Improvement of Selectivity and Kinetics in Lead Refining by Controlled Oxygen Offer and Employment of Rotor Injectors

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Abstract

Lead is one of the oldest metals known to man and found early use in corrosion protection or as a component of ceramic glazes. Today, its production volume is behind aluminium, copper and zinc on fourth place of the non-ferrous metals. Lead production involves several steps beginning with ore mining and processing into a highly enriched lead concentrate followed by processing in lead smelters. The resulting "crude lead” is finally refined in complex processes, which include coarse and fine decoppering or removal of Sn, Sb, As by selective oxidation.

For removing tin, arsenic and antimony from molten lead two methods, the oxidation with air in the boiler and furnace flame and the Harris method are in use. Since the tin-rich refinery product (Sn-dross) can only be processed with difficulties, the Harris method for tin-rich lead bullion offers still an alternative despite economic and ecologic disadvantages. Both methods are based on the oxidation of the accompanying metals at 700-750 °C with an oxygen carrier [1-7]. Depending on the composition, the work-lead tin cuts up to 30% Sn, the arsenic reductions up to 10% As and antimony smear in advance of 1.5-1.8% Sb and 0.05% Sn, about 23-28% Sb, 0 0.8 to 1% As and 0.2 to 0.4% Sn and contain up to 73% Pb [1, 5]. In 60t batch systems (e.g. injection by lances), an oxidation rate of 3.1 kg/m^2*h (surface area 12 m^2) can be reached compared to continuous work with marsh of 13.5 kg/m^2*h (lot 371 t, surface 39 m^2), when starting with lead impurity levels of 1.5-1.8% Sb and 0.05% Sn [2]. As the oxidizing agent (air) is blown in the lead bath, the oxidation rates should be related to the lead bath mass and not to its surface. After converting the data [2] oxidation rates of 620 g/t*h (10.3 ppm/min) at the discontinuous work are present compared to 1422.8 g/t*h (23.7 ppm/min) when working with sump. The injection of the oxidizing agent (oxygen content 20-100%) into the molten lead is typically done by tube with diameters between 1 and 2.5 inches at a gauge pressure of about three bar. The air bubbles formed in this process have a diameter of min. 2.5 to 5 inches. Thus the reaction time is relatively small due to the size of the bubbles as they rise quickly to the metal surface. The tube injection technology leads to long treatment times and low efficiencies. After oxidation of the accompanying elements the oxidation

products are of complex insoluble lead oxides, which are typically named as drosses. The mechanisms responsible for this formation and their influence on the refining process have been repeatedly subject of scientific studies [8-17]. In essence, some questions still remain unresolved so far as to the minimum necessary oxygen supply, the influence of elements interaction on phase composition, the question of maximum achievable refining speed or minimal lead loss by oxidation. From an operational viewpoint, particularly important is a selective removal of tramp elements, the maximum enrichment of the oxide phase with the element (Sb, Sn, As, …) to be removed and the completeness of such removal.

State of Research

The oxidation of binary melts in the system Pb-Sn-As-Sb has been investigated in numerous studies, some of which are essentially contradictory. It is generally assumed on the basis of thermochemical calculations that the oxidation of Sn, As and Sb happens in that order, following the formation enthalpy of the corresponding pure oxides. If so, the order of oxidation must be independent from the activities of the metals, which contradicts the basic thermodynamic principles. The oxidation profile in a multicomponent system is much more complicated than expected, as tin dross compositions reveal. Remarkable are high Sb concentrations, but very low As contents in this phase which should be present according to the heat of formation of Sb_2O_3 and As_2O_3 in inverse ratio. To assess the As-, Sn-, and Sb-removal from the melt during air blow of the melt, the resulting oxide phases direct at the bubble surface have to be forecasted respecting the changing melt composition and oxygen partial pressure there. For this reason, ten years of investigations at IME [18,19] have been made on equilibrium diagrams of lead, its associated metals and the resulting oxides with oxygen. In these publications the triangulation of ternary systems in the higher order systems Pb-As-Sb-O, Pb-Sn-Sb-O Pb-As-Sn-O were presented as well as tetraedration of the respective quinternary systems. By equilibrium calculations it was shown that the oxidation sequence of As, Sn and Sb depend from both the supply of oxygen and from the As-, Sn- and Sb-concentrations in the lead bullion. It was found that in the quaternary systems specific concentration windows exist, which allow a selective oxidation of one single metal just by controlling the concentration/partial pressure of O_2, depending on the melt composition.

Thermochemical modelling of the oxidation process

The oxidation sequence of trace elements as function of the “crude lead” composition and the oxygen offer was determined by FACTSAGE$^{\circledR}$ equilibrium calculations, performed using the databases FACT53, Ftoxid, SCPS, SGTE, FACT-SLAG. The modelling was carried out for 550 and 700 °C. The O_2 content in the gas (mixtures with Ar resp. N_2) was increased in 50 steps each of 0.1 % increased (up to 50 steps), while the total pressure of the gas mixture was set to 3 bar. The calculations show that oxidation of the lead bullion and the oxidation sequence proceeds much more complicated than is generally assumed. Generally a large part of Sn is oxidized first forming SnO_2

while the extend depends on the Sb/Sn ratio as well on the presence of Sb, As or both (table 1). Each step corresponds to a certain composition of the melt, temperature and the oxygen concentration of the gas mixture which is in equilibrium with the melt in contact. To allow for controlling of the oxidation, the dependence of the oxidation selectivity/speed from the oxygen content must be known as exactly as possible.

Table 1: Order of the oxide phase formation during oxidation of lead bullion

°C	ratio Sb/Sn	order of the oxide phases formation
550	Sb/Sn<0.684	**1-$SnO_{2(s)}$ →2-$SnO_{2(s)}$+$PbO_{(SLAG)}$+$As_2O_{3(SLAG)}$+$Sb_2O_{3(s)}$→ 3-$PbO_{(SLAG)}$+$PbO_{(S)}$+$Sb_2O_{3(s)}$ → 4-$PbO_{(S)}$**
	0,684<Sb/Sn<1.026	**1-$SnO_{2(s)}$ →2-$SnO_{2(s)}$+$Sb_2O_{3(s)}$ →3-$Sb_2O_{3(s)}$→ 4-$Sb_2O_{3(s)}$+$PbO_{(SLAG)}$+$As_2O_{3(SLAG)}$ → 5-$Sb_2O_{3(s)}$+$PbO_{(SLAG)}$+$As_2O_{3(SLAG)}$+$PbO_{(s)}$ → 6-$PbO_{(s)}$**
	Sb/Sn>1.026	**1-$SnO_{2(s)}$ →2-$SnO_{2(s)}$+$Sb_2O_{3(s)}$ →3-$Sb_2O_{3(s)}$ → 4-$Sb_2O_{3(s)}$+$PbO_{(SLAG)}$+$As_2O_{3(SLAG)}$ →5-$PbO_{(SLAG)}$ + $PbO_{(S)}$**
650	Sb/Sn<0.684	**1-$SnO_{2(s)}$ →2-$SnO_{2(s)}$+$PbO_{(SLAG)}$+$As_2O_{3(SLAG)}$+$Sb_4O_{6(g)}$→ 3-$PbO_{(SLAG)}$ +$PbO_{(S)}$+$Sb_4O_{6(g)}$→4-$PbO_{(S)}$**
	0.684<Sb/Sn<1.026	**1-$SnO_{2(s)}$ →2-$SnO_{2(s)}$ +$Sb_4O_{6(g)}$ →3-$PbO_{(SLAG)}$ + $Sb_4O_{6(g)}$ + $As_2O_{3(SLAG)}$ →4-$PbO_{(SLAG)}$ + $As_2O_{3(SLAG)}$ + $Sb_2O_{3(s)}$ → 5-$PbO_{(SLAG)}$ + $Sb_2O_{3(s)}$ + $PbO_{(s)}$ →6-$Sb_2O_{3(s)}$ + $PbO_{(s)}$**
	Sb/Sn>1.026	**1-$SnO_{2(s)}$ →2-$SnO_{2(s)}$ + $Sb_4O_{6(g)}$ →3-$Sb_4O_{6(g)}$+$Sb_2O_{3(s)}$ → 4-$Sb_2O_{3(s)}$+$PbO_{(SLAG)}$+$As_2O_{3(SLAG)}$ →5-$PbO_{(SLAG)}$ +$PbO_{(S)}$+$Sb_2O_{3(s)}$ → 6-$PbO_{(S)}$+ $Sb_2O_{3(s)}$**
700	Sb/Sn<0.684	**1-$SnO_{2(s)}$ →2-$SnO_{2(s)}$ + $Sb_4O_{6(g)}$ →3-$Sb_4O_{6(g)}$ +$PbO_{(s)}$ →4-$PbO_{(S)}$**
	0.684<Sb/Sn<1.026	**1-$SnO_{2(s)}$ →2-$SnO_{2(s)}$ + $Sb_4O_{6(g)}$ →3-$Sb_4O_{6(g)}$ + $PbO_{(SLAG)}$ + $As_2O_{3(SLAG)}$ →4-$PbO_{(SLAG)}$ + $As_2O_{3(SLAG)}$ + $Sb_2O_{3(l)}$ → 5-$PbO_{(SLAG)}$ + $Sb_2O_{3(l)}$ →6-$PbO_{(SLAG)}$ + $PbO_{(S)}$ + $Sb_2O_{3(l)}$ → 7-$PbO_{(S)}$ + $Sb_2O_{3(l)}$**
	Sb/Sn>1.026	**1-$SnO_{2(s)}$ →2-$SnO_{2(s)}$ + $Sb_4O_{6(g)}$ → 3-$Sb_4O_{6(g)}$ → 4-$Sb_2O_{3(l)}$+$PbO_{(SLAG)}$+$As_2O_{3(SLAG)}$→5-$PbO_{(SLAG)}$+$Sb_2O_{3(l)}$ → 6-$PbO_{(SLAG)}$+$Sb_2O_{3(l)}$ + $PbO_{(s)}$ → 7-$Sb_2O_{3(l)}$ + $PbO_{(s)}$**

The determination of the maximum permissible oxygen content of the gas mixture can be analytical is shown exemplary for the system Pb-Sb-Sn-O. For other systems, the calculation is made similarly. The tetrahedral Pb-Sb-Sn-O system (Fig. 1) reveals that when oxidizing the Pb melt inside the sub-systems Pb-Sn-Sb-SnO_2 and Pb-Sn-As-SnO_2 the phase SnO_2 is formed with priority. On the other hand all concentrations in the window of Pb-Sb-As -Sb_2O_3 will lead to Sb_2O_3 formation. The Z coordinate represents the maximum oxygen content allowed in the Pb-Sn-Sb-O melt, if only Sn shall be oxidized. At higher oxygen concentrations than that of the plane Pb-Sb-SnO_2 both metals Sn and Sb will be oxidized simultaneously. For all Pb-Sn-Sb melts like "S" the resulting composition can be found on the conode between oxygen and the melt composition. It must be stated that due to kinetics reasons the formation of PbO as an intermediate phase can never be avoided, but will further react if time for equilibrium is given.

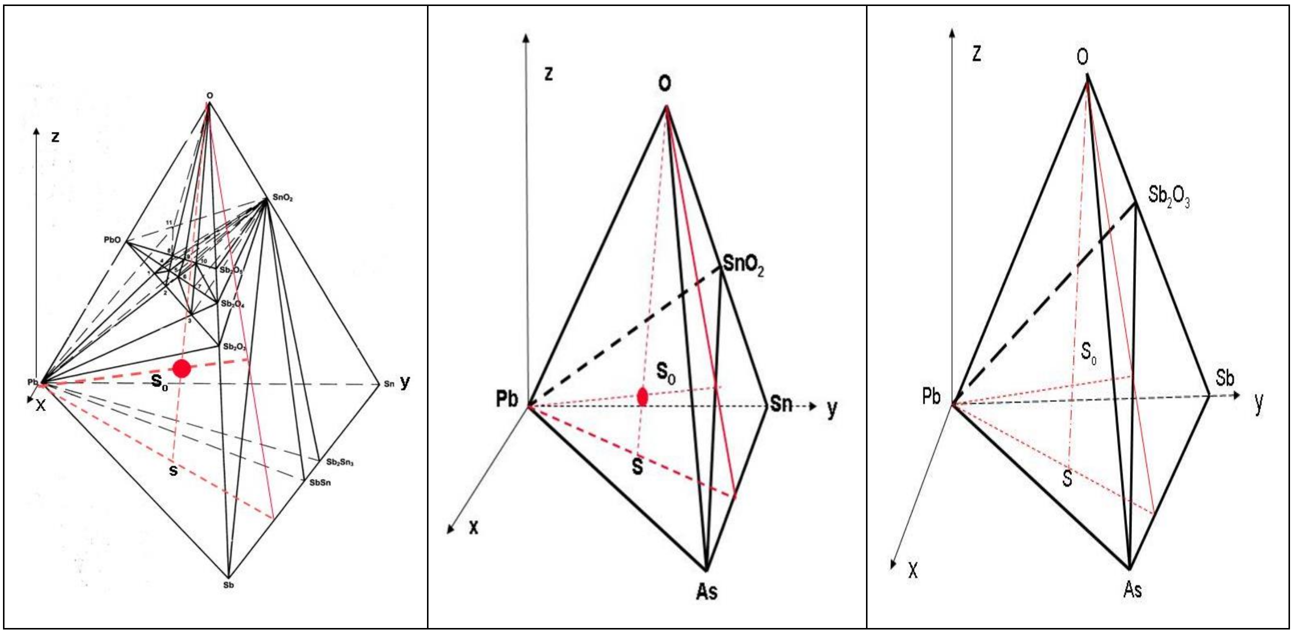

Figure 1: Simplified representation of the Pb-Sn-Sb-O, Pb-Sn-As-O and Pb-Sb-As-O systems as basis for calculating the max. oxygen content allowing for selective oxidation

The intersection point "S_o" of the conode "melt-oxygen" represents the max. permissible oxygen concentration in the Pb-Sb-SnO_2 sub-system where exclusively Sn to SnO_2 is oxidized. For quantifying the maximum oxygen content this conode has been described in analytical form and the system of equations for "z" was solved as to “max. O_2 = 2*[Sn]/(1+2*[Sn])”, values in mass mole fractions, which have to be multiplied by 0.907 to determine the volume fraction of oxygen in the gas mixture. For the system Pb-Sn-Sb-O the formula changes to “max. O_2 = = 3*/(2+3*Sb)”, allowing for As oxidation before Sb.

Experimental studies on a pilot scale

As it follows from the thermochemical calculations an excess of oxygen inside the gas bubble (air) will lead to simultaneous oxidation of all elements of the lead bullion. To ensure a selective oxidation the partial pressure of oxygen in the purge gas must be adjusted. For this purpose a test facility was designed with a volume of 380-400 kg Pb melt. The insertion of the oxidation gases into the Pb melt, which was sealed by a protective gas (Ar) from the environment, is realized by a Foseco rotor injection stirrer (Fig. 2). To adjust the percentage of oxygen inside the gas mixture mass flow meters were used and connected with gas bottles Ar/N_2 and O_2 (or air) as well as with the mixing unit. The use of the rotor system allows the formation of extreme small gas bubbles and such an extreme reaction surface, which thereby accelerates the reaction kinetics.

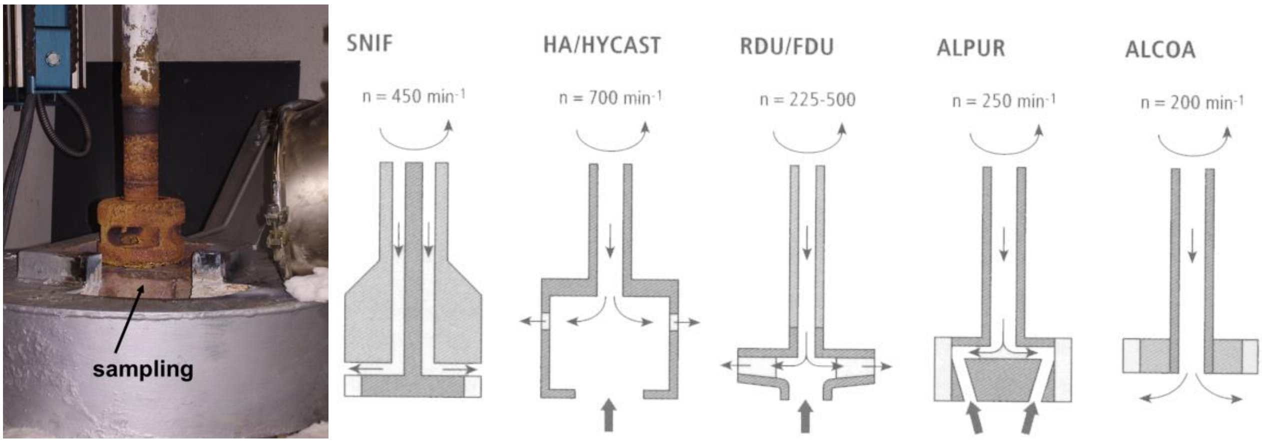

Figure 2: Foseco Rotor Injection set up at the IME for selective oxidation in 400 kg Pb-scale and alternative concepts

Reference tests

To realize industrial conditions reference experiments the Foseco-stirrer (Ǿ 120 mm) was used only as agitator. For selective Sn-oxidation trials were carried out just by stirring the melt under air environment. For As and Sb oxidation (RV6 and RV7) oxygen was blown through a lance onto the stirred melt surface. The experimental parameters of the reference tests and average degradation rates of the accompanying elements are the Table 2.

Table 2: Experimental conditions of reference experiments and average rates of element removal

test no.	°C	time [min]	rpm of stirrer	oxidizing environment	Δ trace-element/Δt ppm/min		
					Sn	Sb	As
rV1	613-620	306	310	air environment	-4.77	-0.95	-0.36
rV2	602-615	115	310	air environment	-6.61	-1.48	-0.26
rV3	615-620	225	425	air environment	-13.3	-0.14	-0.23
rV4	617-620	410	425	air environment	-4.19	-1.97	-0.25
rV5	600-621	170	425	air environment	-2.71	-21.5	-1.76
rV6	640-655	70	425	air+5 l/min O_2	-0.13	-73.6	-0.8
rV7	640-655	75	425	air+5 l/min O_2	-0.13	-48.3	0

Even by stirring the melt with ambient air all accompanying elements oxidize simultaneously. The Sn-removal was significant faster than that of Sb and As (Fig. 3). The analytically determined removal efficiencies of Sn, As and Sb scatter of 10-15% for Sn and values of 30-60% for Sb. With reduction of Sn content in the melt, weaken the Sn-degradation rate from, but it's the Sb-degradation rate. So, for example, the Sn and Sb in an attempt to reduce speeds are RV4 (Sn-Sb and output levels corresponding to 0.048% and 1.676%) ΔSn = -4.19 and -1.97 ppm ΔSb / min and in the attempt RV5 (Sn-Sb and output levels corresponding to 0.005% and 1.454%) ΔSn -2.71 and -21.47 ppm ΔSb min. Additional blowing of oxygen onto the melt surface increases considerably the removal rate. The comparison of the mean values of the reference experiments with industrial data

[2] reveals that the results are comparable. This allows for further tests with this set up improving productivity and selectivity.

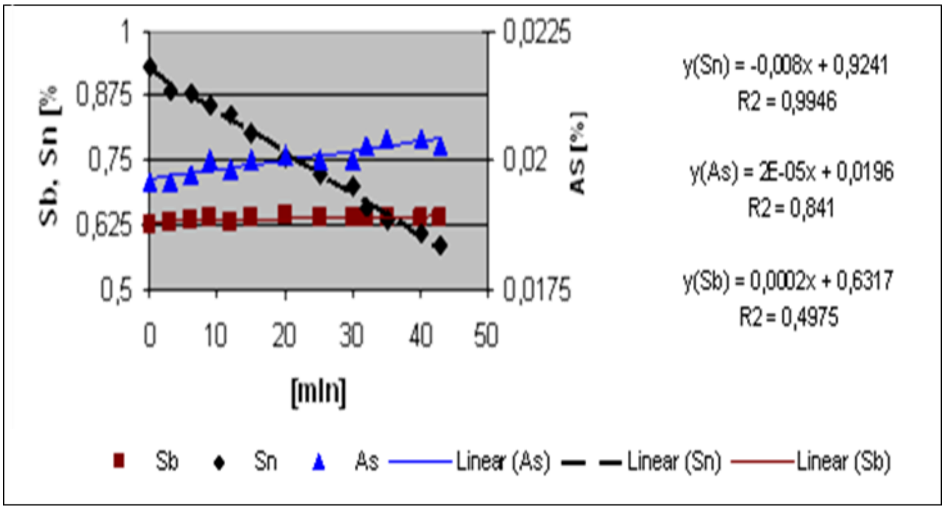

Figure 3: Reference tests - oxidation kinetics of crude lead at 600-617 °C, gas mixture: 50 l/min Ar and 0.9 l/min O_2

Experiments for improved oxidation selectivity

To protect the melt surface from air oxidation and such enable the sole influence of the oxygen content of the gas mixture on oxidation, protective gas of about 30 l/min passed through the lid during the trials. The reaction gas mixture through the Foseco-stirrer was made by 50 l/min Ar resp. N_2 and changing amounts of oxygen respectively air. During heating and melting of the lead bullion the Foseco-stirrer was heated above the melt. After reaching a selected temperature, a melt sample was taken and the Foseco stirrer was immersed in the melt and rotated. During the experiment samples were taken every 2 minutes. After 20-30 minutes the impeller was removed from the melt, allowing for removal of the formed dross from the melt surface. The drosses were weighed, sampled and subjected to wet chemical analysis. Table 3 shows the maximum oxygen levels in the impeller gas for selective oxidation of elements due to thermochemical calculations.

Table 3: Calculated maximum allowed oxygen levels for selective oxidation

trace-elements [%]			max. allowed percentage of oxygen for removal of		Selectivity of oxidation experimental/calculated	
Sn	Sb	As	Sn before Sb	Sb before As	Sn before Sb	Sb before As
0.93	0.63	0.02	0.0282	0.0140	yes/yes	-
0.61	0.64	0.02	0.0186	0.0144	yes/yes	-

The oxidation of the lead examined Pb-bullion (table 4) show high selectivity when an oxygen supply in the gas mixture of 0.9 l/min (0.0177 mole fraction) is applied. Sn and Sb oxidize before

As. The removal rate for Sn was -80.8 ppm/min, while Sb and As increased consequently with a ppm/min rate of +2.9 (Sb) and +0.16 (As).

Table 4: Removal rates of accompanying elements in crude lead during controlled oxidation

Temp. [°C]	oxidation time [min]	Mole fraction of oxygen content in the gas mixture	composition before oxidation [%]			removal rate [ppm/min]		
			Sn	Sb	As	Sn	Sb	As
600-617	43	0.0177	0.9295	0.6272	0.0196	-80.8	+2.9	+0.16

When the bullion reaches tin-values of 0.019%, Sn and Sb oxidize at the same time before As and with the increase of the oxygen content of the gas mixture, all accompanying elements oxidize simultaneously (fig. 4 and table 5).

Table 5: Comparison of calculated and experimental results for selective oxidation at max. allowed oxygen levels

trace-element concentration in lead bullion [%]			Mole fraction of oxygen content in the gas mixture	Calculated max. allowed percentage of oxygen for selective oxidation of		selectivity of oxidation experimental/calculated	
Sn	Sb	As		Sn before Sb	Sb before As	Sn before Sb	Sb before As
0.019	0.852	0.013	0.0099	0.0006	0.0192	no/no	yes/yes
0.003	0.849	0.013	0.0291	9.4*E-5	0.0191	no/no	no/no
0.0005	0.765	0.0077	0.0654	1.6*E-5	0.0173	no/no	no/no

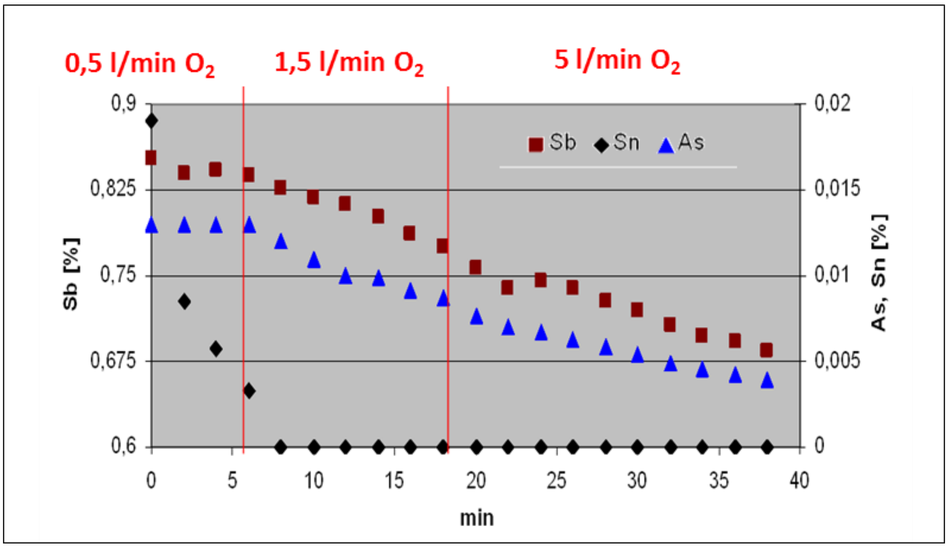

Figure 4: Oxidation kinetics of crude lead with 0.019% Sn, 0.852% Sb and 0.013% As; gas mixture 50 l/min Ar plus O_2 in different volumes

Table 6: Influence of the composition, temperature and oxygen content of the gas mixture on the oxidation rates of the accompanying elements

Temp. [°C]	oxidation time [min]	oxygen content of the gas mixture	composition before oxidation [%]			oxidation rate [ppm/min]		
			Sn	Sb	As	Sn	Sb	As
600-595	6	0.0099	0.019	0.852	0.013	-26.2	-23.3	0
597-608	12	0.0291	0.003	0.849	0.013	-	-60.8	-3.6
603-610	18	0.091	0.0005	0.756	0.0077	-	-39.4	-2.1

On further reducing the oxygen content in the gas mixture by using air instead of O_2 the selectivity of oxidation could be even increased (fig. 5 and table 7).

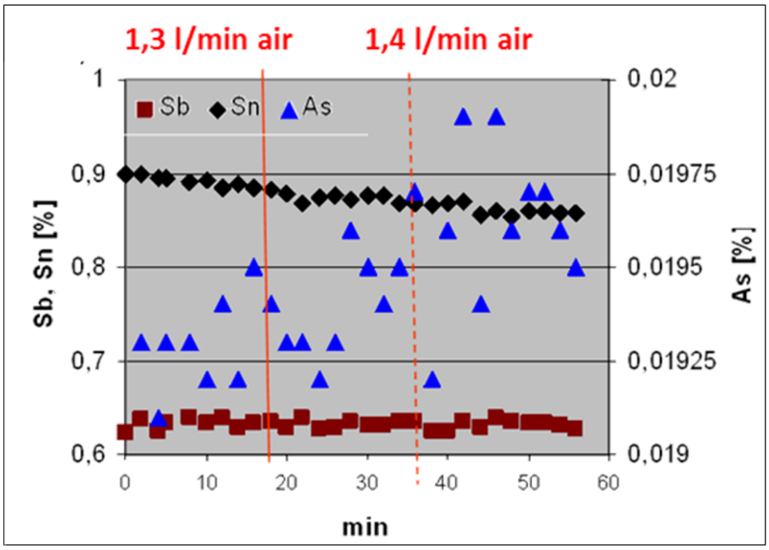

Figure 5: Kinetics of oxidation of the crude lead with 0.9% Sn, 0.64% Sb and 0.02% As with a gas mixture of 50 l min N_2 and two air fractions

Table 7: Comparison of calculated maximum allowed oxygen levels for selective oxidation of crude lead with experimental results

Impurity level [%]			oxygen experiment	Calculated max. allowed oxygen conc. (%) for selective oxidation of		selectivity of oxidation experimental/calculated	
Sn	Sb	As		Sn before Sb	Sb before As	Sn before Sb	Sb before As
0.8998	0.6362	0.0193	0.0053	0.0273	0.0143	yes/yes	yes/yes
0.8822	0.6353	0.0194	0.0057	0.0268	0.0143	yes/yes	yes/yes
0.8753	0.6311	0.0194	0.0057	0.0266	0.0142	yes/yes	yes/yes
0.8663	0.6246	0.0192	0.0057	0.0264	0.0141	yes/yes	yes/yes

Table 8: Influence of the composition, temperature and oxygen content of the gas mixture on the oxidation rates of the accompanying elements

Temp. [°C]	oxidation time [min]	oxygen content of the gas mixture	composition before oxidation [%]	oxidation rate [ppm/min]

			Sn	Sb	As	Sn	Sb	As
495-517	14	0.0053	0.8998	0.6236	0.0193	-11.1	+5	+0.14
536-542	16	0.0057	0.8822	0.6353	0.0192	-7.8	+0.3	+0.16
560-585	16	0.0057	0.8663	0.6246	0.0192	-4.9	+1.7	+0.16

The analysis of all trials shows that the removal/oxidation rates of the accompanying elements depend on the oxygen content of the gas mixture, temperature and number of simultaneous oxidized elements. When Sn, Sb and As are jointly oxidized, the rate is reduced drastically, which can be explained by the formation of $PbO\text{-}As_2O_3$ plus slag (see table 1). In this case the complicated interaction of various factors (composition, temperature, oxygen content of the gas mixture, oxide species of the accompanying elements) does not allow a correct forecast about rates of oxidation. In order to determine the dependencies of the Sn and Sb oxidation rates on the oxygen content of the gas mixture, only the trials were considered where these elements were removed selectively. The corresponding degradation rates follow linearly with the increase of oxygen content in the gas mixture and reached about 75 ppm/min for Sn at an oxygen content of 15 mole% and more than 250 ppm/min for Sb at % oxygen.

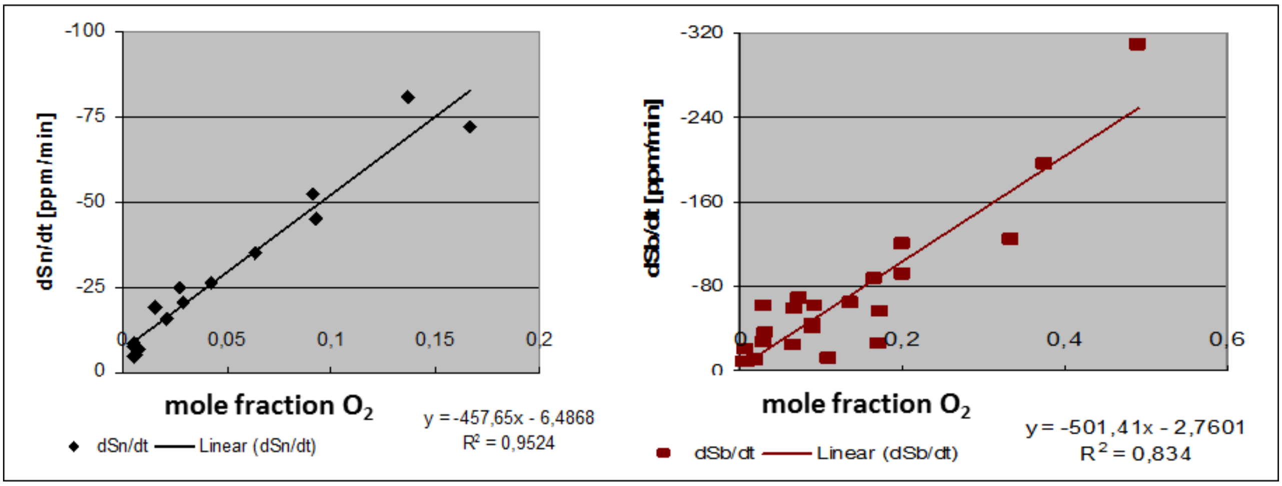

Figure 6: Dependence of impurity oxidation rates Sn (left) and Sb (right on oxygen content of the gas mixture at selective removal conditions

The utilization degree (efficiency) of the introduced oxygen (oxygen mass balance) descends with increasing oxygen content in the gas mixture (fig. 7). It is the proportion of oxygen consumed for the oxidation of the accompanying elements relative to the amount introduced into the melt via the rotor injector. The consequence is, that a high amount of oxygen reacts with Pb, resulting in increasing Pb-loss in dross. The “optimal” oxygen content in the gas mixture (fast process with high Pb-loss and low selectivity or slow selective process with reasonable Pb-loss) can only be determined by economic analysis and may vary from plant to plant.

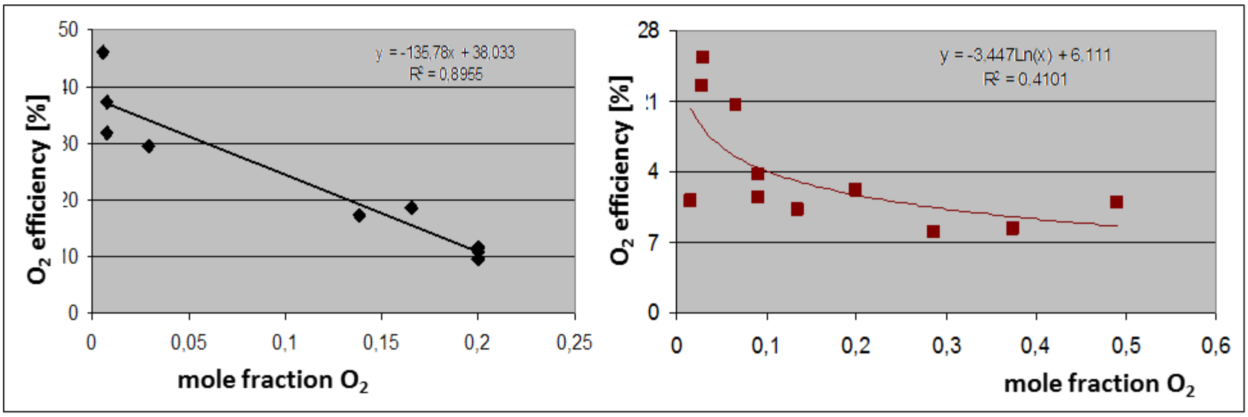

Figure 7: Oxygen efficiency as a function of the oxygen content in the gas mixture at exclusive Sn and Sb oxidation

The experimental results showed further that an increase of the stirrer rotation speed from 265 rpm to 350 rpm does not affect the Sn-degradation rate, but the Sb-degradation rate increases by factor of 5. An influence of the rotation speed on the As-degradation rate could not be determined.

Comparison of the rotational technique with conventional methods

The feasibility of using the rotational injection technique (see fig. 2), which has been established for some time in the aluminium industry for continuous refining of Al-melts, could be a new generation in lead metallurgy for removal of accompanying elements via selective oxidation. From the derived results we see significant advantages (table 9) for this method versus the currently mostly used lance injection route. The use of this technology opens even the way for a continuous process for selective oxidation in lead refining. The obtainable enormous specific surface area of the initiating oxidant (gas) lead to increases of the oxidation rates for Sn by factor of 8 and for Sb of 12 compared to the conventional method. This would result directly in a capacity increase of the entire establishment. Of cause the high level of technology will result in more maintenance as well as labour cost and engineering and material selection for 100t equipment has still to be made. For example the high gas pressures against the lead level, the buoyancy force for the impeller or just its rotor stability are issues to be solved.

Table 9: Comparison of the rotational technique with conventional methods and reverence experiments

	Conventional method	Rotor gas injection
Possibility of ultra-selective oxidation	no	yes
Potential for continuous operation	no	yes
Degree of controlling the oxidation	low	high

Level of technology	low	high
Oxidation rate of the accompanying elements	(10.3-23.7) ppm∑(Sn,Sb,As)/min [3]	to about 80 ppm Sn/min to about 300 ppm Sb/min
	reference experiments (12-16) ppm∑(Sn,Sb,As)/min	

Summary

Thermochemical calculations showed that the oxidation sequence of the accompanying elements in crude lead melts is much more difficult, as commonly believed. Firstly a large part of Sn is oxidized in form of SnO_2. The Sn radicals are oxidized depending on the Sb/Sn ratio, influenced by the fact, whether Sb or Sb and As are present. The modelling also revealed that oxidation sequence depends on oxygen potential and temperature. By controlling the oxygen content of the gas mixture, an ultra- selective oxidation of Sn from As and Sb bearing melts must be possible.

By Tetraedration the quaternary systems Pb-Sn-Sb-O, Pb-Sn-As-O and Pb-As-Sb-O, the concentration volumes have been identified in which Sn, Sb, or As are oxidized with priority. Calculations of the plane intersections Pb-Sb-SnO_2, Pb-As-SnO_2 and Pb-As-Sb_2O_3 with conodes of melt oxygen concentrations resulted in max-values for oxygen in the gas mixture, which still allow a selective oxidation of a single element.

For experimental validation of the selective oxidation a furnace set up (370-400 kg Pb) with a Foseco type stirrer was used, allowing to injecting any gas mixture into the melt. This allows for oxidizing the accompanying elements of the Pb-melt ultra-selectively. The partial pressures were set according to the above mentioned calculations of the max. permissible oxygen content in the gas mixture. Using the rotational injection technique for introducing the gas mixture into the melt with an extreme specific gas surface area an increased productivity of the plant is expected as well as the potential for continuous operations.

Generally the oxidation rates of Sn and Sb increase with increase of oxygen content in the gas mixture. Experimentally achieved removal rates of Sn and reached 80 and 300 ppm/min for Sn respectively Sb. The oxygen efficiency increased to 40% respectively 25% (selective oxidation of Sn respectively Sb, oxygen content <1.5%) compared with less than 10% (oxygen content 20% in air). The Sn- and As-oxidation rates are independent of the rotation speed of the stirrer, while this had a positive effect for Sb.

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