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Development of Secondary Antimony Oxides from Metallurgical Slags for the Application in Plastic Products

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Abstract Recovery of antimony oxide for use in flame retardants from lead refining residues is evaluated using a fuming approach. A process is designed bottom-up. First, thermochemical calculations are made to determine process boundaries for a fuming process. Hence, a fuming model is created based on activity and vapor pressure data from literature, which is practically investigated using synthetic slag mixtures to describe fuming behavior in the binary Sb_2O_3–PbO system. The model shows that drosses can not be used in fuming process in their raw form but have to be preconditioned by the reduction of lead oxide. Preconditioning is investigated to define the best parameters in terms of selectivity and antimony enrichment in the oxide phase.

Keywords Antimony · Antimony white · Fuming · Modeling

Introduction

The use of antimony as a flame retardant in plastic products nowadays plays a major role in the antimony processing industry with antimony trioxide (also called antimony white) accounting for over 70% of today's worldwide antimony consumption [1]. Forecasts estimate further growth of around 4% per year 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—especially 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 less importance [1]. The mentioned developments in the antimony market led to a government-funded research project, carried out at IME. Aim of the project is the development of a pyrometallurgical antimony trioxide winning process from aforementioned lead refining 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 the 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

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evaluate boundaries for the antimony trioxide fuming from antimony-rich drosses, extensive thermochemical modeling is carried out. After the determination of slag composition requirements, the requirements are addressed by slag conditioning. Carbothermic reduction of the named drosses is investigated by thermochemical simulation software and carried out in lab scale to determine optimal parameters.

Process Boundaries

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 offgas due to its high vapor pressure. Production of high-purity antimony trioxide from high-grade antimony metal is considered state of the art. Antimony is melted to around 1000 °C in a suitable furnace while air is blown above the surface. Oxidized and volatilized compounds are carried to the offgas 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. International antimony association specifies antimony trioxide properties as shown in Table 1 [5].

Lead and arsenic oxides are considered most critical condensate impurities as they influence product properties of antimony white and both are often accompanied with antimony. Arsenic oxide will inevitably 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]. As opposed to the oxidation blowing process mentioned above, 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. The 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 the minimum allowed mole ratios in the product which must not be lower than 1353 for Sb/As and 955 for Sb/Pb in the case of Chinese grade 1 antimony white. Using the Clausius–Clapeyron equation, Liu stated that vapor pressure ratios pSb/pAs and pSb/pPb must not undercut these ratios as the mole ratios in the condensate are equal to the vapor pressure ratio of the 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 Pb–As–Sb system. This work adopts the basic principle and applies it to the PbO–Sb_2O_3 system as the aim is to fume antimony white from oxidic slags. Only the relations between lead and antimony oxides are taken into consideration as the As_2O_3 content in the slags is expected to completely volatilize due to its high vapor pressure [10].

The following calculations define the process boundaries. More detailed vapor pressure calculations have been published by the authors in [10].

Product mole fraction is calculated by Eq. 1 according to the International Antimony Association standards shown in Table 1:

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

with x being the product mole fraction, c_{min} the minimal molar Sb_2O_3 product concentration, and c_{max} being 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 value. 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 being the pressure of the pure substance i. Vapor pressures of pure PbO and Sb_2O_3 are calculated for the temperature range of 656–1100 °C according to literature [7]. Activities in the binary system are taken into account and allow partial pressure calculation. Partial pressures are set into relationship by the equation:

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

Table 1 Specifications for antimony trioxide by 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%

with f being the vapor pressure ratio, $p_{Sb_2O_3}$ the partial pressure of antimony trioxide, and p_{PbO} being the partial pressure of lead oxide. Result of the vapor pressure ratio calculation is shown in Fig. 1. The 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 toward 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 and 65 wt% Sb_2O_3 at 900 °C according to the calculation. It can also be seen that the temperatures higher than 900 °C are not suitable for the process as selectivity would decrease further [10].

This model can be seen as a courtesy for process development. Critical assessment of literature shows a large deviation in thermochemical data of the named system. Especially, vapor pressure data for Sb_2O_3 seem to be inconsistent. Therefore, the lowest described vapor pressures as reported in [7] are used for the model in a conservative approach.

Conditioning of Antimony-Rich Drosses for Antimony White Fuming

As mentioned above, industrial Sb-bearing drosses contain about 30–35 wt% Sb_2O_3 and are not suitable for a direct fuming process under the previously described hypothesis. Carbothermic reduction of the drosses is identified as the most practical method for dross enrichment. Sb_2O_3 contents around 70 wt% in the dross phase are set as the target for fuming. The method has previously been described by Foerster et al. [9] in their United States Patent. The aut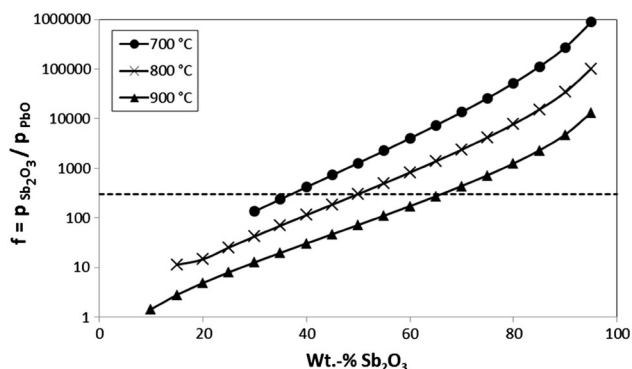hors use drosses containing approximately 70 wt% PbO and 30 wt% Sb_2O_3 claiming that an addition of 3 wt% coke at the reduction temperatures of 840–870 °C yields a slag phase containing 60–65 wt% Sb_2O_3 with the formed metal phase containing not more than 5 wt% antimony.

To validate temperatures and coke addition, thermochemical modeling of the reduction process was executed using FactSage[TM] 6.4. This software does not feature a solution model for the binary PbO–Sb_2O_3 system. As activities are crucial to exact modeling of reduction processes, a custom solution database is created in association with GTT-Technologies based on thermochemical data published by Kopyto et al. [8]. A stoichiometric coke factor is introduced based on the reaction

$$PbO_{(l)} + C_{(s)} \rightarrow Pb_{(l)} + CO_{(g)} \qquad (4)$$
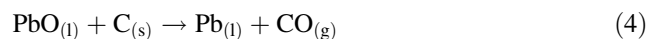
to allow the description of coke addition for varying PbO contents in slags. Slag reduction is simulated for a hypothetical binary slag containing 30 wt% Sb_2O_3 and 70 wt% PbO under varying coke addition according to Eq. 4. Fuming of Sb_2O_3 and PbO is suppressed in the calculation to exclusively describe the reduction behavior. Figure 2 shows the calculated reduction behavior according to the simulation at 800 °C. It can be seen that up to the coke factor value of 0.4 exclusive reduction of PbO takes place with the remaining slag reaching the Sb_2O_3 content of 68 wt%. An increase in Sb_2O_3 content is due to the predominant reduction of PbO to Pb. Further coke addition promotes simultaneous reduction of both oxides. However, PbO reduction is still dominant with the slag reaching 87 wt% Sb_2O_3 at coke factor 0.6. Metal phase reaches 87 wt% Pb under these conditions. Coke additions larger than 0.6 result in higher antimony losses to the metal phase without further enrichment of slags and are therefore not suitable for the desired process.
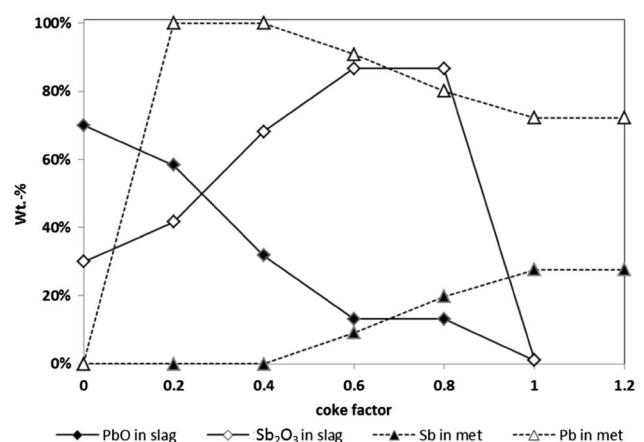

Fig. 1 Calculated vapor pressure ratios as a function of temperature and composition compared to the product mole ratio ($x = 300$)

Fig. 2 Calculated reduction behavior of binary slag containing 30 wt% Sb_2O_3 and 70 wt% PbO at 800 °C

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 Ar to prevent oxidation and coke losses. Three alumina crucibles per trial are placed in the muffle. Figure 3 shows a schematic representation of the trial setup. 300 g of industrial antimony dross (for composition see Table 2) is mixed and milled with the desired amount of petrol coke. The mixture is fed into the alumina crucibles and placed in the muffle. Furnace is heated to the desired temperature with a heating rate of 300 °C/h. After the desired temperature is reached, the melt is held for 60 min before the muffle is taken out of the furnace. Argon cover is kept until the slag was cooled below 300 °C.

Reduction trials are carried out at 700, 800, and 900 °C for stoichiometric coke additions of 0.4–1.2 according to reaction 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 X-ray fluorescence (XRF) spectroscopy. Slag samples are also analyzed by back-scatter detector/energy-dispersive spectrometer (BSE/EDX). Metal phases are remelted for homogenization in a laboratory-scale induction furnace using a clay–graphite crucible. The remelted metal phases are casted into a mold, trimmed, and analyzed by spark emission spectroscopy.

First, fuming tests are simultaneously carried out in a specially designed laboratory-scale installation. The aim of these trials is the validation of the fuming model described above. The fuming reactor is shown in Fig. 4. It consists of a resistance-heated furnace chamber which holds a rotating cylinder. An alumina crucible holding the sample (~ 1000 g) is placed into the cylinder. The furnace chamber is constantly flooded with Argon to prevent Sb_2O_3 from forming higher oxidized, non-volatile Sb–O compounds. Fumes from the furnace chamber are quenched directly after leaving the furnace chamber and carried to a bag filter which is equipped with an aramid fiber/polytetrafluoroethylene (PTFE) membrane filter. The whole furnace is built in a tiltable design.

The first series of trials is carried out with synthetic slags to verify the described fuming model or correct it if necessary. This has to be done due to inconsistent literature data on Sb_2O_3 vapor pressure. In this first trial series, the effect of slag composition is investigated. Slags are prepared by mixing pure Sb_2O_3 and PbO in a composition range from 25 to 80 wt% Sb_2O_3. The mixture is fed into an alumina crucible and heated to 800 °C. Filter suction is applied after complete melting of the mixture. The fuming time is two hours in all trials. The slag is milled after cooling and analyzed by XRF. Condensate is removed from the filter manually and analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-OES).

Results and Discussion

Figure 5 shows the experimental reduction behavior of industrial antimony dross as a function of the amount of coke added at 800 °C. PbO and Sb_2O_3 contents in slag phase are shown together with Pb and Sb contents in the obtained metal phase. As opposed to the calculation, no exclusive PbO reduction is achieved up to a coke factor of 0.4 as the metal phase reaches 4.5 wt% Sb at this point.

Table 2 Composition of antimony dross used for reduction trials (XRF analysis)

Compound	Concentration (wt%)
PbO	62.81
Sb_2O_3	35.79
ZnO	0.89
SnO_2	0.24
As_2O_3	0.09

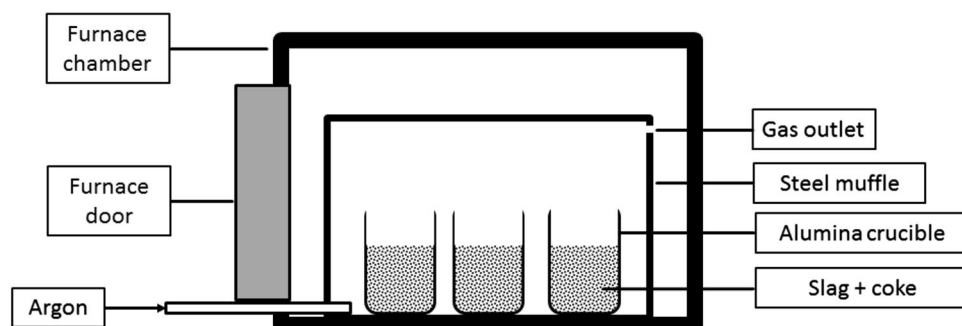**Fig. 3** Schematic of the setup used for slag reduction trials

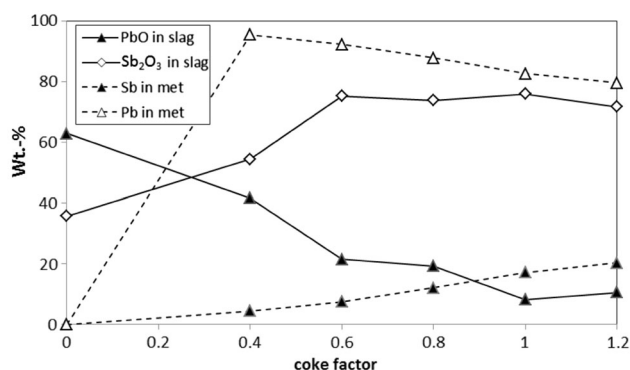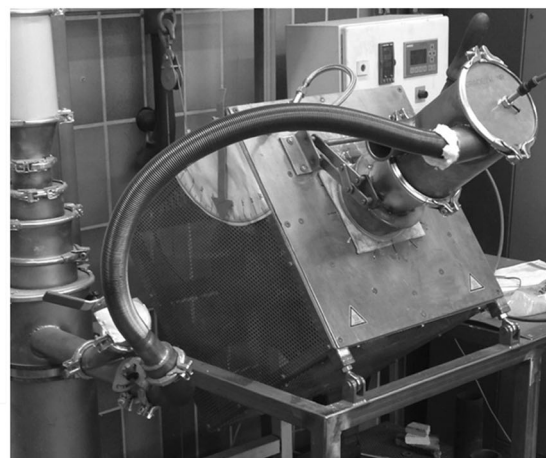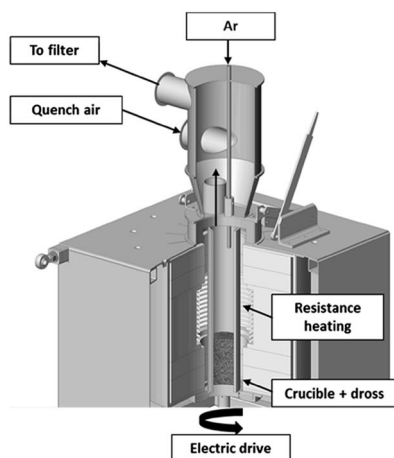**Fig. 4** Laboratory-scale fuming setup: schematic (*left*) and during the fuming process (*right*)

Fig. 5 Experimental reduction behavior of antimony-rich dross under varying coke addition at 800 °C

Fig. 6 Temperature dependency of antimony trioxide enrichment under varying coke addition

However, PbO reduction is dominant and slag enrichment is successful with the slag reaching 75 wt% Sb_2O_3 at the coke addition of 0.6. Compared to the calculated model, antimony trioxide content at this point is 12 wt% lower. As mentioned before, partial Sb_2O_3 reduction is one factor which hinders slag enrichment. Furthermore, fuming of Sb_2O_3 from slag phase can take place in the experimental setup, thus lowering antimony trioxide content in slags compared to the model. This cannot be proven by a mass balance due to small sample sizes and material loss during crushing, milling, and sieving. Coke additions larger than 0.6 do not yield higher enrichment grades of antimony trioxide but promote antimony losses to the metal phase. However, it can be assumed that temporary higher reduction grades are achieved during the trial. As increased Sb_2O_3 content raises activity and therefore antimony trioxide partial pressure, fuming increases in this case and does not allow the detection of higher enrichment grades as the gas phase can leave the system during trials. Complete reduction at the coke factors of 1.0 or higher is not taking place as opposed to the model prediction.

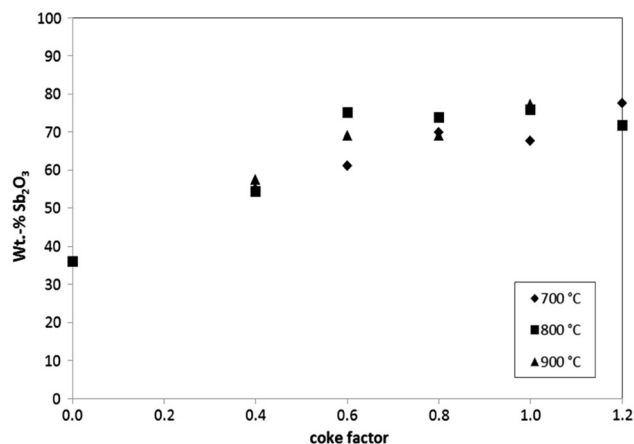Figure 6 shows all the measured antimony contents in the slag phase. It can be seen that enrichment as high as that predicted from calculation cannot be reached with the maximum Sb_2O_3 content for all trials not being higher than 78 wt%. Temperature has no significant influence on reduction grade according to slag analysis; however, it can again be assumed that larger amounts of antimony trioxide have evaporated during the trial at higher temperatures.

Reduction with a stoichiometric factor of 0.6 at 800 °C is considered as an 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. Temperatures lower than 800 °C hinder slag and metal phase separation due to increased viscosity.

Structural analysis of the dross before and after treatment is carried out via scanning electron microscopy (SEM)/EDX analysis in order to confirm the composition changes determined by XRF. Figure 7 shows the BSE image of untreated dross together with an EDX spectrum of the slag matrix. Lighter colored phase in the dross matrix is caused by entrapped metallic lead. Separate EDX analysis not shown here identifies the phase as Lead containing
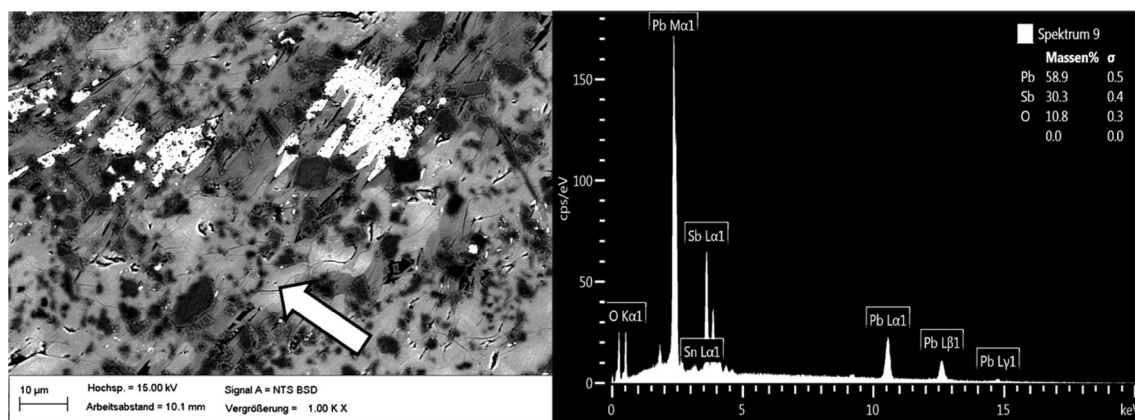
Fig. 7 BSE image and EDX spectrum of industrial lead-rich dross before reductive pretreatment
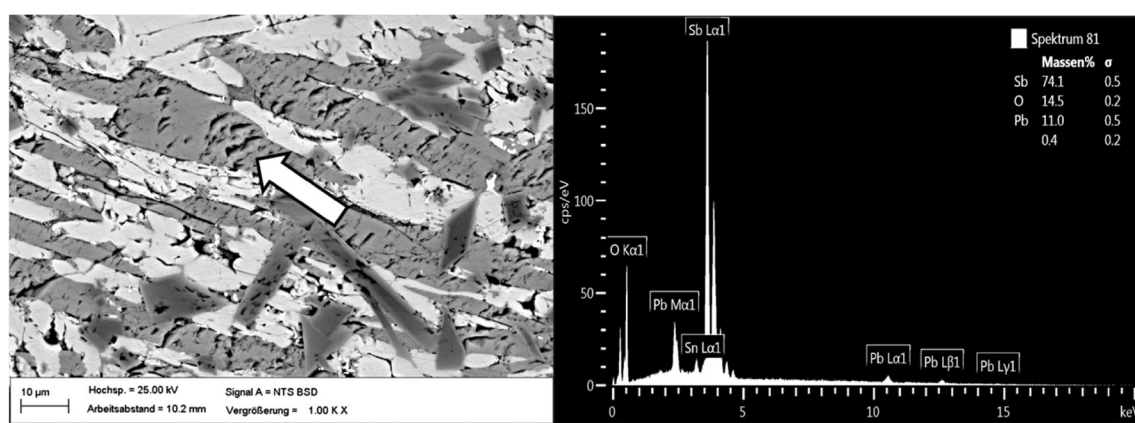

Fig. 8 BSE image and EDX spectrum of antimony-rich phase of preconditioned dross (800 °C, 0.4 stoichiometric coke addition, 60 min holding time)

1.2 wt% Antimony. Darker spots in the image occur due to free spaces in the matrix.

Figure 8 shows the detailed analysis of slag structure after preconditioning at 800 °C and at a coke factor of 0.4. It can be seen that no entrapped lead is found as it settled at the crucible bottom. Slag structure is more regular than in the original drosses. A lighter colored and a darker colored phase can be distinguished in the SEM image. The latter is rich in antimony at 74.1 wt% and only contains 11 wt% Pb. On a molar basis this roughly fits the stoichiometry of pure Sb_2O_3 which solutes a small amount of PbO. The lighter phase is composed of 54.7 wt% Sb, 32.8 wt% Pb, and 12.2 wt% O. This resembles a molar ratio of roughly $PbSb_3O_{4.5}$.

Similar phases can be found in all reduced samples. Phase ratio varies depending on the total antimony content.

Results of the first fuming trial series are compared to the calculated model to evaluate the fuming behavior of binary PbO/Sb_2O_3 mixtures as described above. As dross composition during the trial changes is not known but most of the evaporated material is expected to be Antimony

trioxide—which is confirmed by condensate analysis—average dross composition is calculated from input and output dross in good approximation. Approximation is plausible as Sb_2O_3 contents after the fuming period are not lowered for more than 1.5 wt% compared to the feed.

Figure 9 shows the obtained condensate PbO/Sb_2O_3 ratios as the function of dross composition in comparison to the values calculated from literature. It can be seen that a strong correlation between Antimony oxide content in the drosses and the condensate qualities is confirmed. Slope of the fitted function is very similar to the calculated one, indicating that the characteristics of activity data used for the partial pressure calculations correspond very well to the actual values.

However, the experimental function shows a consistent offset in comparison to the calculated values. The experimental vapor pressure ratios are ~ 2.5–3 times lower than the calculated values. This suggests that vapor pressures on which the model is based are in error. However, the vapor pressure of PbO described in literature is well described. Therefore, the authors conclude that either Sb_2O_3 vapor
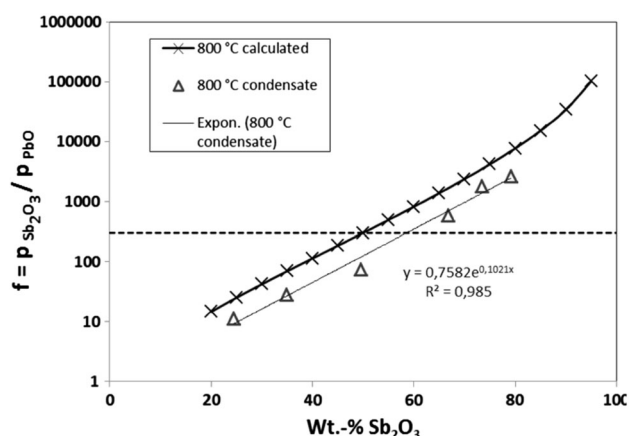
Fig. 9 Vapor pressure ratio at 800 °C as a function of dross composition; calculated values in comparison with the first trials

pressure data are in error being too high although the lowest available pressures from literature were used or a small error in absolute activity coefficients exists. This would have a great effect on vapor pressure ratios as two coefficients are considered in every calculation. This would not be contradictory to the correct behavior of the coefficients as a function of composition as described above.

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 high PbO contents in residues originating from the state-of-the art lead refineries, PbO is identified as the most problematic compound in a fuming process. Extensive thermochemical modeling is carried out in the framework of bottom-up process design to testify the requirements for the feed material of such process. Vapor pressures of antimony trioxide and lead oxide are calculated under consideration of their activities in hypothetical slag compositions and different fuming temperatures. Calculation reveals that the state-of-the art drosses are not suitable for fuming of qualified antimony white. Sb_2O_3 contents in the named slags need to be raised to around 70 wt% for direct fuming. Carbothermic reduction is simulated using FactSage 6.4™ to confirm this enrichment possibility. A series of trials is conducted to prove the principle of antimony enrichment in dross by carbothermic reduction where drosses containing up to 78 wt% Sb_2O_3 are achieved. Optimal reduction parameters are identified in regards to the trial results. The first fuming trials with synthetic mixtures of PbO and Sb_2O_3 at 800 °C indicate that the developed fuming model is able to describe product quality in advance depending on slag composition. However, it needs to be slightly altered due to insufficient data on either vapor pressure of Sb_2O_3 or activities in the binary system. According to the first trials at 800 °C, the dross must contain more than 58 wt% Sb_2O_3 at 800 °C in order to fume a qualified product compared. This value is higher than 49 wt% originally predicted by the model but still reachable via reduction under the right conditions. Future work will focus on more detailed description of fuming characteristics, including different temperature ranges and effects of accompanying oxides.

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