Recovery of Antimony Trioxide Flame Retardants from Lead Refining Residues by Slag Conditioning and Fuming

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Bottom-up process design is performed for a new antimony white fuming approach from antimony-rich lead refining residues. Thermochemical modelling is used to evaluate process boundaries regarding temperature and slag composition allowing the fuming of qualified antimony white from mentioned residues. Two methods are evaluated in laboratory scale to test possibilities of preconditioning for the fuming process. The first one is based on a more selective oxidation during lead softening; the second one on carbothermic reduction of the slag. Antimony enrichment is successfully proven under laboratory scale conditions.

Keywords: Antimony, Antimony white, Fuming, Lead refining, Thermochemical modelling

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1 Introduction

The use of antimony as flame retardants in plastic products nowadays plays a major role in the antimony processing industry with antimony trioxide accounting for over 70 % of today's worldwide antimony consumption [1]. Forecasts estimate further growth of around 4 % a^{-1} regarding the antimony trioxide demand. Currently, China holds a nearly monopolistic market position for primary antimony from which the trioxide is produced by oxidizing smelting. As the Chinese strictly control export rates, they apply strong pressure to the market leading to an uncertain situation regarding the antimony price as well as the availability of antimony for the growing demand of western industrial nations [2]. Therefore, the European Union – for the second time – listed antimony as one of the critical raw materials in 2014 due to its high supply risk and economic importance [3]. Mobilization of new, esp. secondary antimony sources therefore seems inevitable for the future-oriented industry.

Despite the tensed situation on the market, a significant stream of antimony in the form of complex oxidic slags, originating from softening of primary or secondary lead bullion, is left unused in western industrial nations. Antimony-rich drosses from industrial lead refining usually contain ∼30 wt % of antimony and ∼60 wt % of lead in oxide form. These residues have been reduced to hard lead alloys in the past, which were used in lead-acid-battery grids. As the antimony contents in the grids were reduced from ∼12 wt % to less than 2 wt % in the past, application of antimony in lead-antimony alloys is of small importance [1].

The mentioned developments in the antimony market lead to a government-funded research project, carried out at IME. The aim of the project is to develop a process for the winning of antimony trioxide directly from described oxidic residues. The product has to meet the strict regulations of the plastic industry to be applicable in this sector. In case of success, the project provides an innovative reworking route for aforementioned lead refining residues while allowing western industrial nations to partially cover the demand for antimony trioxide from internal sources.

The innovative process is based on a fuming approach. To evaluate boundaries for the antimony trioxide fuming from antimony-rich drosses, extensive thermochemical modelling is carried out. After determination of slag composition requirements, the requirements are addressed by two approaches. The first approach is based on an improved lead refining step to supply suitable drosses, while the second approach uses state of the art drosses which are preconditioned.

2 Thermochemical Modelling of Process Boundaries for Fuming

Antimony trioxide volatilizes easily at higher temperatures. This property is used in different industrial applications such as roasting of sulfidic antimony ores, where the antimony is separated as trioxide via the off-gas due to its high vapor pressure. Production of high purity antimony trioxide from high grade antimony metal is considered state of the

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art. Antimony is melted to around 1000 °C in a suitable furnace whilst air is blown above the surface. Oxidized and volatilized compounds are carried to the off-gas system, quenched and collected in a bag filter or cyclone [4]. Product of the oxidation blowing process is high-grade antimony trioxide which has to meet different requirements depending on customers. The International Antimony Association specifies antimony trioxide properties as shown in Tab. 1 [5].

Table 1. Specifications for antimony trioxide as given by the International Antimony Association.

Physical form	powder
Particle size	0.2 – 44 µm
Sb_2O_3 content	>98.0 wt %
PbO content	<0.25 wt %
As_2O_3 content	<0.1 wt %
Other impurities	<1.75 wt %

Lead- and arsenic oxide are considered most critical condensate impurities as they influence product properties of antimony white and both are often accompanied with antimony. Arsenic oxide will inevitable enter the product due to its high vapor pressure. Therefore, arsenic contents in the feed charge have to be controlled. Lead oxide vapor pressure is considerably lower, but with lead enrichment in the metal bath it may also enter the gas phase in undesired amounts. Therefore, bath composition has to be monitored carefully [4].

Opposing to the oxidation blowing process mentioned, the innovative approach aims to fume antimony white from antimony-rich drosses originating from lead softening. These drosses are complex oxides consisting of PbO, Sb_2O_3, As_2O_3, and other accompanying oxides. Exact composition heavily depends on lead bullion and softening parameters.

Although lead oxide tends to volatilize at higher temperatures than antimony trioxide, it is expected to form the major impurity in the product due to the high contents in the drosses. A vapor pressure calculation is executed to determine the maximum allowed PbO content in the slags for a direct fuming process.

A similar method has recently been used by Liu et al. [6] who calculated the maximum allowed Pb and As contents in antimony metal for an oxidation blowing process using condensate composition standards to determine a boundary for the vapor pressure relations between antimony and lead as well as antimony and arsenic. The authors used the Chinese antimony white standards to determine minimum allowed mole ratios in the product which must not be lower than 1353 for Sb/As or 955 for Sb/Pb in case of Chinese grade 1 antimony white. Using the Clausius Clapeyron equation, Liu stated that vapor pressure ratios p_{Sb}/p_{As} and p_{Sb}/p_{Pb} must not undercut these ratios as mole ratios in the condensate are equal to the vapor pressure ratio of mentioned elements. However, the authors did not take activities into account when calculating the partial pressures as they describe the Sb-rich side of the system Pb-As-Sb. This work adopts the basic principle and applies it to the PbO-Sb_2O_3 system since the aim is to fume antimony white from oxidic slags. Only the relations between lead- and antimony oxide are taken into consideration as the As_2O_3 content in the slags is expected to completely volatilize due to its high vapor pressure.

The product mole fraction is calculated by Eq. (1) according to the International Antimony Association standards from Tab. 1.

$$x_{\left(\frac{Sb_2O_3}{PbO}\right)} = \frac{c_{\min(Sb_2O_3)}}{c_{\max(PbO)}} \tag{1}$$

with x being the product mole fraction, $c_{\min}$ the minimal molar Sb_2O_3 product concentration, and $c_{\max}$ the maximum molar PbO product concentration. The calculation yields a product mole ratio Sb_2O_3/PbO of 300. In order to obtain a suitable product, the vapor pressure ratio of Sb_2O_3 to PbO must not be lower than this.

Partial pressures of substances in solutions can be calculated by the equation

$$p_i = a_i p_i^0 \tag{2}$$

with p_i being the partial pressure of substance i, a_i the activity of substance i in the solution, and p_i^0 the pressure of the pure substance i. Vapor pressures of pure PbO and Sb_2O_3 are calculated for a temperature of 656 °C to 1100 °C according to [7] (Fig. 1). It can be seen that the vapor pressure of pure antimony trioxide is $4.5 \cdot 10^3$ to $1.3 \cdot 10^2$ times higher than the vapor pressure of pure lead oxide in the given temperature range.

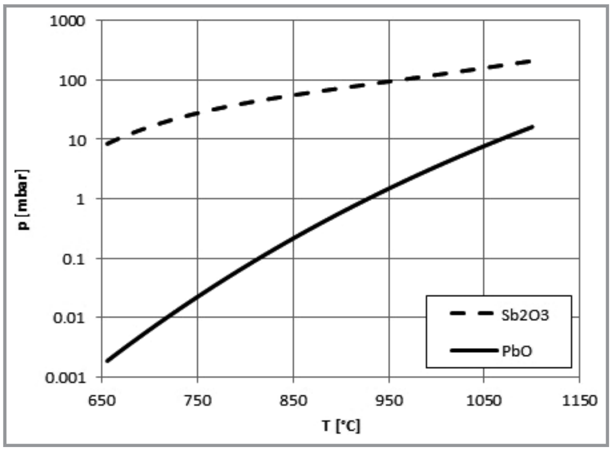


Figure 1. Calculated vapor pressures of pure Sb_2O_3 and pure PbO in the temperature range of 656 – 1100 °C, according to [7].

As slags in the desired process are rich in PbO, activities have to be taken into account. Activities in the binary solution PbO-Sb_2O_3 have been calculated using FactSage 6.4™.

A custom database was designed in cooperation with GTT-Technologies based on the work of Kopyto et al. [8] to supply a solution model for the calculation software in the mentioned system. Using this database, activities of PbO and Sb_2O_3 in a liquid slag phase have been calculated for 700, 800 and 900 °C as function of the antimony trioxide content. Results of the calculation are shown in Fig. 2. Note that no liquid solutions exist in the PbO-rich region at the given temperatures. Hence, activity cannot be calculated for the components for all compositions. Both components show a negative derivation from ideal behavior.

Calculated activities are then used to determine partial pressures of the substances as function of slag composition by Eq. (2). Fig. 3 shows the calculated vapor pressures of PbO and Sb_2O_3 in the liquid slag solution as function of antimony trioxide content in the binary mixture. It can be seen that antimony trioxide vapor pressure varies between 0.5 and 7.3 mbar depending on the influencing factors. Partial pressure of lead oxide is in the range of $1.7 \cdot 10^{-5}$ to 0.53 mbar. Calculation shows that partial pressure of lead oxide is more sensitive to changes in temperature and composition than antimony trioxide vapor pressure. While a change in composition from 30 wt % to 95 wt % Sb_2O_3 raises the antimony trioxide partial pressure by a factor of $3 \cdot 10^1$ to $9.5 \cdot 10^1$ depending on temperature, lead oxide partial pressure is lowered by a factor of $1.3 \cdot 10^2$ to $2.1 \cdot 10^2$ for the same variation in composition. Regarding temperature variation from 700 °C to 900 °C, antimony trioxide partial pressure is raised by a factor of 1.5 to 4.5 depending on composition, while lead oxide partial pressure is raised by a factor of $1.02 \cdot 10^2$ to $3.03 \cdot 10^2$.

Complex dependency of the vapor pressures indicates that the desired process has to be carefully controlled. Understanding temperature and composition dependency is crucial for the process design. Therefore, the vapor pressure ratios are calculated by Eq. (3).

$$f = \frac{p_{Sb_2O_3}}{p_{PbO}} \tag{3}$$

with f being the vapor pressure ratio, p_{Sb2O3} the partial pressure of antimony trioxide, and p_{PbO} the partial pressure of lead oxide. Results of the vapor pressure ratio calculation are shown in Fig. 4. Calculation shows that temperature control is a crucial factor for the desired process. An increase in temperature from 700 to 900 °C favors volatilization of higher lead oxide amounts, hence, reducing the vapor pressure ratio. At 700 °C, the critical boundary ratio of 300 is reached for antimony trioxide contents in the slag higher than 38 wt %. This content boundary moves towards higher required Sb_2O_3 contents with increasing temperature. The desired product can be fumed from slags containing more than 49 wt % Sb_2O_3 at 800 °C or 65 wt % Sb_2O_3 at 900 °C according to the calculation. It can also be seen that temperatures higher than 900 °C are not suitable for the process as selectivity would decrease further. The curves shown in Fig. 4 are fitted with an exponential function $\eta(x)$. Tab. 2 shows the determined functions as well as the coefficient of determination.

As desired fuming process will alter slag composition, a static model as used by Liu et al. [6] and described above does not provide all required information. Therefore, varia-

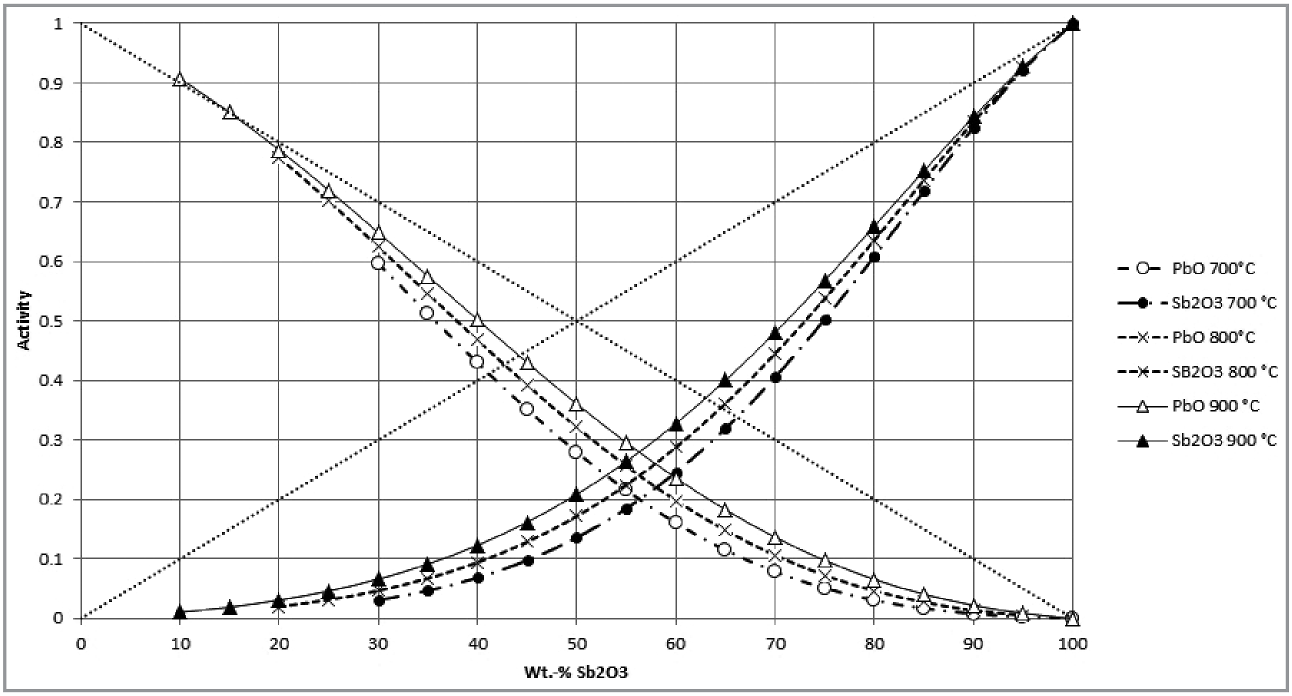


Figure 2. Calculated activities for PbO and Sb_2O_3 in liquid solution at 700, 800 and 900 °C as function of antimony trioxide content.

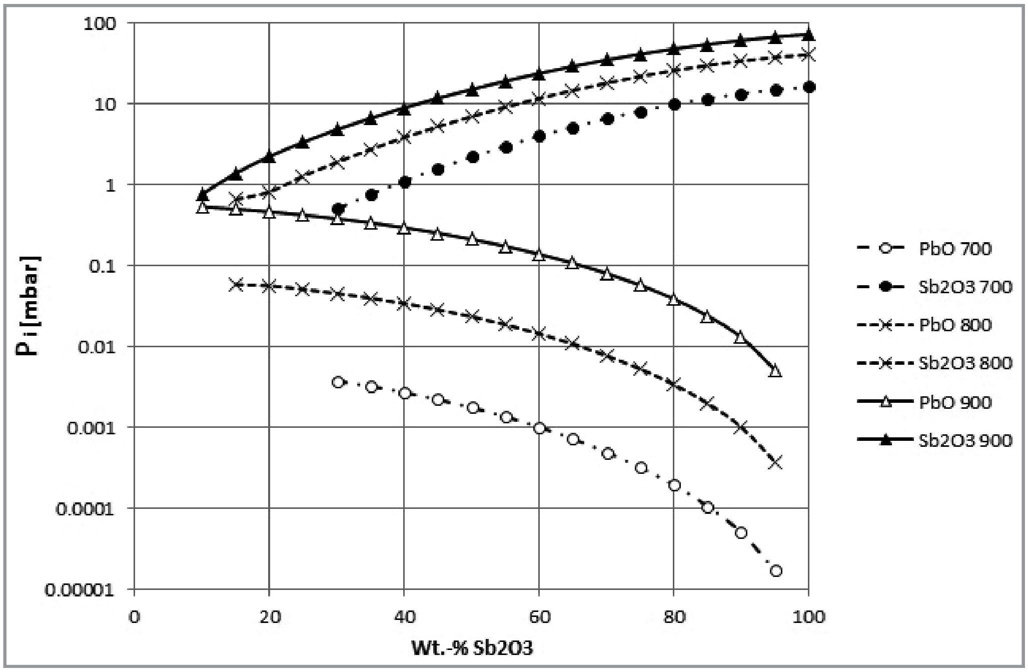


Figure 3. Calculated vapor pressures of PbO and Sb_2O_3 as function of temperature and antimony trioxide content in the binary liquid solution phase.

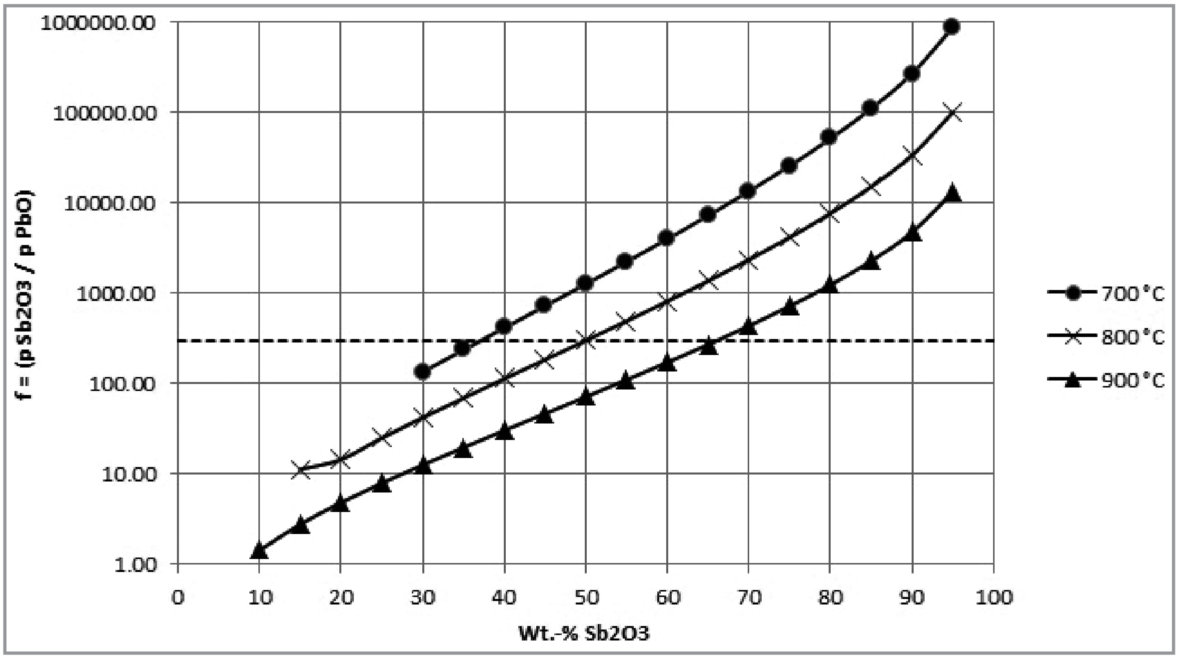


Figure 4. Calculated vapor pressure ratios as function of temperature and composition compared to the product mole ratio ($x = 300$).

tion of slag composition has to be taken into account. Up to this point, the model only yields information on whether or not a suitable product can be fumed at given composition and temperature conditions. The model is upgraded by consideration of the changing composition during the desired process. If fuming starts at conditions where the vapor pressure ratio *f* exceeds 300, thus, forming a condensate of higher purity than the standard, the process can be run not only until a vapor pressure ratio of 300 is reached, but up to conditions where the ratio undercuts a value of 300 as long as the total product composition meets the requirements. Two assumptions are made in this context. First, only antimony

Table 2. Fitted exponential functions $\eta(x)$ describing the vapor pressure ratio depending on temperature and composition.

Fuming temperature	Fitted exponential function	Coefficient of determination
700 °C	$\eta(x) = 2.1531 \cdot \exp(0.1288x)$	0.99
800 °C	$\eta(x) = 1.511 \cdot \exp(0.1089x)$	0.9905
900 °C	$\eta(x) = 0.5828 \cdot \exp(0.0982x)$	0.9924

trioxide is assumed to evaporate during the process, while total lead oxide amount in the slag is held constant due to its lower vapor pressure. Second, the fumed product is assumed to be homogenized in an ideal way after the fuming step.

To calculate suitable fuming composition ranges at a given temperature, a hypothetical fuming scenario is created under mentioned assumptions. Feed charge consists of 100 g slag containing 70 g Sb_2O_3 and 30 g PbO. The vapor pressure ratio is then calculated as function of the evaporated amount taking decreasing Sb_2O_3 content into consideration by Eq. (4).

$$f = \eta\ (100 \frac{m_{Sb_2O_3}}{m_{Sb_2O_3} +\ m_{PbO}}) \tag{4}$$

with η being the fitted vapor pressure ratio function, m_{Sb2O3} the mass of remaining Sb_2O_3 in slag, and m_{PbO} the mass of PbO in slag. Fig. 5 shows the exemplary fuming model at 900 °C. The curves are again fitted with a polynomial function $g(x)$ (Tab. 3) which is integrated to find the abort criterion for the fuming process which is given by

$$\int_0^u g(x) - 300\ \mathrm{d}x = 0 \tag{5}$$

with $g(x)$ being the fitted fuming function and u the maximum fumed amount. Integration yields a maximum fumed amount value which describes the amount of fumed product after which total product composition under the assumption of homogenization undercuts a product mole ratio of 300. Results indicate that at 700 and 800 °C the complete antimony trioxide content of 70 g can be volatilized under given conditions without undercutting the product mole ratio regarding the total product composition. However, the process is limited to a remaining Sb_2O_3 content of 30 wt % at 700 °C or 15 wt % at 800 °C due to solidification of the slag below these contents. At 900 °C fuming has to be stopped after 36.2 g of the antimony trioxide content have been volatilized in order to reach product requirements. Remaining Sb_2O_3 content in the slag at this point is 53 wt %.

A detailed thermochemical examination is applied to a model slag consisting of PbO and Sb_2O_3 with the aim to gather information on how an antimony white fuming process from such slags can be designed. Note that the model only applies for the binary system while common antimony-rich drosses contain other impurities as described before. Kinetics may also change fuming behavior. However, the model provides a first assessment of process boundaries. Following conclusions can be drawn from the preliminary considerations:

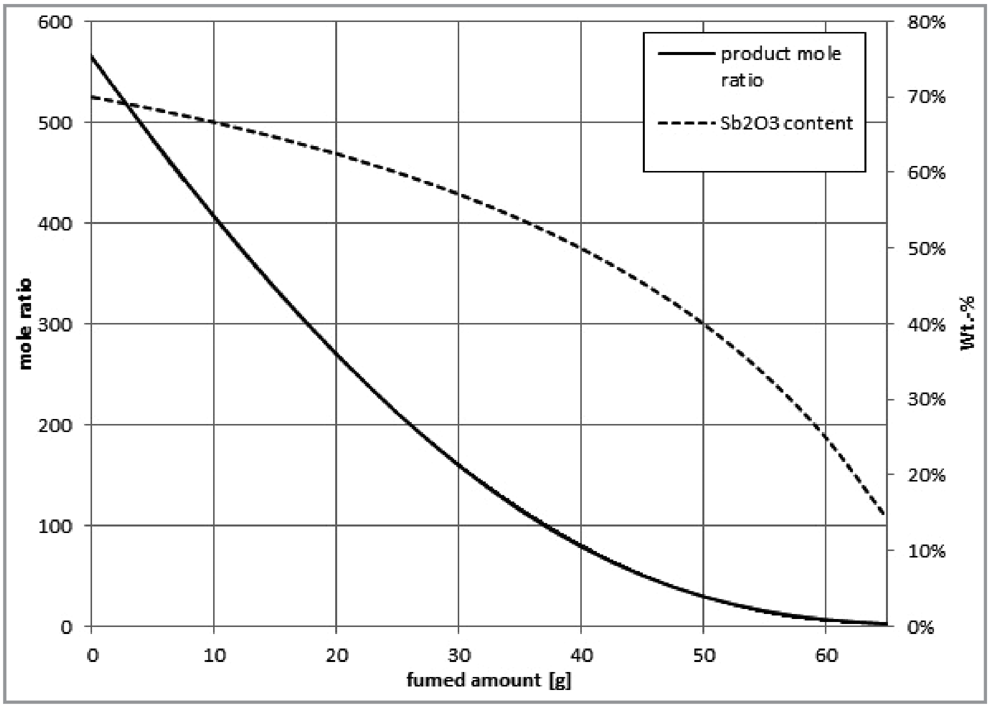


Figure 5. Hypothetical fuming model; product mole ratio and Sb_2O_3 content in the slag as function of the fumed amount originating from 100 g slag containing 70 g Sb_2O_3 and 30 g PbO at 900 °C.

Table 3. Fitted polynomial functions *g* describing the vapor pressure ratio as function of the fumed amount for a model slag of 70 g Sb_2O_3 and 30 g PbO.

Fuming temperature	Fitted polynomial function	Coefficient of determination
700 °C	$g(x) = 5.7983x^2 - 637.63x + 17431$	0.9983
800 °C	$g(x) = 0.8616x^2 - 102.88x + 3086.6$	0.9998
900 °C	$g(x) = 0.1391x^2 - 17.711x + 566.87$	0.9999

- In order to fume a product which reaches the International Antimony Association's low PbO standard, the partial pressure of antimony trioxide must be at least 300 times higher than the lead oxide partial pressure at given conditions.
- Lead oxide vapor pressure is more sensitive to a raise in temperature. Lower process temperatures increase selectivity but lower total vapor pressure results in a trade-off between product quality and fuming speed.
- Slags must not contain less than 30 wt % of Sb_2O_3 at 700 °C or 15 wt % at 800 °C in order to form a liquid solution.
- Fuming temperatures higher than 900 °C result in poor selectivity.
- Drosses have to contain different amounts of antimony trioxide in order to allow fuming of qualified antimony white depending on the fuming temperature. The minimum content is 38 wt % at 700 °C, 49 wt % at 800 °C, and 65 wt % at 900 °C. A process without homogenization (e.g., by refuming) of the product has to be stopped at these compositions.
- If a refuming step is carried out afterwards, a slag containing 70 wt % antimony trioxide and 30 wt % PbO can be fumed until the remaining Sb_2O_3 content reaches 30 wt % at 700 °C or 15 wt % at 800 °C due to slag solidification. At 900 °C, the same slag can be fumed until antimony trioxide content in the slag reaches 53 wt %. Resulting antimony white yields are 81.6 %, 92.4 %, and 51.7 % at the mentioned temperatures.

Preliminary considerations reveal that high antimony trioxide content in the feed material is crucial for an efficient fuming process. Antimony-rich drosses originating from lead refining contain around 30 wt % Sb_2O_3. Therefore, these residues do not provide a suitable raw material for the fuming process in the described condition. Lead oxide content has to be minimized. Two possible solutions are examined in this paper and described below:

1. direct dross conditioning by increased selectivity in lead refining;
2. indirect conditioning by reducing smelting.

Both approaches are evaluated theoretically and experimentally. The aim of the slag conditioning is to achieve antimony trioxide contents ≥ 70 wt %. Fig. 6 shows the proposed flowsheet.

3 Enrichment of Antimony Drosses

3.1 Inline Enrichment

3.1.1 Methodology

Optimization of the lead softening step is carried out according to an approach published by Friedrich & Arnold [9] in 2011. The method aims to achieve an improved selectivity during oxidation of the accompanying elements tin, arsenic, and antimony from lead bullion in lead softening. It is based on a low oxygen partial pressure in the injected gas mixture compared to state of the art techniques. While commercial lead refineries use air or oxygen-enriched air to oxidize mentioned elements, resulting in a poor selectivity and high Pb losses due to the strongly oxidizing conditions, the method proposes defined oxygen partial pressures for the removal of Sn and Sb which can be derived from thermochemical considerations of the quarternary subsytems Pb-Sn-Sb-O, Pb-Sn-As-O and Pb-Sb-As-O. The resulting oxygen partial pressures for selective Sn and a consecutive Sb oxidation depend on composition of the feed charge, but generally are less than half as much as atmospheric oxygen partial pressure. Due to the less oxidizing potential of the injected gas mixture, kinetic disadvantages are inevitable. This negative side effect can be partly compensated by the use of a rotational injection technique.

3.1.2 Experimental

Softening trials are carried out in a resistance heated furnace with a maximum power of 29 kW. The tiltable furnace is fitted with a 35 L iron crucible which measures 365 mm in diameter and 635 mm in height. The furnace lid is attached with an Argon inlet for gas covering of the melt. Melt temperature in the crucible is controlled by a NiCr-Ni

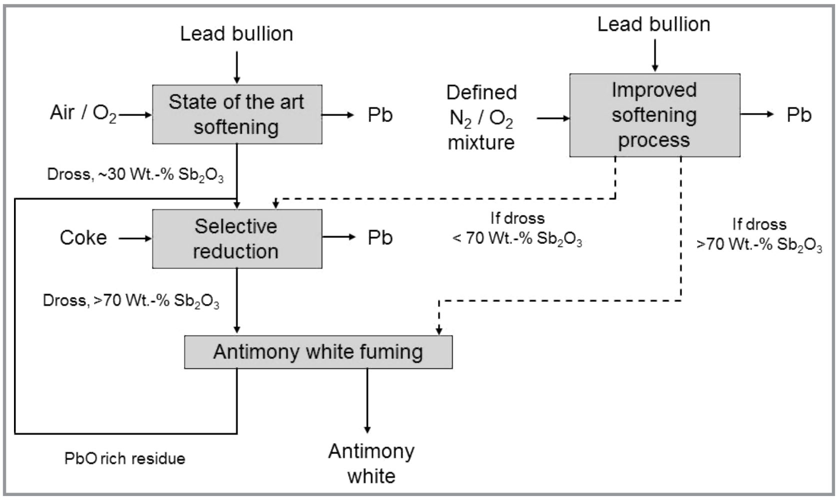


Figure 6. Proposed flowsheet for antimony white fuming including one or two step antimony enrichment in drosses.

thermocouple. An automatic rotary gas injection unit is used for the softening step. Treatment sequences and stirrer rpm are programmable. The graphite shaft measures 45 mm in diameter and 700 mm in length. Fig. 7 shows a schematic representation of the trial setup. The attached graphite stirrer head measures 120 mm in diameter. In operating position,the stirrer head sits 100 mm above the crucible bottom. Gas flow of nitrogen and oxygen is controlled by a digital flowmeter.

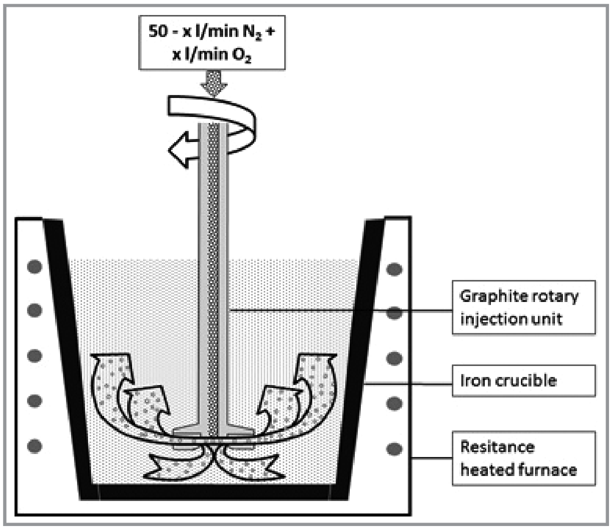


Figure 7. Schematic setup used for lead softening trials.

450 kg of lead bullion are charged into the furnace and melted subsequently. The melt is heated to a softening temperature of 650 °C. After the desired temperature is reached, the stirrer is brought into position and a gas mixture of 0.75 L $\mathrm{min^{-1}}$ O_2 and 49.25 L $\mathrm{min^{-1}}$ N_2 is blown into the melt by the injection unit. The stirrer is operating at 310 rpm during gas treatment. A brown powdery dross is formed during first treatment phase. After a visible change in dross appearance is noted from light brown to a darker color, indicating complete removal of Sn and beginning oxidation of Sb, the gas mixture is changed to a Sb-specific oxygen content of 6.7 L $\mathrm{min^{-1}}$ O_2 and 43.3 L $\mathrm{min^{-1}}$ N_2. A liquid black dross is formed at the lead bath surface during the second oxidation sequence.

During the trial, metal samples are taken every five minutes and analyzed by spark emission spectroscopy. Drosses are removed every 30 min, milled to <90 µm, and analyzed by XRF spectroscopy. Complete treatment duration is 435 min.

3.1.3 Results and Discussion

Metal sampling in small intervals allows calculation of removal rates for the elements Sn, Sb, and As during oxidation treatment. Tab. 4 shows the results for the different treatment sequences divided in Sn and Sb specific oxidation sequences.

Metal phase analysis shows that only tin is oxidized during the treatment with tin-specific oxygen content of 1.5 vol % in the gas mixture. The average removal rate for this treatment phase is 38.75 ppm $\mathrm{min^{-1}}$ while antimony contents show a slight increase and arsenic contents do not change. The tin content is brought down to 26 ppm from an initial content of 0.491 wt % during the first oxidation sequence showing that nearly complete removal is possible without significant antimony losses.

The second oxidation phase with an antimony-specific oxygen content of 13.4 vol % in the gas mixture is crucial for enrichment of antimony in the produced drosses. Metal phase analysis shows that good selectivity in the oxidation process can be achieved with an average antimony removal rate of 50.5 ppm $\mathrm{min^{-1}}$ while Sn and As contents do not change significantly.

Metal phase analysis indicates that the second oxidation sequence should be able to produce oxide mixtures high in antimony while low in As and Sn. Lead content increases by 50 ppm per minute the during second oxidation phase indicating low lead oxide content in the removed slag phases.

Analysis of slag phases which are removed during the second oxidation sequence (Fig. 8) reveal that increased selectivity in oxidation yields slags containing between 39.8 and 56.4 wt % antimony trioxide. Lead oxide content varies between 42.0 and 52.1 wt %, which is more than expected from the analysis of the metal phase. High lead contents in the slag might be due to small metallic lead entrapments which are non-avoidable because of stirrer movement and hand skimming of a thin slag phase.

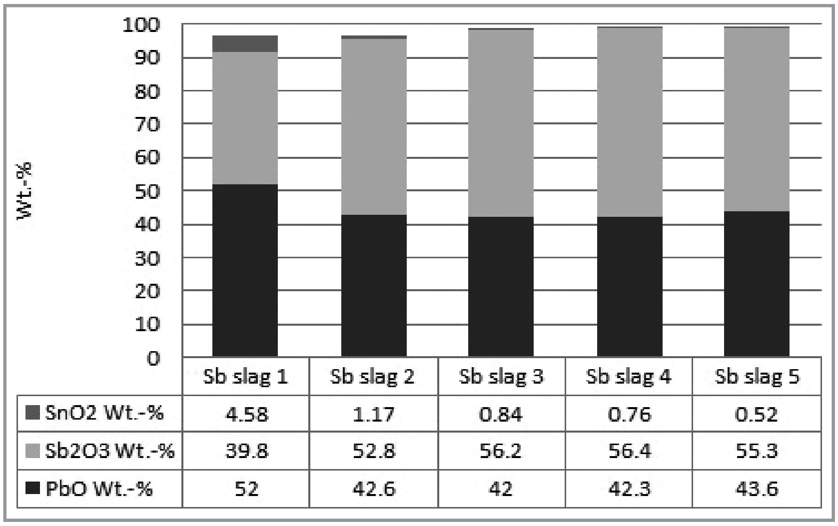
Sb slag 1 represents the first slag skimmed after beginning of the Sb-specific oxidation sequence showing relatively high contents of SnO_2 although Sn is removed nearly completely by the end of the first sequence. The SnO_2 content has to originate from the remaining tin dross which adheres to stirrer and crucible walls and cannot be completely skimmed at the end of the first sequence.

Minor elements such as arsenic, tellurium, cadmium and selenium are also present in the slag phase, but do not make up for more than 0.7 wt % in total, with arsenic accounting for 0.3 – 0.6 wt %.

Inline dross enrichment does not achieve the desired antimony trioxide contents of >70 wt %. However, it is able to reduce contaminations by accompanying oxides. The lead oxide content has to be further reduced by downstream reduction in order to allow effective fuming.

Table 4. Rate of change for the elements Sn, As, and Sb under treatment with varying oxygen partial pressure.

Phase	Duration [min]	Oxygen in gas mixture [vol %]	Element content change [ppm $\mathrm{min^{-1}}$]		
			Sn	Sb	As
Sn-specific	120	1.5	−38.75	5.0	±0
Sb-specific	315	13.4	−1.3	−50.5	−0.52



	Sb slag 1	Sb slag 2	Sb slag 3	Sb slag 4	Sb slag 5
■ SnO2 Wt.-%	4.58	1.17	0.84	0.76	0.52
■ Sb2O3 Wt.-%	39.8	52.8	56.2	56.4	55.3
■ PbO Wt.-%	52	42.6	42	42.3	43.6

Figure 8. Composition of antimony-rich drosses won by selective oxidation.

3.2 Indirect Dross Conditioning

3.2.1 Methodology

Downstream conditioning of industrial drosses by selective reduction of lead oxide provides the second possibility of antimony enrichment in the mentioned drosses. The method has previously been described by Foerster et al. [10] in their United States Patent. The authors use drosses containing approximately 70 wt % PbO and 30 wt % Sb_2O_3 claiming that an addition of 3 wt % coke at reduction temperatures of 840 – 870 °C yields a slag phase containing 60 to 65 wt % Sb_2O_3 with the formed metal phase containing not more than 5 wt % antimony.

To validate temperatures and coke addition, thermochemical modelling of the reduction process was executed using FactSage 6.4 with the aforementioned custom solution database. A stoichiometric coke factor is introduced based on the reaction

$$PbO_{(l)} + C_{(s)} \rightarrow Pb_{(l)} + CO_{(g)} \tag{6}$$

to allow the description of coke addition for varying PbO contents in slags. 300 g of antimony dross with the aforementioned composition are taken as base for the calculation. Reduction is modelled in equilib mode. Fig. 9 shows calculated Pb and Sb distribution as function of the coke addition at 800 °C. The model indicates that exclusive reduction of lead oxide is possible up to a stoichiometric coke factor of 0.4. Remaining slag has an antimony trioxide content of 71 wt %. Larger coke additions promote reduction of antimony which is not desired during the process. As kinetics are not considered in the model, a wider range of coke additions is selected for the experimental part.

3.2.2 Experimental

Reduction trials are carried out in a resistance heated furnace with a maximum power of 14 kW. The furnace chamber measures 200 mm in height, 270 mm in width, and 450 mm in depth. Automatic furnace control allows exact temperature setting as well as realization of temperature profiles. A steel muffle is placed in the furnace chamber and purged with 3 L min^{-1} Ar to prevent oxidation and coke losses. Three alumina crucibles per trial are placed in the muffle. Fig. 10 shows a schematic representation of the trial setup.

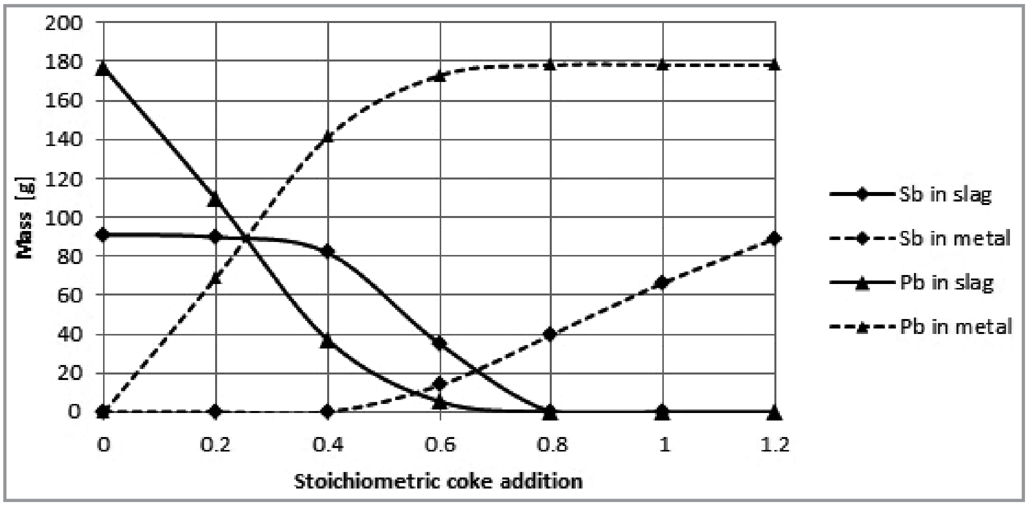


Figure 9. FactSage calculation of lead and antimony distribution in the slag and metal phase originating from 300 g slag as function of coke addition at 800 °C.

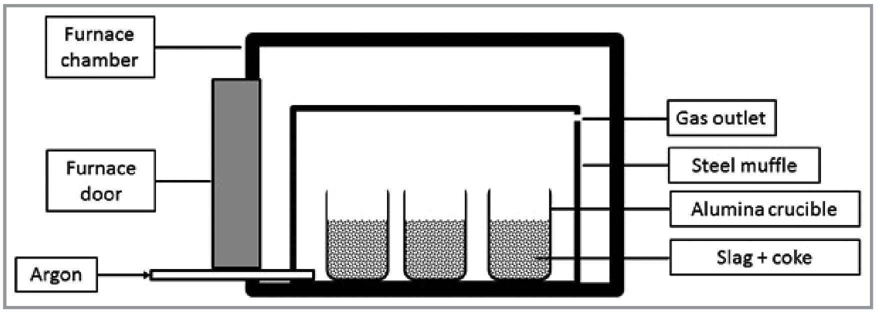


Figure 10. Schematic setup used for reduction trials.

300 g of antimony dross is mixed and milled with the desired amount of petrol coke. The mixture is fed into the alumina crucibles and placed in the muffle. The furnace is heated to the desired temperature with a heating rate of 300 °C h^{-1}. After the desired temperature is reached, the melt is held for 60 min before the muffle is taken out of the furnace. The argon cover is kept until the slag has cooled below 300 °C.

Reduction trials are carried out at 700 °C, 800 °C, and 900 °C for stoichiometric coke additions of 0.4 to 1.2 according to Eq. (6) resulting in 15 parameter sets. Every parameter set is run three times. Therefore, the total number of trials is 45.

Slag and metal phase are separated and weighed. The slag is milled to <90 µm and analyzed by XRF spectroscopy. Metal phases are remelted for homogenization in a laboratory scale induction furnace using a clay graphite crucible. Remelted metal phases are casted into a mould, trimmed and analyzed by spark emission spectroscopy.

3.2.3 Results and Discussion

The metal phase composition is shown in Fig. 11. Depending on reduction temperature and coke addition, the metal phase contains between 2.02 and 22.5 wt % antimony. Lead accounts for the remaining metal phase content nearly completely since all minor elements together are found to be lower than 2000 ppm in sum. Results show that larger coke additions decrease the selectivity of the reaction which is predicted by the model. The same relation applies for an increase in temperature.

Analysis of the slag phase reveals that the Sb_2O_3 content can be raised to over 70 wt % by reduction of the slag. However, the stoichiometric factor of coke addition should not be chosen larger than 0.6 as selectivity decreases and antimony losses to the metal phase increase.

Distribution of Sb and Pb in slag and metal phase are calculated from weights and analytic results. Result of the calculation is shown for a reduction temperature of 800 °C in Fig. 12. The results show the same trend as the calculated behavior (see Fig. 9). However, antimony is reduced at lower coke additions than predicted from calculation.

800 °C is considered as suitable temperature for the reduction step as increased viscosity at 700 °C does not allow complete separation of metal and slag phase. At 900 °C, antimony trioxide losses increase due to higher evaporation rates.

Metal yield is calculated for antimony and lead. Fig. 13 shows the experimental result. Lead metal yield varies between 64 and 95.5 % depending on coke addition, while

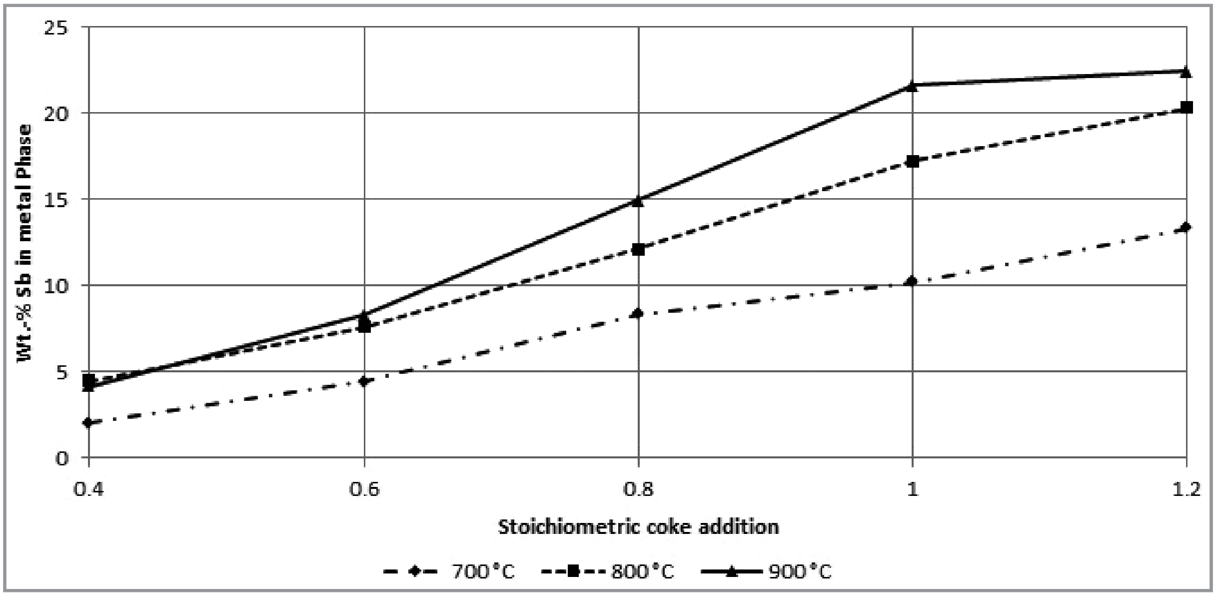


Figure 11. Antimony content in the metal phase as function of coke addition and temperature.

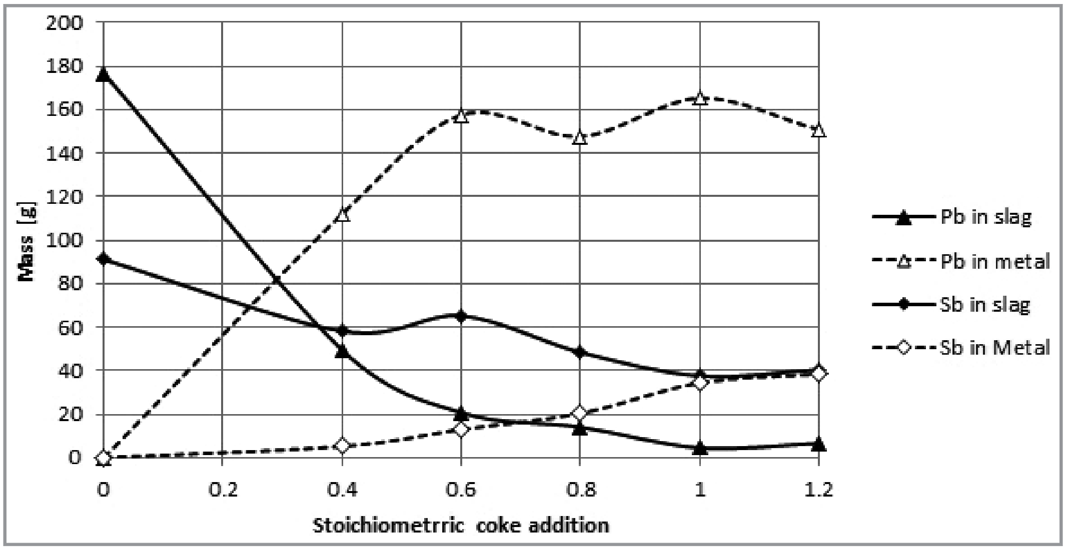


Figure 12. Distribution of antimony and lead in the slag and metal phase as function of coke addition after reduction of 300 g slag at 800 °C.

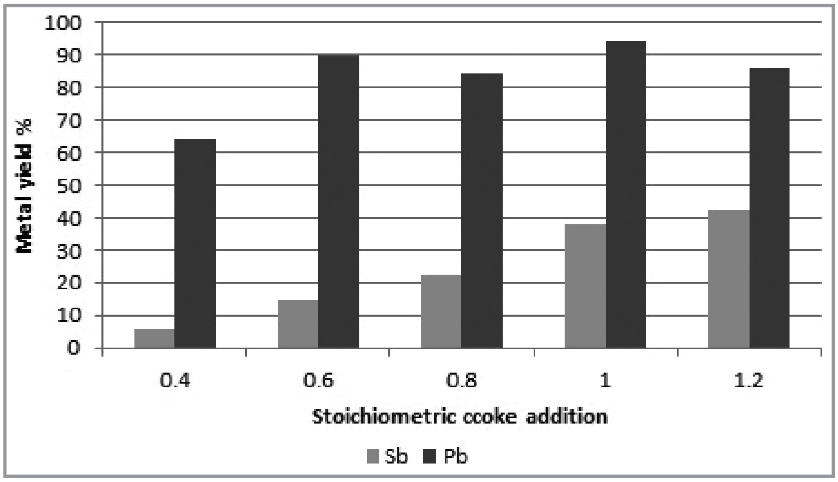


Figure 13. Antimony and lead metal yield after reduction at 800 °C as function of stoichiometric carbon addition.

antimony yield is more dependent on the amount of reduction agent. At a stoichiometric carbon addition of 0.4, only 5.86 % of total antimony input are found to be in metallic form while nearly doubling if the coke amount is raised to a factor of 0.6 resulting in a Sb-yield of 14.43 %. As antimony is desired to be kept in the slag phase for effective fuming, not more than 15 % of antimony input should be brought to the metal phase. Results reassure that stoichiometric coke addition should not exceed a factor of 0.6.

Reduction with a stoichiometric factor of 0.6 at 800 °C is considered as optimal parameter set yielding a slag containing 75.2 wt % Sb_2O_3 with high lead yield and low antimony loss to the metal phase.

4 Summary

A new pyrometallurgical process is currently being developed for antimony white production from antimony rich lead refining residues by direct fuming. The mentioned residues contain about 30 wt % Sb_2O_3 and 60 wt % PbO as well as oxides of arsenic, tin, and other elements. Antimony white products for the application in plastic industry have to meet strict requirements regarding lead and arsenic contents. Due to the large PbO contents in residues originating from state of the art lead refineries, PbO is identified as the most problematic compound for a fuming process. Extensive thermochemical modelling is carried out in the framework of a bottom-up process design to test requirements for the feed material of such a process. Vapor pressures of antimony trioxide and lead oxide are calculated under consideration of their activities in hypothetical slag compositions and different fuming temperatures. Although lead oxide vapor pressure is up to 4500 times lower than the vapor pressure of antimony trioxide in pure form depending on temperature, calculations show that vapor pressures are influenced by high lead oxide activity to a large extent. Slag composition and possible product compositions are brought into relation by introduction of a partial pressure ratio. Antimony white product requirements of the International Antimony Association are used to define a boundary for such a ratio because the partial pressure ratio of Sb_2O_3 and PbO is directly linked to the product composition. It is found that Sb_2O_3 partial pressure has to be at least 300 times higher than PbO partial pressure to fume a suitable product. Boundaries for minimal Sb_2O_3 content in the feed material to achieve this vapor pressure ratio are found to be 38 wt % at 700 °C, 49 wt % at 800 °C, and 65 wt % at 900 °C. As antimony trioxide content in the slags decreases during fuming, the feed material has to contain higher contents plus the fuming would have to be stopped at said boundaries. It is also found by implementation of a dynamic fuming model that fuming can be run to lower Sb_2O_3 contents under assumption of condensate homogenization. An enriched slag containing 70 wt % Sb_2O_3 can be fumed down to antimony trioxide contents of 30 wt % at 700 °C or 15 wt % at 800 °C due to solidification. At 900 °C, the same process can be run down to 53 wt %. Resulting antimony white yields are 81.6 %, 92.4 %, and 51.7 % at mentioned temperatures. Calculation shows that state of the art drosses are not suited for fuming without enrichment of antimony content. Therefore, two conditioning methods are experimentally tested with the aim to produce slags containing ≥ 70 wt % antimony trioxide. Direct conditioning of slags by increased selectivity during lead softening under use of low oxygen partial pressures yields slags containing up to 56.4 wt % Sb_2O_3. The indirect method by reduction smelting of state of the art antimony-rich drosses yields a slag phase containing 75.2 wt % Sb_2O_3 without significant antimony losses to the metal phase. The indirect approach is considered as the best solution for Sb_2O_3 enrichment due to the described results. Further enrichment methods such as reduction by gaseous reduction agents are currently being investigated at IME.

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