Equilibria in Pb-As-Sb-O-melts

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1 Introduction and description of the task

The classical procedure for the separation of tin, arsenic and antimony from lead is the selective oxidation of these metals with the oxygen of air in a refining furnace. As oxidation products from this process complex lead oxides develop, that are called skimming. Up to now some questions are still unanswered: the formation of the oxides, the necessary oxygen, the influence of the interaction of the different trace elements in lead on the phase composition of the oxides as well as the maximum possible refining grade and minimal lead loss. From the view of the industry most important are: the selective separation of the trace elements at the same time the maximal enrichment of these elements in the oxidation product as well as the lowest possible oxidation of lead and a total removal of the trace elements.

There is a lot of literature about the oxidation of Pb-Sn-As-Sb-melts that are in some cases contradictory. In general it is assumed on the base of thermodynamic calculations and practical knowledge that the oxidation of Sn, As and Sb runs in this sequence because in this sequence the heat of formation of the pure oxides decreases. That the oxidation process is far more complex shows the composition of tin skimmings. Interesting are the high Sb-concentrations and the low As contents of the tin skimming that should appear according to the heat of formation of Sb_2O_3 and As_2O_3 the other way around.

A great number of investigations on the oxidation of Pb-melts with trace elements was conducted on unmoving air. These investigations show that the oxidation on unmoving air is restricted by diffusion in the oxide layer. In the industry the air is injected into the melt so that on permanently new forming surfaces the diffusion restriction is overcome. Therefore the oxidation is restricted by the through heterogeneous reactions at the phase boundary melt-bubble-surface developing solid-liquid oxide layer. The developing oxides rise to the melt surface and are oxidised further depending on the atmosphere in the furnace. But this oxidation only plays a minor part in the separation of As-, Sn- and Sb. To evaluate the As-, Sn- and Sb-separation from lead during injecting of air the developing oxide phases at the air bubble surface with the permanently changing melt composition and oxygen concentration have to be understood. An answer to this question can be the phase diagrams of lead and its trace elements with oxygen as well as the phase diagrams of the developing oxide systems that give an overview of the possible phase transitions in all possible systems lead-trace elements-oxygen.

The knowledge about possible more component compounds of the trace elements, reaction of the compounds with oxygen and the by this way developing reaction products in a lead melt is required for the estimation of the efficiency of the trace element separation as well as the type and amount of the developing oxides. Phase diagrams show these conditions in a graphical form.

2 Methodology

To clarify which reactions run in a ternary system and which final products do develop W. Guertler did propose so called "clarifying intersections" [1]. With this procedure phase diagram triangles that contain compounds are divided into sub triangles by quasi binary lines. By these means the ternary system is broken up into a series of secondary sub-systems whose components are simple compounds and show the equilibrium of the sub-system [2]. This division of ternary systems in a series of secondary sub-systems is called triangulation.

The division of a ternary system with for example two binary compounds M_1 and M_2 in a binary system is trivial (Figure 1), whereby the ternary system A-B-C is divided by quasi binary cuts C-M_1 and C-M_2 in three secondary sub-systems A-M_1-C, M_1-C-M_2 and M_2-B-C.

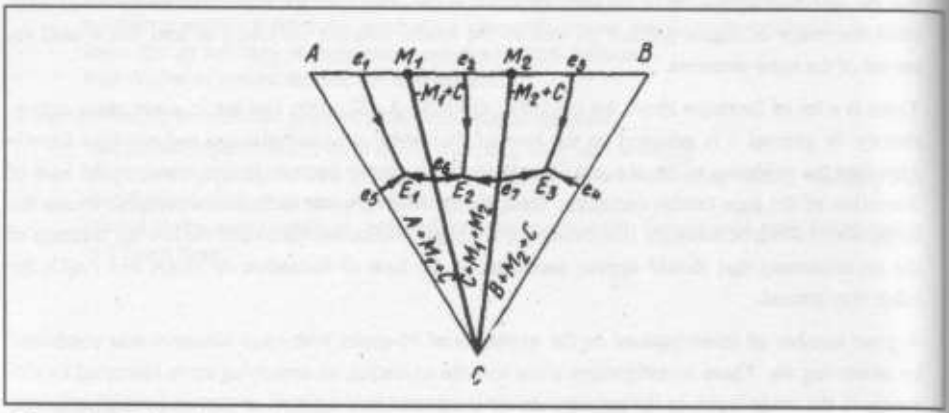

Figure 1: Triangulation of a ternary system with two congruent melting binary compounds M_1 and M_2 in the system A-B

More complex is the case when in two binary boundary systems and in the ternary system binary compounds do form.Here two possibilities of triangulation can be performed (Figure 2 and Figure 3). The quasi binary cut M_2-B (Figure 2) or the quasi binary cut M_1-C (Figure 3). With both variants the cut M_1-M_2 is quasi-binary.

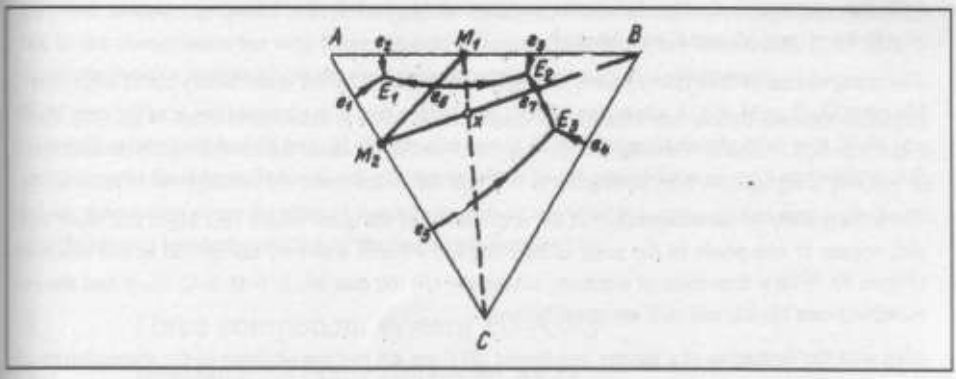

Figure 2: Triangulation of a ternary system with two congruent melting binary compounds M_1 and M_2 in the boundary systems A-C and A-B (first variant)

In case of the quasi binary cuts M_2-B and M_1-M_2 (first variant) the system A-B-C is divided into three sub-systems: A-M_1-M_2, M_1-M_2-B and M_2-B-C. Are the cuts M_1-M_2 and M_1-C quasi-binary (second variant) the primary system is divided into the following sub-systems: A-M_1-M_2, M_1-M_2-C and M_1-B-C.

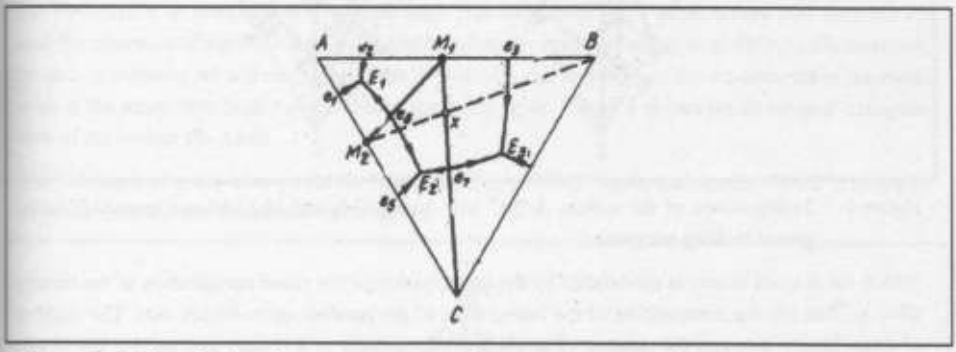

Figure 3: Triangulation of a ternary system with two congruent melting binary compounds M_1 and M_2 in the Boundary systems A-C and A-B (second variant)

An investigation of the first variant shows that the compound M_1 can not be in equilibrium with the component C but the compound M_2 is in equilibrium with the component B. With the second variant the compound M_1 is in equilibrium with the component C but the compound M_2 can not be in equilibrium with the component B. In case the cut M_2-B is quasi binary (Figure 2), no reaction will occur during the melting of compound M_2 with the component B. But during melting of the compound M_1 with the component C a reaction M_1+C=M_2+B will run and M_2 and B will develop. In case the cut M_1-C is quasi binary (Figure 3), no reaction will occur during melting of compound M_1

with the component C, but during the melting of M_2 and B the following reaction will run: $M_2+B=M_1+C$ and M_1 and C will develop.

The triangulation of the system A-B-C can only be conducted by the quasi binary cut of both possible cuts (M_2-B or M_1-C). A admission of both cuts means that at the intersection x of the cuts M_2-B and M_1-C four solid phases (components B, C and compounds M_1 and M_2) of the ternary alloy with the composition x are in equilibrium, based on the phase rule this is not allowed at all temperatures.

The ternary alloy of the composition at the intersection of the quasi binary cuts M_2-B and M_1-C can also appear in one phase in the solid in case the alloy forms a ternary compound at this position (Figure 4). With a formation of a ternary compound (S) the cuts M_1-S, S-B, S-C, M_2-S and the intersecting cuts M_1-M_2 and A-S are quasi-binary.

Also with the formation of a ternary compound (S) there are two possibilities of the triangulation of the ternary system A-B-C: by the quasi binary cuts M_1-S, S-B, S-C, M_2-S and M_1-M_2 (Figure 4/1) or by the quasi binary cuts M_1-S, S-B, S-C, M_2-S and A-S (Figure 4/2)

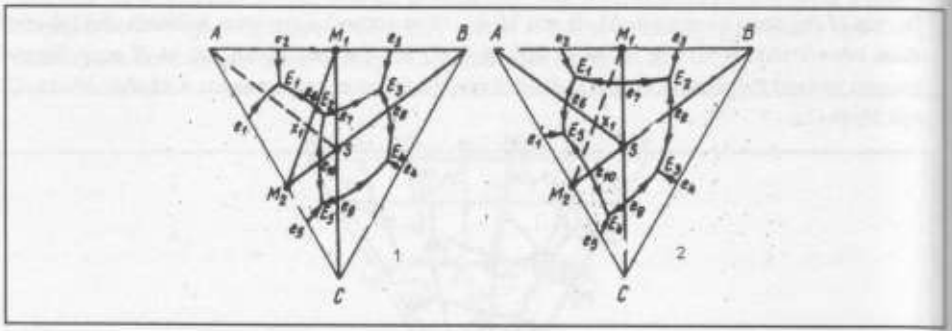

Figure 4: Triangulation of the system A-B-C with binary (M_1 and M_2) and one ternary (S) congruent melting compound.

Which cut is quasi binary is established by the investigation of the phase composition of the ternary alloy x_1, that has the composition of the intersection of the possible quasi-binary cuts. The number of quasi binary cuts and the number of secondary sub-systems in a ternary system that are developed by triangulation is equal [6]:

$$R=N_b+3N_t \quad \text{(Eq. 1)}$$

$$T=1+N_b+2N_t \quad \text{(Eq. 2)}$$

With: R-Number of developed quasi binary cuts; N_b- Number of binary compounds in the ternary system; N_t- Number of ternary compounds in the ternary system; T- Number of developed ternary sub-systems

The development of these "clarifying intersections" for multi component systems were conducted by [3]-[6], where first a triangulation of the ternary systems was performed. The tetrahedron space

of a four component system is divided by quasi binary planes in secondary tetrahedrons (comparable to the triangulation but with planes instead of lines). Each secondary tetrahedron is for equilibrium conditions a system where the components are simple materials (compounds).

This division of multi component systems in secondary sub-systems can lead to answers about possible reactions, concentration areas in which reactions run and possible products that develop in multi component systems by these reactions. For the investigation of a metallurgical process for which the precise phase diagram of the components is not valid it is advisable to start with the triangulation and tetrahedronisation of the respective systems [6].

3 Three component system Pb-As-O

3.1 Triangulation of the system Pb-As-O

The triangulation of the system Pb-As-O (Figure 5) can be conducted with the help of the boundary systems of the system Pb-As-O [7];[8], the publicised cuts $PbO\text{-}As_2O_5$- and $PbO\text{-}As_2O_3$- [9] as well as the indication of a lead precipitation from $PbO\text{-}As_2O_3$-and the As-distribution between metal and slag [9];[10].

Because from $PbO\text{-}As_2O_3$-mixtures products of the $PbO\text{-}As_2O_5$-cut form [9], the $PbO\text{-}As_2O_3$ is not, the $PbO\text{-}As_2O_5$ in comparison is quasi binary. But there have to be quasi binary cuts between Pb and the arsenates of the $PbO\text{-}As_2O_5$ cut, that confirm the lead precipitation of $PbO\text{-}As_2O_3$-mixtures, as well as between As and arsenates of the $PbO\text{-}As_2O_5$ cut, that explain the As-contents in the metal with at the same time high As-contents in the oxide layer. Figure 6 shows the developed triangulation of the system Pb-As-O.

The existence of quasi-binary cuts $Pb\text{-}3PbO{*}As_2O_5$, $As\text{-}3PbO{*}As_2O_5$ and $As_2O_3\text{-}3PbO{*}As_2O_5$ was confirmed by thermo dynamical calculations.

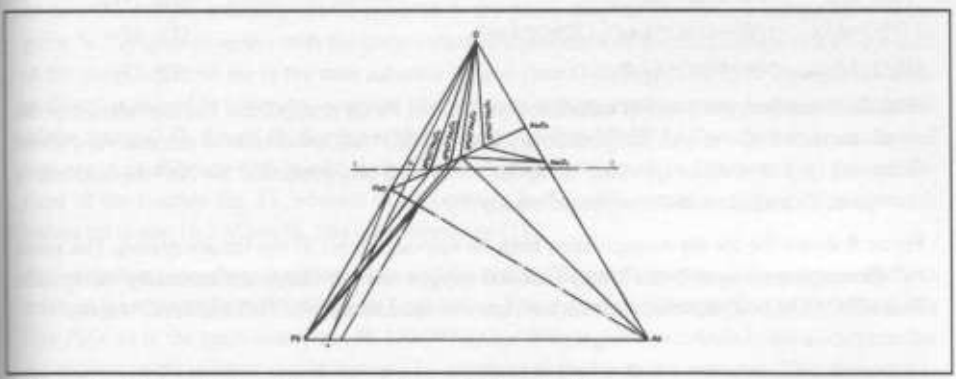

Figure 5: Triangulation of the systems Pb-As-O (Atomic.-%)

From the triangulation of the system Pb-As-O follows, that lead precipitations from the PbO-As_2O_3-mixtures can be described by the following reactions:

$10<PbO> + <As_2O_3> = 2(Pb) + <8PbO*As_2O_5>$ (Eq. 3)

$16<PbO> + 2<As_2O_3> = 4(Pb) + <8PbO*As_2O_5> + <4PbO*As_2O_5>$ (Eq. 4)

$6<PbO> + <As_2O_3> = 2(Pb) + <4PbO*As_2O_5>$ (Eq. 5)

$11<PbO> + 2<As_2O_3> = 4(Pb) + <4\ PbO*As_2O_5> + <3PbO*As_2O_5>$ (Eq. 6)

$5<PbO> + <As_2O_3> = 2(Pb) + <3PbO*As_2O_5>$ (Eq. 7)

$7<PbO> + 3<As_2O_3> = (Pb) + 2\underline{As}_{Pb} + 2*<3PbO*As_2O_5>$ (Eq. 8)

According to these reaction equations (Eq. 3 - Eq. 8) no pure As_2O_5 is formed but mixed oxides do develop. The per mol As_2O_3 conducted metal precipitation increases according to the equations (Eq. 3 - Eq. 5) from 20 % up to app. 32,5 %. Above that amount they sink again according to (Eq. 6) to app. 9 % increase again according to reaction Eq. 7 to 20 % and finally sink again according to (Eq. 8). Because the formed oxide phases and their mixtures have very different melting temperatures the conduct of the reaction can be handicapped by this reasons as well. The intersection of the connection line PbO-As_2O_3 with the quasi binary cut Pb-$3PbO*As_2O_5$ in Figure 5 shows the minimal value of the metal precipitation. It shows a As_2O_3-content in the mixture of app. 15-16 % (As-content app. 12 %), that complies good qualitatively und quantitatively with experimental results [10].

The arsenic distribution between metal and slag can be described by the following reaction equations (As-separation from Pb-melts). (Intersections of the tie-line PbO-As with the cuts of the secondary sub-system Figure 5):

$13PbO + 2As = 5Pb + 8PbO*As_2O_5$ (Eq. 9)

$22PbO + 4As = 10Pb + 8PbO*As_2O_5 + 4PbO*As_2O_5$ (Eq. 10)

$9PbO + 2As = 5Pb + 4PbO*As_2O_5$ (Eq. 11)

$17PbO + 4As = 10Pb + 4PbO*As_2O_5 + 3PbO*As_2O_5$ (Eq. 12)

$8PbO + 2As = 5Pb + 3PbO*As_2O_5$ (Eq. 13)

With these reactions per 1 mol of transferred As, 2,5 mol Pb are precipitated. The intersection of the connection line PbO-As with the quasi binary cut Pb-$3PbO*As_2O_5$ delivers the minimal As-content in the slag (app. 8 % As or app. 10,5 % As_2O_3) where a As-precipitation of the PbO-As-mixtures is conducted. This agrees with experimental results [9].

Figure 6 shows the for the As-separation from Pb relevant corner of the ternary system. The point "x" (heterogeneous equilibrium ("x_1")-melt and oxygen line I-I) lies in the secondary sub-system PbO-$8PbO*As_2O_5$-O, therefore the melt oxidises with the formation of PbO and $8PbO*As_2O_5$.

The As-content in the oxide layer should not be lower than 5 Mass.% at the direct oxidation of As by oxygen (Intersection of the line of the oxygen concentration and the quasi binary cut $8PbO*As_2O_5$-O), that does not lie in good relation to results from laboratories and the industry (app. 16 Mass.%) [11].

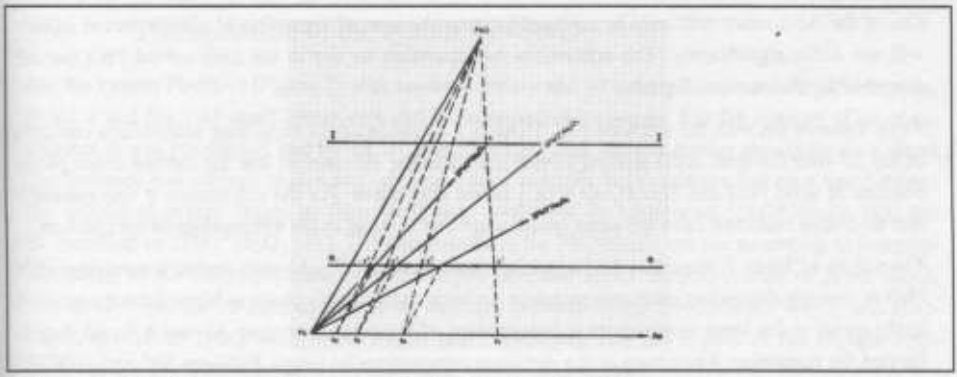

Figure 6: The Pb-corner of the system Pb-As-O (schematically)

Because as mentioned above the activity of lead is 1 and the activity of arsenic is below 0,01 [12];[13], during the injection of air in a Pb-As-melt at first a Pb oxidation is conducted. The formed PbO is solved in the melt (solvability of PbO at 800°C is app. 0,45 Mass.-% [14] and oxidises the As according to the reaction (Eq. 9 - Eq. 13). The by the reactions (Eq. 9 - Eq. 13) formed mixed oxides can contribute to the As-separation as well:

$$8As+9*(8PbO*As_2O_5)=20Pb+13*(4PbO*As_2O_5) \quad \text{(Eq. 14)}$$

$$2As+8*(4PbO*As_2O_5)=5Pb+9*(3PbO*As_2O_5) \quad \text{(Eq. 15)}$$

In case the oxygen solubility (PbO) is added in the phase diagram Pb-As-O, a composition at the point "x^1" (Figure 6) agrees with the composition in equilibrium of the composition of a Pb-As-melt at the point "x^1" with the in the melt solvable oxygen (line O-O, Figure 6). This "equilibrium composition" is moved to lower As –contents with constant oxygen concentrations in the melt (direction of the arrow O-O, Figure 6). By the oxidation of As at first $3PbO*As_2O_5$-compounds are formed that are in equilibrium with the Pb-melt. The As-content in the melt is determined by the equilibrium of the reaction Eq. 13, whereas the As-content in the oxide layer can at the beginning reach values up to app.16,7 Mass.-%, this is confirmed by [11].

As is possible to see from the triangulation of the system (Figure 5) an As-oxidation from a PbO-As mixture is only conducted in the oxide layer above 8 % As content (Intersection of the connection line PbO-As in the quasi-binary cut Pb-$3PbO*As_2O_5$). With higher As-content in the oxide layer the As-content in the mixture should increase by reactions of lead with the arsenates. This discovery is in accordance to qualitative and quantitative results [9];[15];[16].

3.2 Thermodynamic boundaries of the As-separation by oxidation of Pb-As-melts

Because of thermo dynamical data of compounds of the cut $PbO-As_2O_5$ only data for the compound $3PbO*As_2O_5$ is available only this data was used for the calculations. The deviation for the calculation of the As-content will only be minimal because the heat of formation of similar mixed oxides will not differ significantly. The achievable As-separation by the in the melt solved PbO can be described by the reaction Eq. 13.

Table 1 shows the with the software FACTSAGE 5.1 calculated As remaining equilibrium contents of Eq. 13 with different As/O starting conditions under the assumption that the formed oxide phase consists of solid PbO and $3PbO*As_2O_5$ or a liquid slag phase. For the calculation it was assumed that all charge materials have the same temperature that is equal to the temperature of the reaction.

The values of Table 1 show that the remaining As-content in a Pb-As-melt during a oxidation with PbO is strongly dependent on the temperature. In case a solid oxide phase is formed the As-content in the metal at the same temperature is independent of the surplus oxygen. In case a liquid slag is formed the remaining As-content in the metals is substantionally lower. Between 800 and 1000 °C the As-content has therefore a minimum when a oxygen surplus O/As > 4/1 is present. The remaining As content is then substantionally lower because of the formation of liquid oxide phases in comparison to the formation of solid oxides (4-19 ppm in comparison to 255 ppm,

Table 1). For a comparison equilibrium calculations were conducted for the application of gaseous oxygen for the separation of As from lead melts. According to these calculations during the oxidation of Pb-As-melts by oxygen simultaneously PbO and PbO und As_2O_3 can develop.

Table 1: Selected calculations for the equilibrium of the reaction
$8\langle PbO\rangle + 2\underline{As}_{Pb} = 5(Pb) + \langle 3PbO*As_2O_5\rangle$

Charge mixture [Mol]			Temperature	Calculated As-contents [ppm] under consideration of the formation of:	
Pb	As	PbO	in [°C]	$PbO_{(s)}$; $As_2O_8Pb_{3(s)}$	$PbO_{(l)}$; $As_2O_{3(l)}$
100	1	4	350	255	-
			500	907	388
			800	3602	584
		20	350	255	-
			500	907	19
			800	3602	4
100	2	8	350	255	-
			500	910	720
			800	4687	978
		20	350	255	-
			500	907	19
			800	4687	4

The in the Pb-As-melt injected oxygen oxidises at first Pb to PbO that in a subsequent step reacts with As.

4 Three component system Pb-Sb-O

4.1 Triangulation of the system Pb-Sb-O

For the system Pb-Sb-O (Figure 7) with known 4 binary and 10 ternary compounds result according to Eq. 1 and Eq. 2 34 quasi binary cuts and 25 secondary sub systems. For the conduct of the triangulation it was considered that by the oxidation formed high valence oxides should lie on a direct line between low valence oxides and oxygen. Also a complex oxide mixture lies on a line between the individual oxides. Based on these geometric conditions the compound $5PbO*2Sb_2O_3$ [19] can be modified as $3PbO*Sb_2O_3$ [21]. The compounds of the PbO-Sb_2O_4 cut are according to these observations $8PbO*2Sb_2O_4$ instead of $8PbO*Sb_2O_4$ [19] and $4PbO*2Sb_2O_4$ instead of $2PbO*Sb_2O_x$ $3<x<5$ [19] and lie on an intersection of the lines between $5PbO*Sb_2O_3$-$3PbO*Sb_2O_5$ and PbO-Sb_2O_4 as well as $3PbO*Sb_2O_3$-$PbO*Sb_2O_5$ and PbO-Sb_2O_4. The sub system of the triangle PbO-Sb_2O_3-O describes the oxidation of PbO-Sb_nO_m-mixtures as follows:

During oxidation $5PbO*Sb_2O_3$ reacts step wise to higher valence oxides under the formation of PbO, following the reactions:

$$2*(5PbO*Sb_2O_3)+O_2 = 2PbO+8PbO*2Sb_2O_4 \quad \text{(Eq. 16)}$$

$$8PbO*2Sb_2O_4+O_2 = 2PbO+2*(3PbO*Sb_2O_5) \quad \text{(Eq. 17)}$$

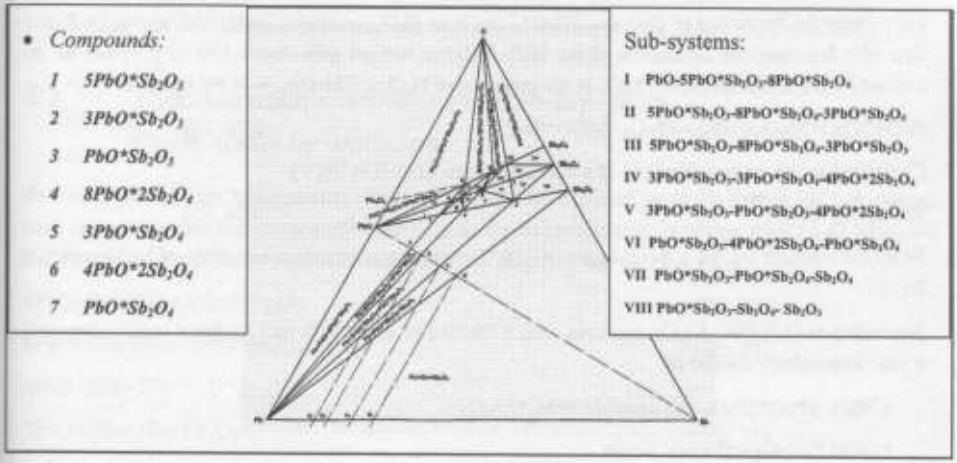

Figure 7: Triangulation of the system Pb-Sb-O (Atomic %)

In dependence of the oxygen supply in a $5PbO*Sb_2O_3$-$3PbO*Sb_2O_3$ mixture the phases are oxidised as follows:

$3PbO*Sb_2O_3+1/2O_2 = 3PbO*Sb_2O_4$ (Eq. 18)

$3PbO*Sb_2O_3+O_2 = 3PbO*Sb_2O_5$ (Eq. 19)

During the oxidation of $3PbO*Sb_2O_3$-$PbO*Sb_2O_3$ mixtures can additional to the oxides of Eq. 18 and Eq. 19 form the following oxide phases in dependence of the mixtures composition and the oxygen supply:

$PbO*Sb_2O_3+1/2O_2 = PbO*Sb_2O_4$ (Eq. 20)

$3PbO*Sb_2O_3+ PbO*Sb_2O_3+O_2 = 4PbO*2Sb_2O_4$ (Eq. 21)

$PbO*Sb_2O_3+O_2 = PbO*Sb_2O_5$ (Eq. 22)

$3PbO*Sb_2O_3+3(PbO*Sb_2O_3)+4O_2=2(3PbO*2Sb_2O_5)$ (Eq. 23)

The accuracy of the triangulation of the system Pb-Sb-O can be validated by the comparison with publicised experimental results of different mixtures.

In [17] the oxidation of two mixtures with the molar composition $3PbO/2Sb_2O_3$ and $PbO/3\ Sb_2O_3$ were investigated. Based on the experimental results it was concluded that during oxidation of PbO-Sb_2O_3-mixtures Sb_2O_5 in the form of antimonates develop. Into consideration can be taken pyroantimonate ($2PbO*Sb_2O_5$) and metaantimonate ($PbO*Sb_2O_5$). Whereas in mixtures with a PbO-content lower than 50 Mol-% also the formation of free Sb_2O_4 is possible.

The oxidation of mixtures with a concentration relation up to $PbO/Sb_2O_3=5$ is conducted theoretically under the formation of PbO and $8PbO*2Sb_2O_4$ or PbO and $3PbO*Sb_2O_5$ and not with a formation of a homogenous antimonite phase [19]. Relative weight gain above 130 % [19] can be described by the stabilisation of Pb_3O_4 at the presence of H_2O or OH-groups in the mixture:

$PbO+5PbO*Sb_2O_3+3/2O_2=Pb_3O_4+3PbO*Sb_2O_5$ (Eq. 24)

Compared to the assumption [19] of a oxidation from Sb(III) to Sb(V)

$Sb_2O_3+O_2=Sb_2O_5$ (Eq. 25)

From the reaction Eq. 24 a weight gain of 150 % results in comparison to 100 % of by the reaction Eq. 25.

According to [19] PbO-Sb_2O_4-mixtures with a fraction of up to 70% Sb_2O_4 after a heat treatment in a inert atmosphere consist of:

- PbO, $3PbO*Sb_2O_4$ and possible $8PbO*Sb_2O_4$
- $3PbO*Sb_2O_4$ and $PbO*Sb_2O_4$

After [17] Sb_2O_4 is broken up at the presence of PbO under the formation of $PbO*Sb_2O_3$, $2PbO*Sb_2O_5$ and $PbO*Sb_2O_5$.

The triangulation leads to the assumption that in an inert atmosphere only the compounds of the $PbO\text{-}Sb_2O_4$-cut are broken up and the following phases appear:

$<8PbO*2Sb_2O_4> = <5PbO*Sb_2O_3> + <3PbO*Sb_2O_5>$ (Eq. 26)

$2*<3PbO*Sb_2O_4> = <3PbO*Sb_2O_3> + <3PbO*Sb_2O_5>$ (Eq. 27)

$<4PbO*2Sb_2O_4> = <3PbO*Sb_2O_3> + <PbO*Sb_2O_5>$ (Eq. 28)

$2*<PbO*Sb_2O_4> = <PbO*Sb_2O_3> + <PbO*Sb_2O_5>$ (Eq. 29)

During the oxidation of $PbO\text{-}Sb_2O_4$-mixtures compounds of the $PbO\text{-}Sb_2O_5$-cut are formed.

The triangulation of the system Pb-Sb-O predicts that the following phases can appear in a $PbO\text{-}Sb_2O_5$-mixture at the same time:

- PbO and $3PbO*Sb_2O_5$
- $3PbO*Sb_2O_5$ and $3PbO*2Sb_2O_5$
- $3PbO*2Sb_2O_5$ and $PbO*Sb_2O_5$
- $PbO*Sb_2O_5$ and Sb_2O_5

This is in accordance with experimental results in [19]. In an inert atmosphere the compounds $3PbO*Sb_2O_5$ and $PbO*Sb_2O_5$ can form compounds of the $PbO\text{-}Sb_2O_4$-cut under the formation of oxygen after the following reactions:

$3PbO*Sb_2O_5 = 3PbO*Sb_2O_4 + 1/2O_2$ (Eq. 30)

$PbO*Sb_2O_5 = PbO*Sb_2O_4 + 1/2O_2$ (Eq. 31)

A according gas development in connection with characteristic boiling noises were noticed by [17].

4.2. Thermodynamic boundaries of Sb-sep. from Pb-Sb-melts by oxidation

As can be seen in the triangulation (Figure 7) Sb can be oxidised by in Pb solved PbO as well as with oxygen in case the oxygen concentration in the oxygen carrier is higher than 16,47 Mass.-% O_2. The oxidation of Sb by PbO is described by the reactions Eq. 32 - Eq. 35:

$8PbO + 2Sb = 3Pb + 5PbO*Sb_2O_3$ (Eq. 32)

$6PbO + 2Sb = 3Pb + 3PbO*Sb_2O_3$ (Eq. 33)

$4PbO + 2Sb = 3Pb + PbO*Sb_2O_3$ (Eq. 34)

$3PbO + 2Sb = 3Pb + Sb_2O_3$ (Eq. 35)

In case the oxygen concentration is above app. 16,5 Mass.-% O_2 (the oxygen concentration of Sb_2O_3 is 16,47 Mass.-% O_2) in the oxygen carrier a simultaneous oxidation of Pb and Sb is conducted:

$5(Pb)+2\underline{Sb_{Pb}}+5\{O_2\}=2<PbO>+<3PbO*Sb_2O_5>$ (Eq. 36)

Because thermo dynamical data for the compounds of the system Pb-Sb-O are not available except for Sb_2O_3, Sb_2O_4 and Sb_2O_5, for the calculations only the available data was used. This can lead to a too high equilibrium concentration of Sb in Pb melts in comparison to the true values that adjust during the formation of Pb-Sb mixed oxides. Table 2 shows some by the software FACTSAGE 5.1 calculated values of Sb-equilibrium concentrations in Pb-melts at 500 to 800 °C.

Based on this values it can be assumed that a temperature increase of 500 to 800 °C increases also the Sb-content in the melt substantionally. The required oxygen supply for the Sb-oxidation is O/Sb=3/2 (Mol) according to the compound Sb_2O_3.

Table 2: Selected calculations of the equilibrium of the reaction $3<PbO>+2\underline{Sb_{Pb}}=3(Pb)+Sb_2O_3$ (*-liquid; **-solid)

Educts [Mol]			Tem-perature	Products [Mol]				$\underline{Sb_{Pb}}$-content
				Metal phase		Slag phase		
Pb	Sb	<PbO>	[°C]	Pb*	Sb*	PbO	Sb_2O_3	[ppm]
100	1	1	500	101,00	0,33451	-	0,33274*	1950
		2	500	101,41	0,05948	0,5892**	0,47026**	345
		3	500	101,41	0,05948	1,5892**	0,47026**	345
		2	800	102,52	0,3501	-	0,32495*	2017
		3	800	102,45	0,24430	0,5498**	0,37785*	1400
		5	800	101,48	0,27544	3,5164**	0,36228*	1595
100	2	2	500	102,00	0,66746	-	0,66627**	3845
		3	500	102,91	0,06036	0,0906**	0,96982**	345
		6	500	102,91	0,06036	3,0905**	0,96982**	345
		10	500	102,91	0,06036	7,0905**	0,96982**	345
		2	800	102,00	1,00490	-	0,49756*	5790
		3	800	103,00	0,52759	-	0,73621*	3000
		6	800	103,96	0,24791	2,0357**	0,87604*	1400

A further increase of oxygen supply leads to a formation of PbO. After [17];[19] the melting temperature of a $PbO-Sb_2O_3$-mixture decreases to app. 550°C by the addition of app. 40 Mol % Sb_2O_3. Based on this fact the slag phase should be liquid at 800°C. In contradiction the calculation program shows at 800°C solid PbO and liquid Sb_2O_3. Because the literature about the melting temperature of $PbO-Sb_2O_3$-mixtures can be viewed as significantly representative the conclusion has to be drawn that the database of Fact Sage 5.1 is not complete in this area. The question how this impacts on the calculated Sb-contents is open. The calculated Sb-equilibrium content in Pb-melts after the Sb-oxidation by PbO at 500°C is about 345 ppm independent on the starting concentration of the Pb-melt. The Pb-content in the metal phase increases with the turnover of Sb to Sb_2O_3 by PbO. A surplus oxygen supply compared to the stoichometrical necessary amount for the oxidation leads to an increased Pb oxidation and a decreased Sb content in the slag phase. The relation of Sb/O of the

quasi binary cut Pb-Sb_2O_3 with given Sb-content provides the maximal oxygen concentration in the Pb-melt at which a "pure" Sb-oxidation is conducted.

5 Three component system As-Sb-O

5.1 Triangulation of the system As-Sb-O

The triangulation of the system As-Sb-O shows Figure 8.

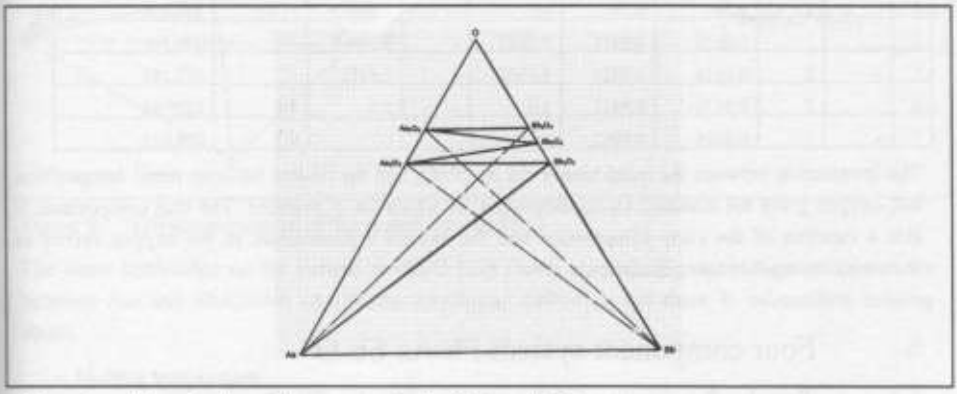

Figure 8: Triangulation of the system As-Sb-O (Atomic %)

With the help of FACTSAGE the equilibrium fractions of the phases with the reaction between Sb and As_2O_5, Sb and As_2O_3, As and Sb_2O_5 as well as As and Sb_2O_4 were calculated (Table 3).

The calculations show that Sb is oxidised at 500°C by As_2O_3 and As_2O_5. In return As is oxidised by Sb_2O_5 and Sb_2O_4, depending on the concentration conditions. This result complicates a direct answer about the possible quasi binary cut in the system As-Sb-O.

The sequence of the formed oxide phases by the application of different oxygen carriers with an increasing oxygen content remains undisturbed:

$Sb_2O_3 \rightarrow Sb_2O_3+As_2O_3 \rightarrow Sb_2O_3+As_2O_3+Sb_2O_4 \rightarrow As_2O_3+Sb_2O_4 \rightarrow As_2O_3+As_2O_5+Sb_2O_4$

The triangulation of the system As-Sb-O (Figure 8) confirms that by the oxidation of an As-Sb-melt different oxide types depending on the oxygen concentration and the melt composition are formed. Sb can be oxidised selectively by As_2O_3 and As_2O_5 in a As-Sb-melt to Sb_2O_3 (Sub-system As-Sb_2O_3-Sb), As in comparison can only be oxidised together with Sb

Table 3: Selected calculation for the equilibrium of the reaction between Sb and As_2O_3 resp. As_2O_5 at 500 °C

Educts [Mol]			Products [Moll in						-ΔG [kJ/turnover]
			Metal phase		Slag phase				
Sb	As_2O_3	As_2O_5	Sb	As	As_2O_3	As_2O_5	Sb_2O_3	Sb_2O_4	
5	1	-	0.6	0.4	-	-	1.0	-	95.016
2	1	-	0.0175	0.9825	0.0175	-	0.9825	-	65.014
1	1	-	0.0175	0.9825	0.50875	-	0.49125	-	36.140
1	2	-	0.0175	0.9825	1.5087	-	0.49125	-	43.407
4	-	1	0.25	0.75	-	-	1.6667	-	320.676
2	-	1	0.0175	0.9825	0.6725	-	0.99417	-	276.585
3	-	2	0.0175	0.9825	1.8362	-	1.4971	-	527.162
6	-	5	0.0175	0.9825	5.0	-	2.0	1.0	1229.86
1	-	1	0.0038	0.9962	1	-	-	0.5	226.059

The intersection between the quasi binary cut As-Sb_2O_3 and the tie-line between metal composition and oxygen gives the maximal O_2-concentration, at which Sb is oxidised. The slag composition is also a function of the alloy composition and the oxygen concentration in the oxygen carrier as shown by the equilibrium calculations.

6 Four component system Pb-As-Sb-O

6.1 Tetrahedronisation of the system Pb-As-Sb-O

The tetrahedronisation of the system Pb-As-Sb-O was conducted on the basis of the triangulisation of the ternary boundary systems and the topology rule of multi component systems (Figure 9).

The thermodynamic existence of some quasi binary planes was confirmed by in-house calculations.

According to Eq. 2 the system Pb-As-Sb-O consist of 27 quaternary sub-systems, when only 6 binary and 14 ternary compounds are considered (4 in the system Pb-As-O and 10 in the system Pb-Sb-O).

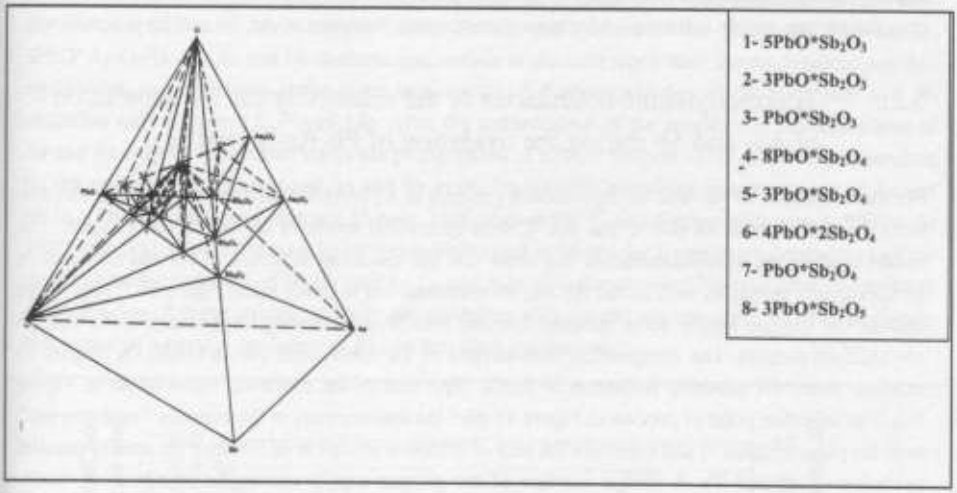

Figure 9: Tetrahedronisation of the system Pb-As-Sb-O

The latest knowledge on the system As-Sb-O [22] shows a series of gaseous ternary compounds between As- and Sb-Oxides ($As_3Sb_2O_6$, $As_2Sb_2O_6$, $AsSb_3O_6$), but there is information missing about:

- Melting temperature
- Type of melting (congruent, not congruent)
- Temperature range of existence
- Existence of this compound only in the gaseous phase,

By which the consideration of these compounds is not possible for a tetrahedronisation. The limitation for the tetrahedronisation of the system Pb-As-Sb-O does not pose any significant disadvantages for the interpretation of the oxidation of Pb-As-Sb-melts, because the oxygen concentration for an oxidation on air is already between the oxygen content of Sb_2O_4 (20,8 Mass.-%) and Sb_2O_5 (24,73 Mass.-%) in the system Sb-O, between As- and As_2O_3 (24,26 Mass.-%) in the system As-O, PbO (7,17 Mass.-%) and oxygen in the system Pb-O. Therefore the oxidation products in the subsystem of the oxygen corner at the side of Pb-O and As-Sb-mixed oxides do not have any influence. The „oxidation equilibrium products" during the oxidation on air are in the sub-systems PbO-$3PbO*Sb_2O_5$-$8PbO*As_2O_5$ and $3PbO*Sb_2O_5$-$8PbO*As_2O_5$-$4PbO*As_2O_5$. The formed oxides are oxidised further because additional oxygen is added to the melt at all times. Therefore skimming can contain all oxides, that form in the system PbO-Sb_2O_4-$3PbO*As_2O_5$.

As can be derived from the tetrahedronsation, the system is characterised by the quasi binary plane Pb-As-Sb_2O_3. At low oxygen concentrations a Sb-oxidation is favoured and at first with increasing

oxygen concentrations and decreasing Sb-concentration a parallel oxidation of As and Sb runs. In case the oxygen supply is increased further a simultaneous oxidation of As, Sb and Pb is conducted.

6.2. Thermodynamic boundaries of the selectivity for the separation of As- and Sb during the oxidation of Pb-As-Sb-melts

For the evaluation of As- and Sb Equilibrium contents in a Pb-As-Sb-melt thermodynamic calculations were conducted for 600°C and 800°C with theoretical mixtures of As, Sb and oxygen. The results confirm the tetrahedronisation and show that the oxidation sequence of As and Sb depends on the oxygen supply as well on the As and Sb concentration in crude lead (Figure 10, Table 4). In case of low oxygen supply Sb is oxidised first and then with increasing oxygen supply As and Sb are oxidised parallel. The composition melt-oxygen of the sub-system Pb-As-Sb-Sb_2O_3 (Figure 9) oxidises under the selective formation of Sb_2O_3 (first arm of the oxidation curve of Sb in Figure 10). The inflexion point of the line in Figure 10 give the intersections of the conodes "melt-oxygen" with the plane (Figure 9) and separates the area of selective oxidation of Sb from the area of parallel oxidation of As and Sb. A further increase of the oxygen supply moves the composition "melt-oxygen" in the sub-system of the quadrangle Pb-PbO-Sb_2O_3-3PbO*As_2O_5 (Figure 9) where Pb, As and Sb are oxidised parallel (Figure 11- Mol=6400 ppm) at 600 and 800 °C (Figure 11–Figure 12, Table 4).

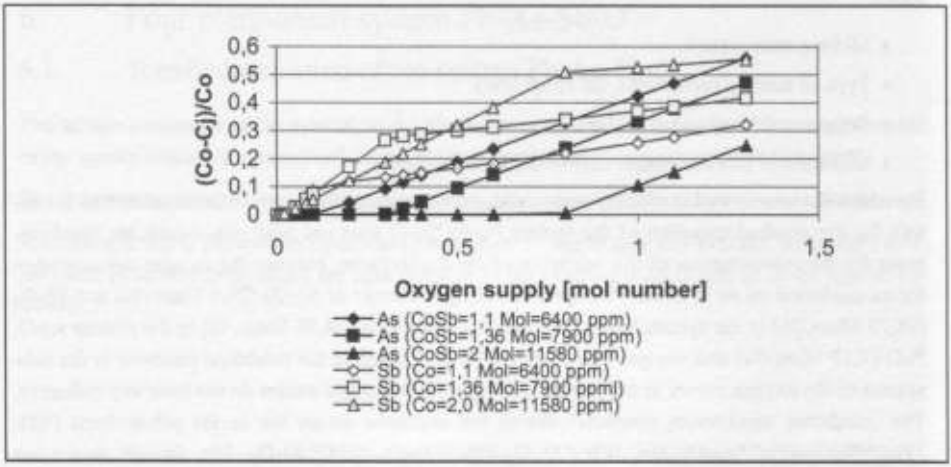

Figure 10: As and Sb-separation by oxidation of a Pb-melt (Pb 100 Mol; As 0,8 Mol=2850 ppm; Sb 1,1-2,0 Mol) at 600 °C

For the control of the oxygen supply (low oxygen concentration) up to 50 % of the Sb-content of the melt can be removed selectively (Sb_2O_3) without an oxidation of As at the same time (Sub-system Pb-As-Sb-Sb_2O_3 in Figure 9). Because of the shift of the composition "melt-oxygen" in the

sub-system Pb-As-As_2O_3-Sb_2O_3, As and Sb are oxidised parallel later. With increased oxygen supply the composition of "melt-oxygen" shifts into the sub-systems of the quadrangle PbO-Sb_2O_3-3PbO*As_2O_3-O, the As and Sb-contents that remain in the melt reach their thermodynamic possible equilibrium concentrations at the given temperature. A further oxidation of the melt leads to a Pb oxidation only (Figure 11; Figure 12). After the achievement of the equilibrium concentrations of As and Sb only Pb is oxidised under the precipitation of <PbO> (Figure 11; Figure 12). Independent on the starting concentrations of As and Sb in the Pb-melt the remaining concentrations of As and Sb in a Pb-melt after oxidation are 15 resp. 1100 ppm at 600°C and 5 resp. 1400 ppm at 800°C. At 500°C the Sb-contents decrease to 345 ppm. This result confirms the temperature dependency of the thermodynamic potential of Sb_2O_3 und As_2O_3 and is in accordance to in [23] calculated temperature dependencies of these oxides. In technical oxidation with air the oxygen concentration is already that high that a parallel oxidation of Pb, As and Sb is conducted.

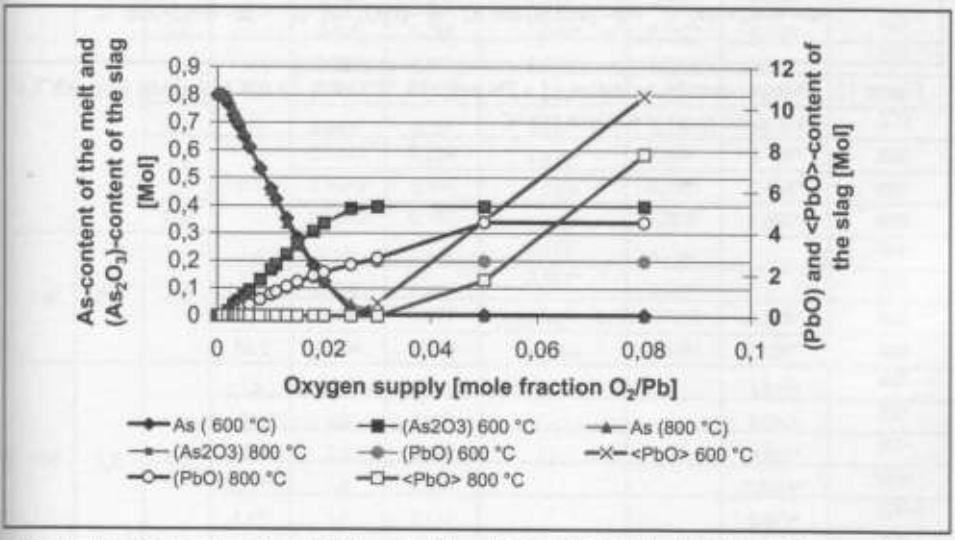

Figure 11: As-separation by oxidation of a Pb-melt (Pb 100 Mol; As 0,8 Mol=2850 ppm; Sb 1,1 Mol=6400 ppm) at 600 and 800 °C

The Sb-oxides of the Sb oxidation can be in gaseous, liquid or solid form. The As-oxidation is always combined with a Pb-oxidation, the developing slag is liquid (Table 4).

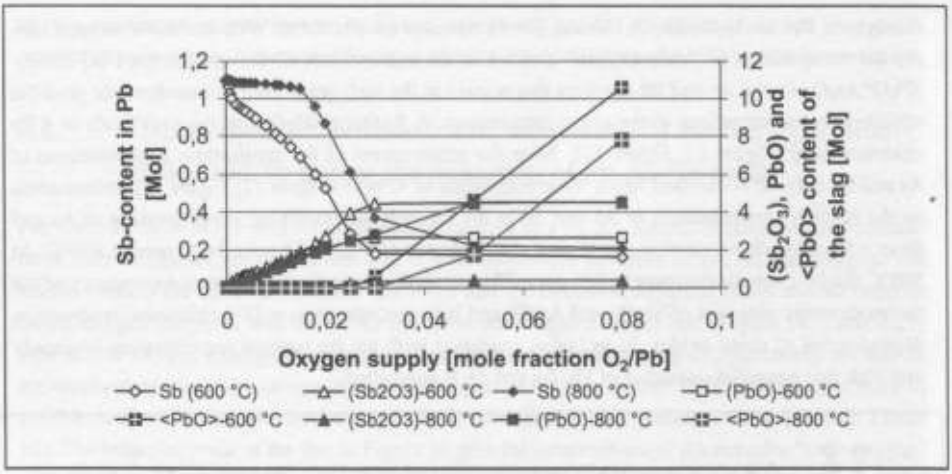

Figure 12: Sb-separation by oxidation of a Pb-melt (Pb 100 Mol; As 0,8 Mol=2850 ppm; Sb 1,1 Mol=6400 ppm) at 600 and 800 °C

Table 4: Selected calculations for the equilibrium of the As and Sb-separation by oxidation 600 and 800 °C (*-liquid; **-solid);***-3 bar; *'-10 bar

Educts [Mol]				Products [Mol]					Temperature [°C]
Pb	As	Sb	O_2	As	Sb	PbO	As_2O_3	Sb_2O_3	
100	0,8	1,1	0,2	0,795	1,088	0,01*	0,002*	(0,003)	800
				0,765	0,970	0,098*	0,017*	0,0513*	600
		2,0		0,799	1,758	-	-	0,1073*	600
		1,1	0,5	0,666	1,085	0,401*	0,066*	(0,004)	800
				0,649	0,917	0,443*	0,075*	0,078*	600
		2,0		0,799	1,363	-	-	0,305*	600
		1,1	1,8	0,173	0,961	1,962*	0,313*	0,043*	800
				0,186	0,602	1,859*	0,307*	0,236*	600
		2,0		0,416	0,788	1,144*	0,192*	0,593*	600
		1,1	3,0	0,0083	0,371	2,810*	0,396*	0,339*	800
				0,0047	0,183	2,648*	0,398*	0,445*	600
		2,0		0,0471	0,383	2,350*	0,376*	0,795*	600
		1,1	8,0	0,0013	0,209	4,532*	0,399*	0,420*	800
				0,0042	0,164	2,650*	0,398*	0,455*	600
		2,0		0,0043	0,167	2,650*	0,398*	0,903*	600
100	3,0	1,0	2,0	2,161	0,996	2,445*	0,416*	-	800
			2,0	2,098	0,989	2,587*	0,447*	-	600
			12,0	0,0012	0,197	17,017*0,217**	1,499*	0,378*	800
			12,0	0,004	0,124	9,976*	1,498*	0,438**	600
100	1,0	4,0	1,5	0,998	2,201	-	-	0,873*	800
			1,5***	1,0	2,200	-	-	0,891*	800
			1,5	1,0	2,020	-	-	0,985*	600
			1,5***	1,0	2,020	-	-	0,988**	600
			1,5*'	1,0	2,199	-	-	0,897*	800
			1,5*'	1,0	2,019	-	-	0,990**	600

7 Summary

From the thermodynamic investigation of the oxidation of Pb-As, Pb-Sb, As-Sb and Pb-As-Sb-melts the following conclusions can be drawn:

- The sequence of the oxidation of As and Sb in a Pb-melt depends on the concentration of the trace elements, the oxygen supply and the temperature,
- During a "dry" oxidation of a Pb-melt the following remaining contents of As and Sb can be reached:

- In binary Pb-Me-melts:
  - 19 ppm As and 345 ppm Sb at 500 °C
  - 4 ppm As and 1400 ppm Sb at 800 °C
- In ternary Pb-As-Sb-melts:
  - 15 ppm As and 345 ppm Sb at 500 °C
  - 5 ppm As and 1400 ppm Sb at 800 °C

- The As-Oxidation in a Pb-As and Pb-As-Sb-melt is always combined with a Pb-oxidation,
- Sb can be oxidised selectively in a Pb-melt by a directed control of the oxygen supply (partial pressure),

Because the oxidation of As and Sb in a Pb-melt is a heterogeneous reaction "melt-gas" by the application of appropriate mixtures of "nitrogen-air" and "nitrogen-oxygen" the selective oxidation of As and Sb can be controlled,

- Recommendations for an improved selective oxidation of As and Sb in Pb-melts in industrial processes can only be given after experimental investigations of the kinetics.

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