DEVELOPMENT OF SECONDARY ANTIMONY OXIDES FROM METALLURGICAL SLAGS FOR THE APPLICATION IN PLASTIC PRODUCTS

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Abstract

Bottom-up process design is performed for an 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. Fuming boundaries indicate that state of the art drosses are not suitable for fuming qualified antimony white. Slag conditioning by antimony enrichment of the slag has to be carried out in advance. Carbothermic reduction of lead oxide from named oxides is simulated and evaluated in lab scale to achieve optimal slag enrichment while avoiding antimony losses to the metal phase.

Introduction

The use of antimony as flame retardant 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 % 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 are of small importance. [1] The mentioned developments in the antimony market lead to a government funded research project, carried out at IME. Aim of the project is to develop a process for antimony trioxide winning 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 slag conditioning. Carbothermic reduction of 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 temperatures above 600 °C. 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 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 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].

Table 1. Specifications for antimony trioxide by
International Antimony Association [5]

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 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 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 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 respectively 955 for Sb/Pb in case of Chinese grade 1 antimony white. Using the Clausius Clapeyron equation, Liu [6] stated that vapor pressure ratios pSb/pAs and pSb/pPb 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$_2$O$_3$ System as 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$_2$O$_3$ content in the slags is expected to completely volatilize due to its high vapor pressure.

Product mole fraction is calculated by equation 1 according to the International Antimony Association standards from Table 1.

$$x_{(\frac{Sb_2O_3}{PbO})} = {c_{\min(Sb_2O_3)}}\big/{c_{\max(PbO)}} \qquad (1)$$

With x: product mole fraction, c_{min}: minimal molar Sb$_2$O$_3$ product concentration, c_{max}: maximum molar PbO product concentration. The calculation yields a product mole ratio Sb$_2$O$_3$/PbO of 300. In order to obtain a suitable product, vapor pressure ratio of Sb$_2$O$_3$ to PbO must not be lower than this. Partial pressures of substances in solutions can be calculated by the equation [5]

$$p_i = a_i * p_i^0 \qquad (2)$$

With pi: partial pressure of substance I, ai: activity of substance i in the solution, pi0: pressure of the pure substance i. Vapor pressures of pure PbO and Sb$_2$O$_3$ are calculated for a temperature of 656 °C to 1100 °C according to literature. [7] Activities in the binary system are taken into account and allow partial pressure calculation. Vapor pressures are set in to relationship by the equation

$$f = {p_{Sb_2O_3}}\big/{p_{PbO}} \qquad (3)$$

With f: vapor pressure ratio, p_{Sb2O3}: partial pressure of antimony trioxide, p_{PbO}: partial pressure of lead oxide. Result of the vapor pressure ratio calculation is shown in Figure 1. 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$_2$O$_3$ contents with increasing temperature. Desired product can be fumed from slags containing more than 49 Wt.% Sb$_2$O$_3$ at 800 °C respectively 65 Wt.% Sb$_2$O$_3$ 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.
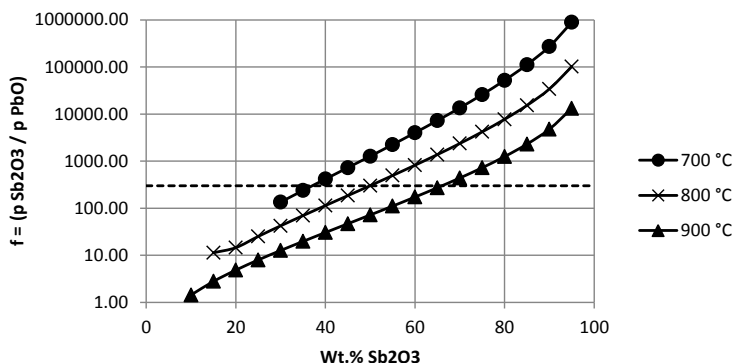
Figure 1. Calculated vapor pressure ratios as function of temperature and composition compared to the product mole ratio (x = 300)

Conditioning of antimony rich drosses for antimony white fuming

As mentioned above, industrial Sb-bearing drosses contain about 30 to 35 Wt.% Sb_2O_3 and are not suitable for a direct fuming process under previously described hypothesis. Carbothermic reduction of the drosses is identified as most practical method for dross enrichment. Sb_2O_3 contents around 70 Wt.% in the dross phase are set as target for fuming. The method has previously been described by Foerster et al. [9] in their United States Patent. The authors used drosses containing approximately 70 Wt.% PbO and 30 Wt.% Sb_2O_3 and found that an addition of 3 Wt.% coke at reduction temperatures of 840-870 °C yields a slag phase containing 60 to 65 Wt.% Sb2O3 and a 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. Named software does not feature a solution model for the binary PbO-Sb_2O_3 system. As activities are crucial for accurate modelling 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

$$PbO_{(l)} + C_{(s)} \rightarrow Pb_{(l)} + CO_{(g)} \qquad (4)$$
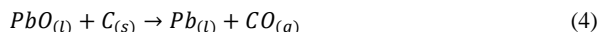
to allow description of coke addition for varying PbO contents in slags. Slag reduction is simulated for a hypothetical binary slag containing 30 Wt.% Sb_2O_3 and 70 Wt.% PbO under varying coke addition according to equation 4. Fuming of Sb_2O_3 and PbO is suppressed in the calculation to exclusively describe reduction behavior. Figure 2 shows calculated reduction behavior according to the simulation at 800°C. It can be seen that up to coke factors of 0.4 exclusive reduction of PbO takes place with remaining slag reaching Sb_2O_3 content of 68 Wt.%. Further coke addition promotes simultaneous reduction of both oxides. However PbO reduction is still dominant with 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 metal phase without further enrichment of slags and are therefore not suitable for desired process.
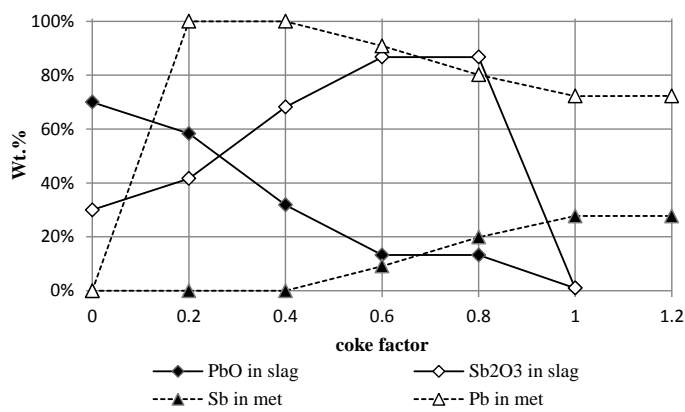

Figure 2. Calculated reduction behavior of binary slag containing 30 Wt.% Sb_2O_3 and 70 Wt.% PbO at 800 °C

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 (composition see Table 2) is mixed and milled with 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 desired temperature is reached, the melt is held for 60 minutes before the muffle is taken out of the furnace. Argon flow is kept until the slag has cooled below 300 °C.

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

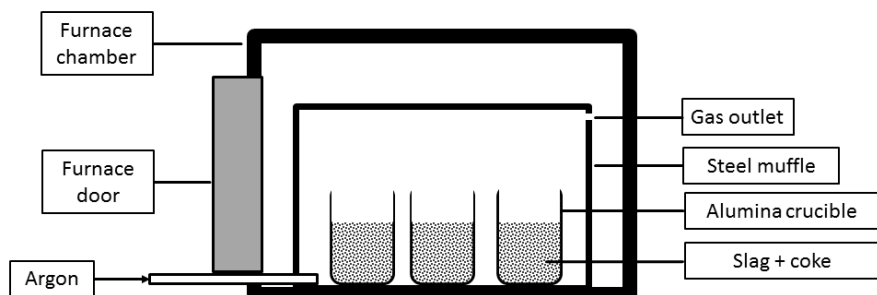| Compound	Concentration [Wt.%]
PbO	62.81
Sb_2O_3	35.79
ZnO	0.89
SnO_2	0.24
As_2O_3	0.09

Figure 3. Schematic setup used for slag reduction trials

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 reaction 6 resulting in 15 parameter sets. Every parameter set is run three times. Therefore total number of trials is 45. Slag and metal phases are separated and weighed. The slag is milled to < 90 μm and analyzed by XRF spectroscopy. Slag samples are also analyzed by SEM/EDX. 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.

Results and Discussion

Figure 4 shows experimental reduction behavior of industrial antimony dross as function of coke addition at 800°C. Opposing to the calculation no exclusive PbO reduction is achieved up to coke factor of 0.4 as metal phase reaches 4.5 Wt-% Sb at this point. However PbO reduction is dominant and slag enrichment is successful by reaching 75 Wt.% Sb_2O_3 at 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 during experiments thus lowering antimony trioxide content in slags compared to the model. 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 higher reduction grades temporary are achieved during the trial. As increased Sb_2O_3 content raises activity of Sb_2O_3 and therefore antimony trioxide partial pressure, fuming is promoted in this case. This temporary state can not be detected by analysis as the gas phase can leave the system during trials. Complete reduction at coke factors of 1.0 or higher is not taking place opposing to the model prediction.
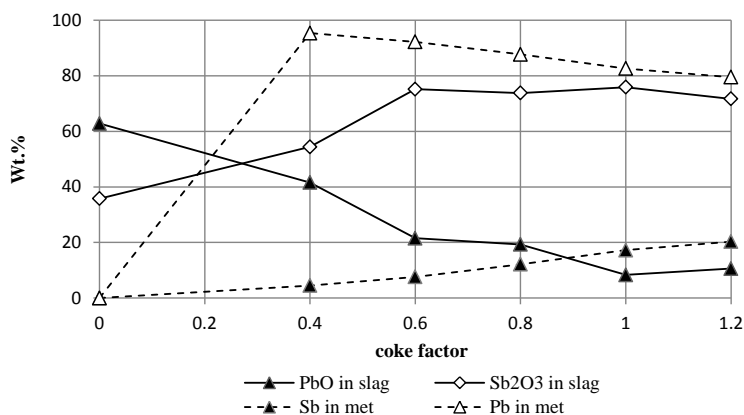
Figure 4. Experimental reduction behavior of antimony rich dross under varying coke addition at 800 °C

Figure 5 shows all measured antimony contents in slag phase. It can be seen that enrichment rates as high as predicted from calculation can not be reached. Maximum Sb_2O_3 content for all trials is not 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.
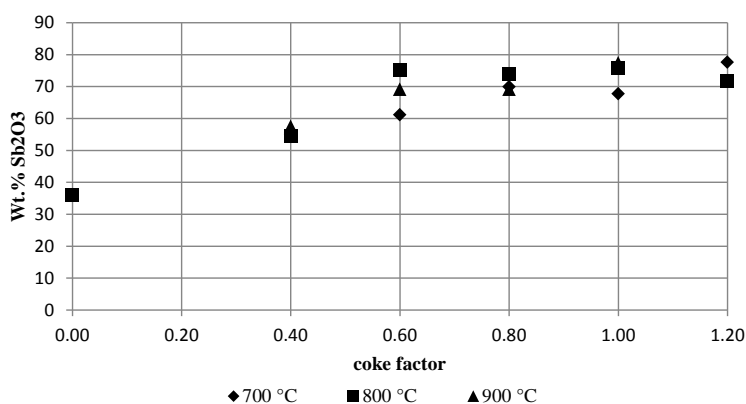

Figure 5. Temperature dependency of antimony trioxide enrichment under varying coke addition

Reduction with a stoichiometric factor of 0.6 at 800 °C is considered as optimal operating condition 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.

Summary

A new pyrometallurgical process is currently being developed for antimony white production from antimony rich lead refining residues by direct fuming. 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 most problematic compound for a fuming process. Extensive thermochemical modelling is carried out in the framework of bottom up process design to testify 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 state of the art drosses are not suitable for fuming of qualified antimony white. Sb_2O_3 contents in 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 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. As conditioning of the drosses is successful, future work will focus on optimizing fuming parameters.

Acknowledgements

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