-component subsystems.

In accordance with the tetrahedration rule the number of the secondary quaternary systems, which are formed with the tetrahedration of a quaternary system, is determined by a formula with T: Number of the secondary quaternary systems, ZV: Number of the two-material compounds in all two-component systems, DV: Number of the three-material compounds in all ternary systems:

$T = 1 + ZV + 2*DV$ [20]

For the system Cu-Sb-As-Sn ZV amounts to 11 and DV to 2. This leads to 16 secondary quaternary systems!

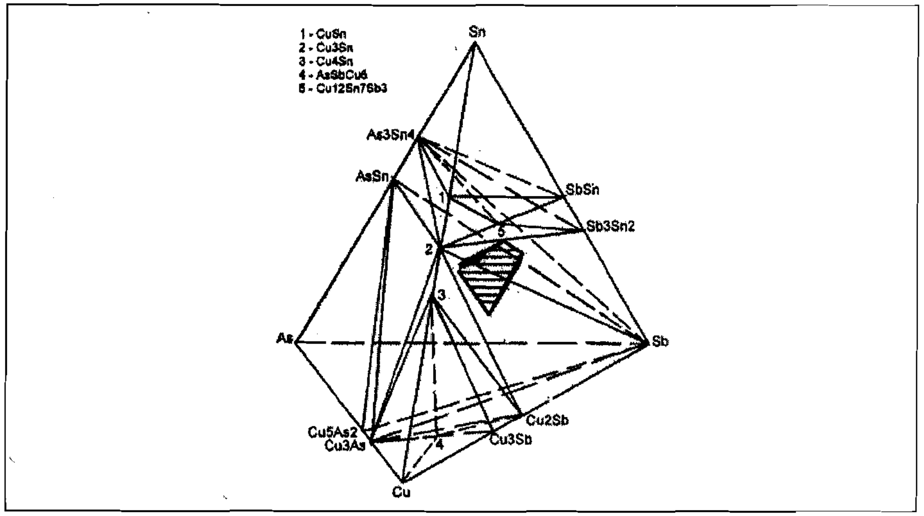

Figure 10: Tetrahedration of the system Cu-Sb-As-Sn

The following secondary sub-systems are formed:

- $Cu-Cu_6SbAs-Cu_4Sn-Cu_3As$
- $Cu-Cu_6SbAs-Cu_4Sn-Cu_3Sb$
- $Cu_6SbAs-Cu_4Sn-Cu_3Sb-Cu_2Sb$
- $Cu_6SbAs-Cu_4Sn-Cu_3As-Cu_2Sb$
- $Cu_3As-Cu_4Sn-Cu_2Sb-Cu_3Sn$
- $Cu_3As-Cu_2Sb-Cu_3Sn-Sb$
- $Cu_3As-AsSn-Cu_3Sn-Sb$
- $Cu_3As-AsSn-Cu_5As_2-Sb$
- $AsSn-Cu_5As_2-Sb-As$
- $AsSn-As_3Sn_4-Cu_3Sn-Sb$
- $As_3Sn_4-Sb_3Sn_2-Cu_3Sn-Sb$
- $As_3Sn_4-Sb_3Sn_2-Cu_3Sn-Cu_{12}Sn_7Sb_3$
- $As_3Sn_4-Sb_3Sn_2-SbSn-Cu_{12}Sn_7Sb_3$
- $As_3Sn_4-Cu_3Sn-CuSn-Cu_{12}Sn_7Sb_3$
- $As_3Sn_4-SbSn-CuSn-Cu_{12}Sn_7Sb_3$
- $As_3Sn_4-SbSn-CuSn-Sn$

The crude lead composition from battery recycling followes typically on the cut As-Sb-Sb/Cu ≈ 9,5 (figure 11). Since the arsenic and tin contents are usually very small in a production lead a bullion, the composition moves mainly into the sub-system $Sb-Cu_3Sn-Cu_3As-Cu_2Sb$ (field 8 in figure 11). Copper is present here in form of three intermetallic compounds. Thus also the copper dross should contain this compounds (beside lead oxide).

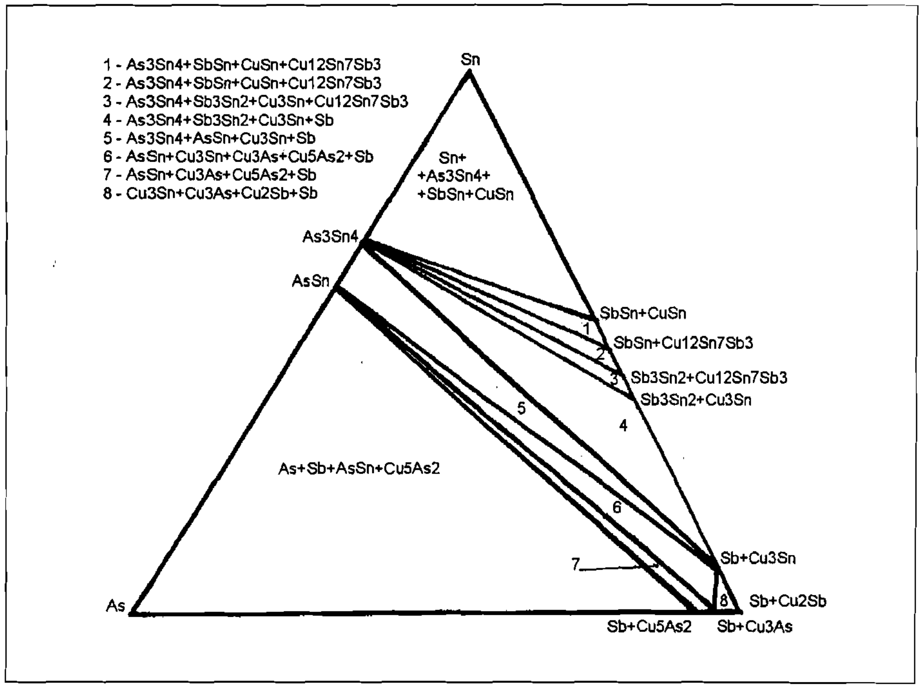

Figure 11: Polythermic cut As-Sn-Sb/Cu = 9,5 (bullion from battery recycling)

3 Copper removal by precipitation with sulphur (second step)

3.1 Equilibrium Pb-Cu-S

Since the copper content of the lead bullion after dross removal is still too high (negative copper impacts in further refining steps), and to meet the specification for battery electrodes, a second and advanced copper removal step must be executed. This is done by heating the pre-refined lead after dross removal and adding several portions of sulphur (pyrite, sodium-sulphide) [2]. Insoluble sulphides are formed, which can be separated.

Table 2: Copper removal from lead with sulphur in different plants (production data)

enterprise	Cu-content before S-treatment [weight-%]			Cu-content after S-treatment [weight-%]			process of S-addition $[kg/t_A]$	temperature [°C]	batch size [t Pb]	reaction time [min]	dross weight [t] $([kg/t_{Pb}])$
	Cu	Ag	Sn	Cu	Ag	Sn					
A	0,04	0,1		0,002	0,1		0,8 kg/t with a shovel during 3 min (2,1)	320	90	10	4-5 (44,4–55,5)
B	0,42	0,21	0,14	0,01	0,23	0,07	2,1 kg/t with a shovel during 5 min (5,13)	350	60	60	3-4 (50-67)
C	0,06	0,001	0,15	0,001	0,001	0,15	1 kg/t in 10 doses during 10 min (1,67)	370	100	10	0,7 (7)
D	0,06			0,01	0,1	0,01	0,5-1 kg/t (1 – 2)	340-350	100	20-30	3 (30)
E	0,5	0,8	0,7	0,05	0,8	0,7	0,8 kg/t in 10 doses (0,18)	350-370	30	15-20	0,1 (3,3)
F	0,1	0,37		0,03	0,32		0,7 kg/t (1)	340	230	90	5 (21,7)
G	2,28	0,55	2,0	0,05	0,59	0,99	1,25 kg/t during 25 min (0,06)	320	200	65	25 (125)
H	0,08	0,73	0,07	0,009	0,73	0,017	2,2 kg/t with a shovel during 45 min (3,1)	330	220	90	8 (36,4)
I	0,12	0,16	0,01	0,06	0,16	0,01	0,2-0,25 kg/t with a shovel during 2 min (0,3 – 0,4)	380-400		30	30 (30)
J	0,3	0,15	0,05	0,08	0,15	0,01	0,5 kg/t (0,23)	370-390	60	30	2 (33,3)
K	0,1	0,01		0,009	0,01		1,5 kg/t (1,65)	345	230	25	9 (39,1)
L				0,02	0,02	0,68	0,6 kg/t (k. A.)	335	100	360	
M	0,5			0,008	0,01		0,9 kg/t during 30 min + 1,8 kg/t FeS_2 (0,18)	360-400	200	120-180	5 (25)

An overview of the process of copper removal processes in different plants gives table 2. It shows that in all plants individual, adapted procedures for copper removal from lead with sulphur are used. The procedures differ by the sulphur quantity, the degree of the copper removal and the quantity of formed dross. The sulphur demand varies from 0,055 kg per kg copper in the lead (factory G) up to 2.75 kg sulphur per kg copper (factory H). A logical explanation for these enormous differences is missing.

In practice crude lead is decopperized with sulfur to about 0.001 % Cu and less. Theoretically and thermodynamically this concentration can hardly be reached. The final thermodynamic concentration limit. is approx. 0.05 % Cu. The potential phases, being in equilibrium with sulfur during decopperization of lead, are shown in the phase diagram Pb-Cu-S. [21,33] (figure 12)

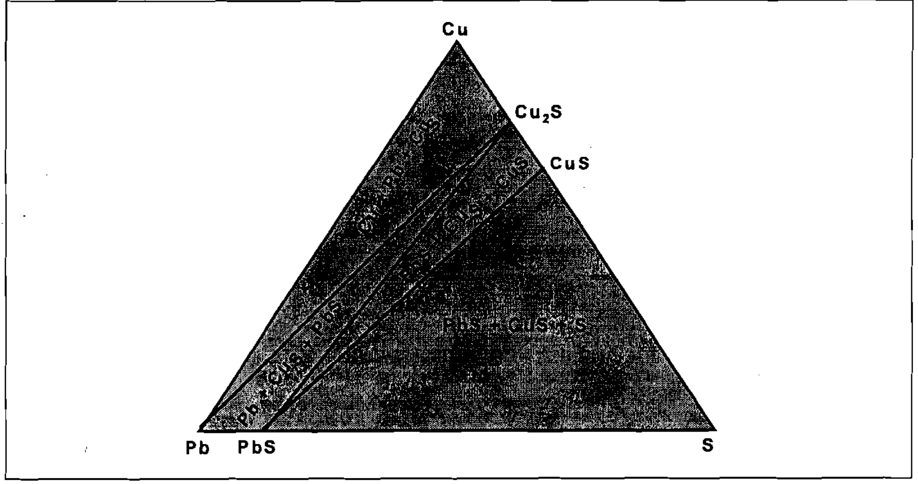

Figure 12: System Pb-Cu-S [33]

According to this, the following reactions are expected:

$(Pb) + (S) = \langle PbS \rangle$ (1)

$\underline{Cu}_{Pb} + (S) = \langle CuS \rangle$ (2)

The gross reaction of (1) and (2) is: $(Pb) + CuPb + 2\,(S) = \langle PbS \rangle + \langle CuS \rangle$ (3)

with the secondary reaction $\langle CuS \rangle + Cu_{Pb} = \langle Cu_2S \rangle$ (4)

the gross reaction of (3) and (4) is: $\langle PbS \rangle + 2\underline{Cu}_{Pb} = (Pb) + \langle Cu_2S \rangle$ (5)

Using the phase-diagram (figure 12), the entire solubility of copper in lead is determined by the individual solubilities of Cu and Cu_2S in the Pb-Cu-Cu_2S-system, or by the solubility of Cu_2S in the Pb-Cu_2S-PbS-system. In [32] the following reaction-process was assumed, based on experimentally produced phases:

very fast: $(Pb) + (S) \rightarrow \langle PbS \rangle$ (6)

fast: $\langle PbS \rangle + Cu_{Pb} \rightarrow \langle CuS \rangle + (Pb)$ (7)

Decopperize-reaction

moderate fast: $\langle CuS \rangle + \underline{Cu}_{Pb} \rightarrow \langle Cu_2S \rangle$ (8)

Decopperize-reaction

slow: $2\langle CuS \rangle + (Pb) \rightarrow \langle Cu_2S \rangle + \langle PbS \rangle$ (9)

very slow: $\langle Cu_2S \rangle + (Pb) \rightarrow \langle PbS \rangle + 2\underline{Cu}_{Pb}$ (10)

lead-sulfide-coating

But due to figure 12 it is impossible that copper sulfide is formed from lead sulfide and reacting back to lead sulfide without changing temperature, pressure or other reaction-parameters. In our (IME)-understanding the following reaction is more probable:

$$\begin{tikzcd}
 & 2\underline{Cu}_{Pb} + \underline{PbS}_{Pb} \rightarrow \langle Cu_2S \rangle + (Pb) \\
\mathbf{(Pb) + \underline{Cu}_{Pb} + (S) \rightarrow \langle PbS \rangle / \underline{PbS}_{Pb} + CuS} \arrow[ur] \arrow[r] \arrow[dr] & (Pb) + \underline{Cu}_{Pb} + 3\langle CuS \rangle \rightarrow \langle PbS \rangle + 2\langle Cu_2S \rangle \\
 & (Pb) + 2\,\langle CuS \rangle \rightarrow \langle PbS \rangle + \langle Cu_2S \rangle
\end{tikzcd}$$

PbS and CuS as stable phases are formed when liquid or gaseous sulfur comes in contact with lead containing copper. CuS originates by a heterogeneous reaction between copper dissolved in lead and sulfur. It is there produced where sulfur is in a local surplus. According to the reactions (4) and (5) CuS contributes to a further decopperization [1, 35].

As it results from the tetraedation of the system copper occurs in crude lead in different phases. It can occur elementary (as segregated phase) or in dissolved copper compounds combinations depending on the content of alloying elements (Sn, As, Sb, etc.). In all external examinations presented above, which are concerned with the reaction mechanism in crude lead only the free copper is looked at. However, the alloying elements of lead can fundamentally influence the reaction mechanism and the cinetics of the decopperication.

3.2 The influence of alloying elements on decopperization with sulphur

In practice much lower Cu contents are reached than thermodynamically possible. The reason is seen in the positiv effect of tin [36], silver [38] and bismuth [37], the influence of antimony is discussed controversary [37,38,12]. From [12] is published that antimony impedes the process in the systems Pb-Cu-Sn-Sb and Pb-Cu-As-Sb especially at high Sb-contents (fig. 13). The influence of Zn in Pb-Cu-Sb-As and As in Pb-Cu-Sb-As show, that there are further phase equilibria in the systems (fig. 14).

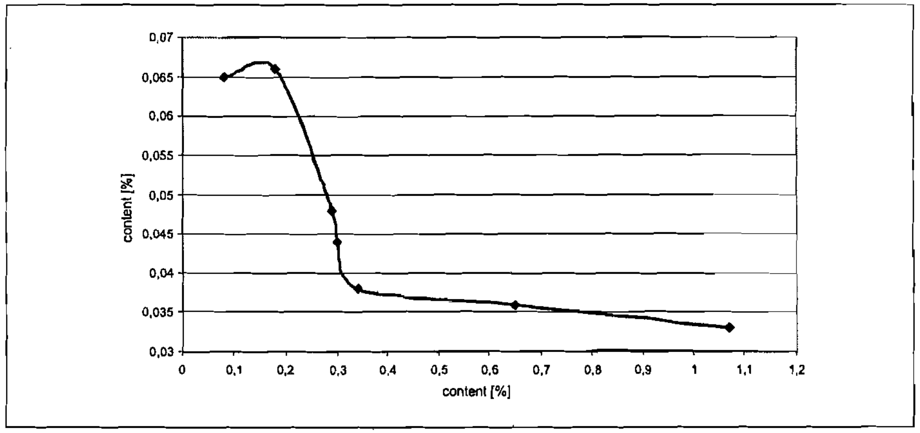

Figure 13: Influence of tin concentration on copper removal in Pb-Cu-Sn-Sn-melts at 285 °C (single sulphur addition 100 % related to Cu_2S, Cu initial content 0.15 to 0.30 %, Sb initial content 9.0 %) [12]

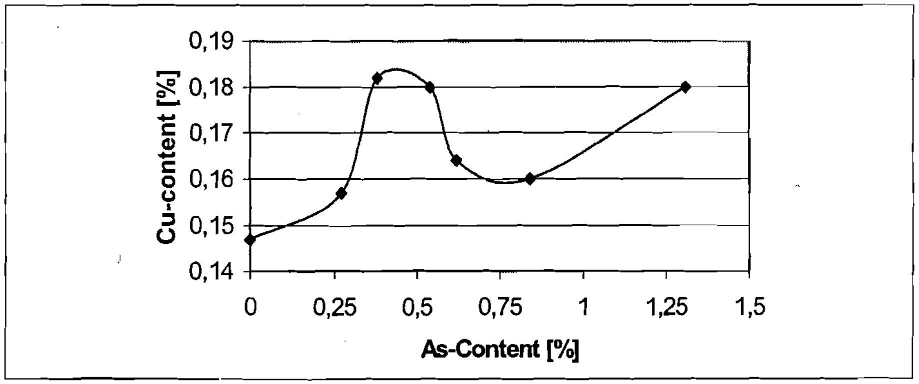

Figure 14: Influence of arsenic on the copper removal in the system Pb-Cu-Sb-As (single sulphur addition 100 %, Cu initial content from 0,30 to 0,50 %, Sb initial content 9 %)

3.3 Copper removal kinetics at presence of sulphur

3.3.1 Published knowledge

Published data on kinetics of the copper removal from lead bullion with sulphur [1,39] showed that within 2 - 4 minutes the minimum concentration of copper in the melt is reached, which thereafter again rises (figure 15). The backward reaction 10 between lead and Cu_2S is assumed to be the reason [40], which accelerates with increasing contact time between dross and the lead melt [41]. In most publications, dealing with kinetics of the copper removal, the specification concerning the composition of the used lead is missing, which makes a interpretation of the complex effects of the individual alloying elements impossible.

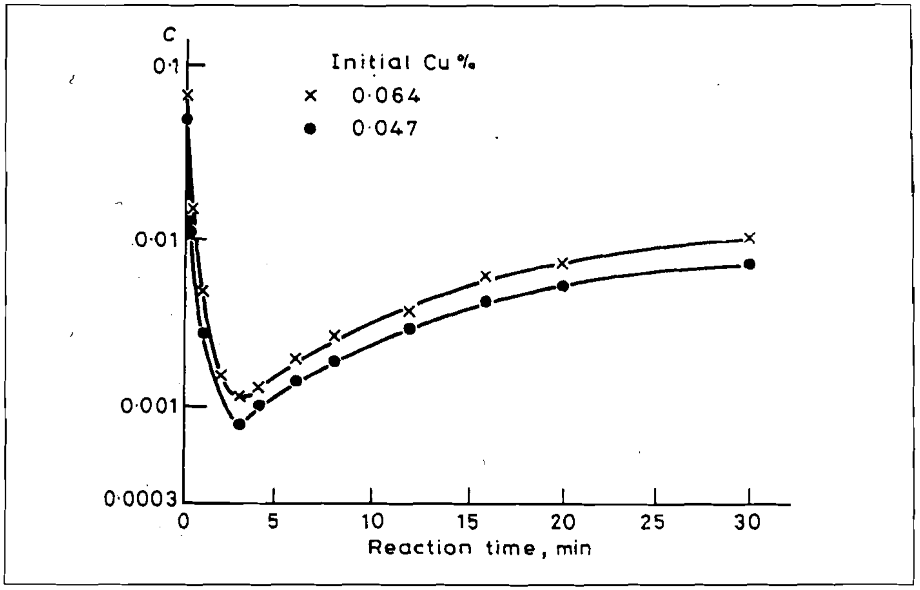

Figure 15: Kinetics of the copper removal from lead with sulphur [40]

A different shape of the kinetic-curves is found at presence of elements, which form compounds with copper (e.g. Tin) and of non-compound-forming elements (e.g. Silver). The decline of the copper concentration happens with presence of silver steadily. The lower the temperature, the more rapidly and more completely. At presence of tin the Cu-level first rapidly decreases, in the further run the copper content rises again. The temperature influence is completely reverse to the silver presence. The causes of this different effect are not published yet. The often assumed backward reaction from Cu_2S and lead to PbS and Cu however is thermodynamically impossible. The third elements, in the intermetallic phases have a much lower affinity to sulphur and react much slower. This could lead to higher dissolved levels than initially present.

3.3.2 Experimental investigations

The copper removal in lead using sulphur and pyrite was investigated at Varta Recycling, Krautscheid under special consideration of Arsenic, Tin and Antimony. Before and whilst copper removal with sulphur and pyrite samples were taken with a special developed sampling device about 50 cm under the surface as well as the temperature of the melt was measured at this location.

After immersing the sampling device in the melt, it was opened by removing a lid, which was immediately closed again in order to avoid dross. The device was pulled out and samples were cast. One of the samples was vacuum filtered through a mineral felt at sampling temperature. Both were analysed on Cu, Sb, As, Sn, Te and Se.

The concentration of copper, tin, arsenic and antimony in the non-filtered = standard samples show a similar trend (s. fig. 16). Noticeable is again the rise and decline of the values. After approx. 40 minutes reaction time the copper, tin and arsenic content came to a relative constant level.

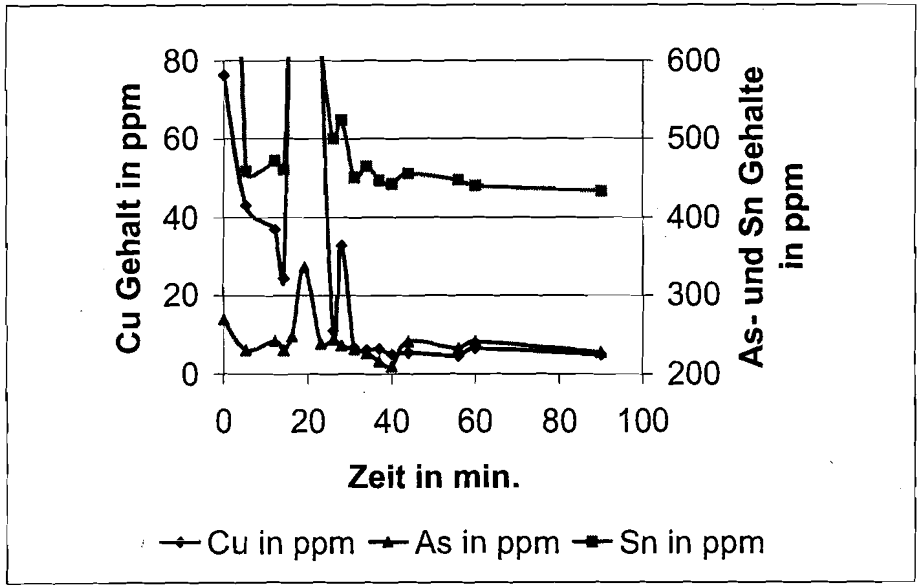

Figure 16: Kinetic curves of copper, tin and arsenic concentration by copper removal in lead with sulphur and pyrite (production samples)

The comparison of the copper concentration curves before and after filtration (Fig. 17a) shows concentration peaks for the not filtered sample and a steady decreasing curve of the filtered sample. The starting copper concentration of the not filtered sample was 76,3 ppm, of the filtered sample 49.9 ppm. After 40 - 50 minutes the concentrations reached the same level. The unsteady course of the copper concentration in the not filtered samples is pointing to segregation processes and not separated inclusions of copper-bearing compounds. Focussing on the copper reduction curve after filtration in detail a slight periodical rise and decline of copper concentration is observed (fig. 17b). After 10 - 12 minutes the copper concentration slope delays and slight increases can be observed in the following hour. Such delays were also noticed in laboratory scale trials but repeated in smaller periods of 2,5 to 3 minutes. Figure 18 collects the kinetics results for tin, arsenic and antimony. Non filtered samples show again the presence of suspended not settled particles.

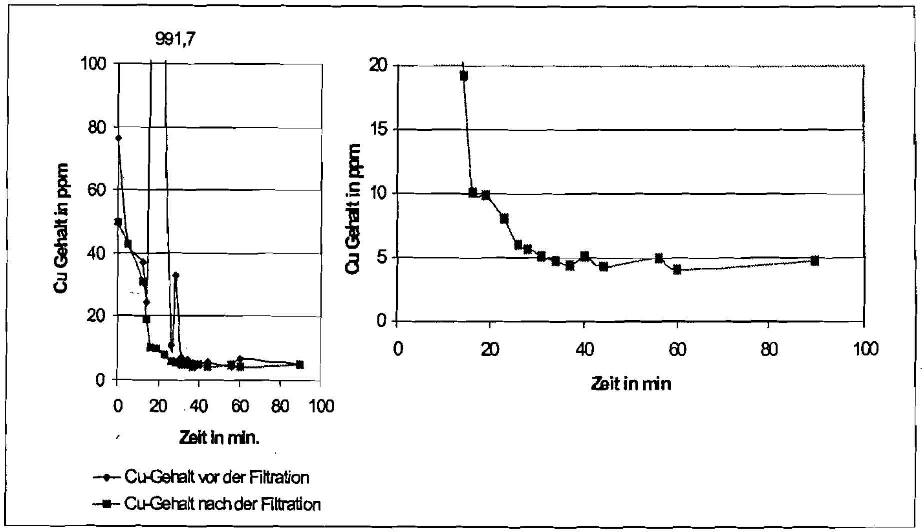

Figure 17: Copper concentration versus reactiontime
a) before and after filtration b) detail after filtering

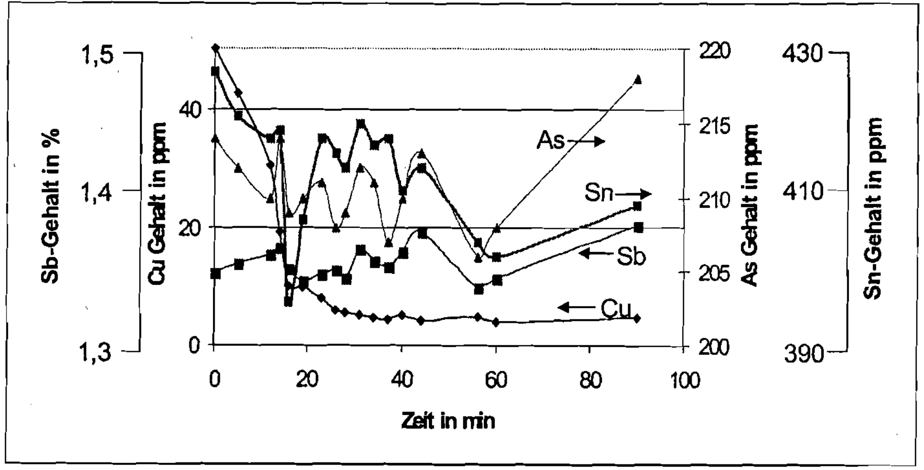

Figure 18: Concentration of copper, tin, arsenic and antimony during sulphur addition treatment (after sample filtration)

A different presentation (fig. 19) shows a close connection between rise and fall of the elements An, As and Sb, which leads to the assumption, that the same mechanism applies for these elements.

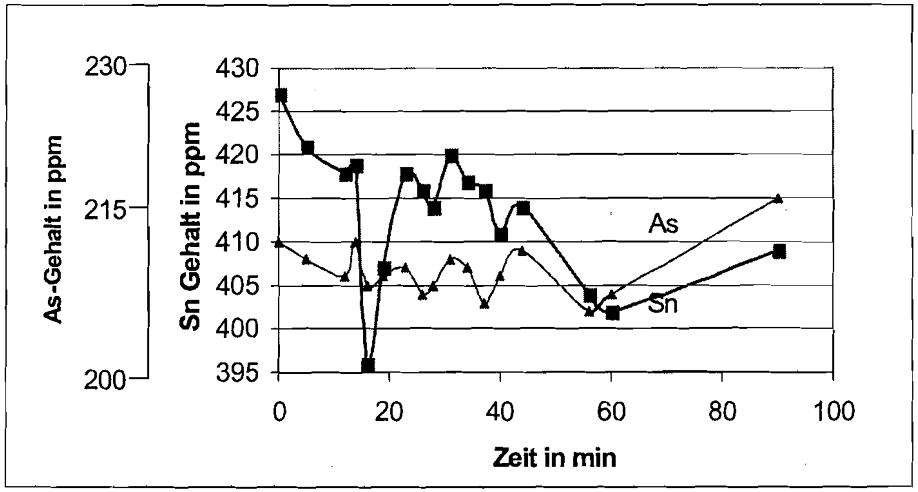

Figure 19: Concentration of tin and arsenic (filtered samples)

3.4 Mechanism of the decopperization of crude lead with presence of sulphur

The different courses of copper removal with sulphur in presence of alloying elements leads to two different mechanisms depending whether these elements form compounds with copper or not. In pure Pb-Cu-melts and also in Pb-Cu-Me1-melts (Me1 is a metal, which does not form compounds with copper) dissolved copper reacts with dissolved PbS or sulphur forming Cu_2S. Thus the copper content of the melt decreases below the copper solubility in lead at that temperature. Due to the fact that re-dissolving of suspended or dross contained high melting copper metal (from first stage of Cu-refining, see. 3.2) needs more time than the reaction of dissolved copper with sulphur at 350 - 400 °C it is most likely that copper is not quantitatively dissolved. In Pb-Cu-Me2-melts (Me2 is a metal which forms compounds with copper) dissolved copper in the lead react with dissolved PbS and sulphur forming Cu_2S. Again the copper content of the melt decreases below the copper solubility at that temperature. Suspended copper intermetallic compounds (about 90 % of the copper in the dross occurs as intermetallic compounds) can be quickly re-dissolved in the melt, due to the lower melting point. The copper content of the melt rises to the thermodynamic solubility and reacts again with sulphur (sulphur carrier).

The comparison of the concentration change of the investigated elements and of copper show, that parallel to the primary reduction of the copper concentration the tin and arsenic values decrease also, but not antimony. At the points of retardation or reversal of the copper reduction the contents of these elements increase intensively and particularly a parallel progress can be detected (see figure 19). Because of these results it can be concluded, that during the removal of copper reactions are taking place, which implicates also a removal of Sn, As, Sb from the molten lead bullion, but to a certain degree these reactions may force copper to dissolve again. As published and shown by tetraedration of the multi-component system (see 3.2) copper in crude lead is present in form of various intermetallic compounds. A copper enrichment of the lead bullion can take place in the presence of third elements, which form with copper intermetallic compounds. The reported experimental results confirm the following proposed mechanism of lead decopperization.

A minor part of the intermetallic compounds (copper and third elements) is dissolved in lead, but the largest part is suspended in the melt in solid form. With the addition of a sulphur carrier (sulphur, pyrite) CuS and predominantly PbS is formed corresponding to the ternary-phase-diagram (figure 8). This happens by heterogenous reaction of the melt with liquid respectively gaseous sulphur, because the lead activity is closed to 1. PbS dissolves in lead at 350 - 400 °C to approximately 0,7 – 0,8 %, which is equivalent to a solubility of sulphur of 0,1 – 0,12 %. Through homogenous reaction in the lead dissolved PbS reacts with dissolved third elements (intermetallic compounds). The homogenous liquid reaction is kinetic perferred to a heterogeneous liquid solid reaction. Single and double sulphides of copper and of third elements are formed. The solid and in lead insoluble sulphides rise to the melt surface, thereby the content of copper and impurities in the melt decreases. A lead melt with contents of copper and those third elements is formed, with concentrations below the solubility of a sulphur free lead melt. Thereafter intermetallic compounds, which are suspended in the melt, can dissolve in the lead melt, supported by stirring. Because of the affinity of copper to sulphur in opposite to the impurities, already dissolved copper sulphidizes and immediatly segregates, the copper content of the melt remains more or less unchanged or increases only slightly. But the concentration of the third elements in the melt increases because they do not react as fast with sulphur as copper does.

An approach to draw this mechanism is given in figure 15 schematically. Cycles of decopperization and re-dissolution exist and last as long as in the melt disperred but soluable intermetallic compounds exist. This mechanism of periodic decopperization and enrichment as well as the increase and decrease of the impurity contents in lead during the treatment with a sulphur can be described thermodynamically by the phase-diagram (figure 12). The assumption of forming double sulphides ($n*Cu_2S*m*Me_xS_y$) leads to a larger equilibrium constant of the decopperation reaction and thus to lower copper concentrations in the lead bullion. Thus the contradiction is solved between the practical achievable and the thermodynamical computed values of the copper concentration in lead after decopperization with sulphur. The very small re-enrichment of copper in the lead in pure Pb-Cu-melts while decopperization with sulphur can be explained with the very slow re-dissolution of unsolved metallic copper in the lead.

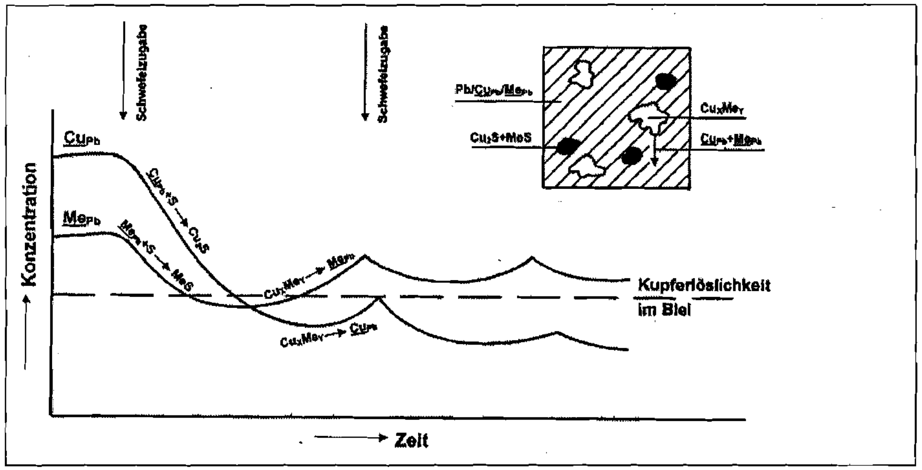

Figure 20: Schematic illustration of proposal mechanism for copper removal

4 Conclusions

Due to these considerations the following suggestions for a practical compared to sulfide formation realisation of the decopperization of crude lead with sulphur can be made:

Decopperization of the lead by thermal segregation prior to a sulphur addition has to be completely undertaken, to avoid dispersed metallic copper or intermetallic copper compounds in the lead melt.

The sulphur quantity has to be below 0,1 % of the lead quantity per addition step (solubility of sulphur). A surplus leads only to sulphur losses.

In order to avoid re-dissolution of intermetallic compounds in lead, the sulphurization has to be undertaken quickly and the formed dross has to separated from the lead melt immediately.

5 Literature

[1] T.R.A Davey: The physical chemistry of lead refining; Lead-Zinc-Tin 80 Proceedings of a World Symposium on Metallurgy and Environmental Control sponsored by the TMS-AIME Lead, Zinc, and Tin Committee at the 100th AIME Annul Meeting, February 24-28, 1980, in Las Vegas, Nevada, p. 477-507

[2] W.W. Krysko: Die Entkupferung des Bleies; Erzmetall Vol. 17 (1964) no. 6, p. 285-291

[3] W.W. Krysko: Die Entkupferung des Bleies (Part 3 and 4): Erzmetall Vol. 19 (1966) no. 1, p. 12-20

[4] R. Kleinert: Gegenwärtiger Stand der Blei-Raffinationsverfahren; Erzmetall Vol. 22 (1969) no. 9, p. 327-338

[5] F. Johannsen, B. Rose: Untersuchungen zur Entkupferung von Werkblei; Erzmetall Vol. 16 (1963) no. 9, p. 443-451

[6] T.B. Massalski, H. Okamoto: Binary Alloy Phase Diagramms; Copyright by ASM International, 2nd printing, August 1992

[7] W.W. Krysko, J. Drinkwater: Die Entkupferung des Bleies (Part 8); Erzmetall Vol. 20 (1967) no. 4, p. 171-173

[8] T.R.A. Davey: Phase Systems concerned with the Copper Drossing of Lead; Bulletin of the Institution of Mining and Metallurgy, October 1962, no. 671, p. 553-620, Transactions, Vol. 72, 1962-63, Part 1, p. 1-60

[9] H. Hartmann, F. Ensslin, E. Wunderlich: Untersuchungen über die Entkupferung des Bleies in Gegenwart von Zinn, Arsen und Antimon (Part 1); Erzmetall Vol. 12 (1959) no. 8, p. 374-381

[10] H. Hartmann, F. Ensslin, E. Wunderlich: Untersuchungen über die Entkupferung des Bleies in Gegenwart von Zinn, Arsen und Antimon (Part 1); Erzmetall Vol. 12 (1959) no. 9, p. 437-443

[11] A. Schrader, H. Hanemann: Über das System Blei – Antimon – Kupfer; Zeitschrift für Metallkunde, Vol. 33, Feb. 1941, no. 2, p. 49-60

[12] H. Hartmann, F. Ensslin, E. Wunderlich: Untersuchungen über die Entkupferung des Bleies in Gegenwart von Zinn, Arsen und Antimon (Part 2); Erzmetall Vol. 12 (1959) no. 11, p. 537-543

[13] E. Günzel, K. Schubert: Strukturuntersuchungen im System Kupfer-Antimon; Z. Metallkunde Vol. 49 (1958) no. 3, p. 124-133

[14] Konstitution der ternären metallischen Systeme (Page 29-50-51); Kompendium Lose-Blatt-Sammlung; Ed.: W. Guertler, Berlin - Istanbul 1956/57, 1st Volume

[15] W. Guertler: Betrachtungen zur theoretischen Metallhüttenkunde; Metall und Erz Vol. 17 (1920) no. 8, p.192-195

[16] R. Vogel: Die heterogenen Gleichgewichte; 2nd printing, Akademische Verlagsgesellschaft GEEST & PORTIG K.G, Leipzig 1959, p. 389-393

[17] L.S. Palatnik, L.I. Landau: Fazovye Ravnovesiya v. Mnogokomponentnykh Sistemakh (Phase equilibria in multiple component systems), Kharkovs Stats University, Kharkov, 1961 (russian)

[18] N. S. KURNAKOV: Einführung in die physikalisch-chemische Analyse; Verlag AN UdSSR, 1940 (russian)

[19] A. PRINCE: Alloy phase equilibria; Elsevier publishing company, Amsterdam-London-New York, 1966

[20] M. ZAKHAROV: Mehrkomponentige metallische Systeme mit Mischphasen; Moskau, Verlag Metallurgie, 1985 (russian)

[21] W. GUERTLER, G. LANDAU: Beiträge zur Kenntnis des System Kupfer-Blei-Schwefel; Metall und Erz Vol. 31 (1934) no. 8, p. 169-179

[22] H. HARTMANN, F. ENSSLIN, W. DAVIDSON: Untersuchungen über die Entkupferung des Bleies in Gegenwart von Zinn, Arsen und Antimon (Part 3); Erzmetall Vol. 13 (1960) no. 2, p. 53-58

[23] K.L. MEIßNER: Gleichgewichte zwischen Metallpaaren und Schwefel; V. Das System Kupfer-Zinn-Schwefel; Metall und Erz Vol. 18 (1921) no. 18, p. 466-468

[24] M.E. DRITZ et. al.: Handbook: Binary and multiple component copper systems; Moskau, Verlag Nauka, 1979 (russian)

[25] J.V. HARDING et.al.: The constitution of Tin-rich Tin-Antimony-Copper Alloys; The Journal of the Institute of Metals Vol. 75 (1948-49), Ed.: Lieut.-Colonel S.C. Guillan; London, Inst. of Met. 1949, p. 115-130

[26] Phase Diagrams for Ceramics; Ed.: M.K. Reser; 4th printing 1979, Copyright, 1964, by the American Ceramic Society

[27] W. BONSACK: Über das System Zinn-Kupfer-Antimon; Zeitschrift für Metallkunde (1927) no. 3, p. 107-110

[28] I. BARIN: Thermochemical Data of Pure Sybstances; VCH Verlag Gesellschaft, Weinheim 1989

[29] I. BARIN: Thermochemical Data of Pure Sybstances; VCH Verlag Gesellschaft, Weinheim 1993

[30] I. BARIN, O. KNACKE, O. KUBASCHEWSKI: Thermodynamic Properties of Inorganic Substances; Springer-Verlag, Berlin and New-York, NY, 1973, Supplement 1977

[31] O. KNACKE, O. KUBASCHEWSKI, K. Hesselmann: Thermodynamic Properties of Inorganic Substances; Springer-Verlag, Berlin-Heidelberg 1991

[32] I.R.S. CLARK: Mechanismus und Kinetik der Entkupferung des Bleis mit Schwefel; Erzmetall Vol. 21 (1968) no. 11, p. 497-501

[33] K.L MEIßNER: Gleichgewichte zwischen Metallpaaren und Schwefel; Das System Kupfer-Blei-Schwefel; Metall und Erz Vol. 18 (1921) no. 7, p. 146-152

[34] G.M. WILLIS, T.R.A. DAVEY: Mechanismus und Kinetik der Entkupferung des Bleis mit Schwefel; Erzmetall Vol. 22 (1969) no. 8, p. 382-383

[35] I.S.R. CLARK, L.A. BAKER, A.E. JENKINS: Decoppering of lead alloys with sulphur: I – reactions in the binary Pb+Cu System; Institution of Mining & Metallurgy, Transactions/Section C, Transactions Vol. 81 1972, Bulletin no. 784 March 1972, p. C195-C203

[36] R. KLEINERT: Über die Entkupferung von Hartblei; Metall und Erz 1945 no. 1/4, p. 18-20

[37] W. KRYSKO: Die Entkupferung des Bleies (Part 9); Erzmetall Vol. 20 (1967) no. 5, p. 214-217

[38] J. BLANDERER: Gedanken über die Theorie der Blei-Raffination; Metall 1957, no. 8, p. 662-667

[39] M.P. SMIRNOV, G.B. BELETZKIJ, G.A. BIBENINA: Examination of the macro kinetics of fine decoppering of lead; Cvetnye Metally 1970, no. 9, p. 18-20 (russian)

[40] H.A. SIMSON, F. LAWSON: Mathematical model for fine decoppering of lead; Transactions of the Institution of Mining and Metallurgy, Section C, Mineral Processing and Extractive metallurgy, Transactions Vol. 94, March 1985, p. C83-C88

[41] B.S. TERRY, C.L. HARRIS, D.G.C. ROBERTSON: Decoppering of liquid bullion by elemental sulpher additions; Part 1: sulphidation of lead by elemental sulfur; Transactions of the Institution of Mining and Metallurgy, Section C, Mineral Processing and Extractive Metallurgy, Transactions Vol. 102, January – April, 1993, p. C57 – C61; Part 2: mechanism and model for decopperize; Transactions of the Institution of Mining and Metallurgy, Section C, Mineral Processing and Extractive Metallurgy, Transactions Vol. 102, January – April, 1993, p. C63 – C69