



# Development of Secondary Antimony Oxides for the Application in Plastic Products

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## Abstract

IME together with four industrial partners is currently developing a new pyrometallurgical process route for the production of secondary antimony oxides from metallurgical residues, namely lead drosses. The 36 month project is funded by the German federal ministry of education and research. Antimony trioxide is widely used as flame retardant in plastics accounting for more than 70 % of today's antimony consumption. The growing demand by western industrial nations combined with the uncertain primary antimony supply by China leads to the necessity of mobilizing new antimony trioxide sources.

To achieve this goal, the project chooses an integrated approach to cover every aspect of the new process route. Namely these aspects are optimization of the lead refining process towards a more differentiated separation of accompanying elements in the different drosses, winning of antimony oxide from the antimony rich fraction and proving the applicability of the product in plastic goods.

Optimization of the metallurgical steps is done by combination of thermochemical modelling and laboratory scale trials to define the process windows of the mentioned steps. To evaluate the applicability of these findings, pilot scale trials are run in a lead refinery as well as in a TBRC for the trioxide winning process.

The full paper will be published soon after the conference in a scientific journal.

## 1 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 [2]. Currently China holds a nearly monopolistic market position for primary antimony. As the Chinese strictly control export rates of 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. 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.

## 2 The s-AmOx Project

“S-AmOx” is an abbreviation for secondary antimony oxides. The joint project – started in January 2014 - is funded as part of the German federal ministry for education and research’s MatResource call which focuses on materials for a resource efficient industry and society. The call addressed the topics substitution, corrosion protection and catalysis with the mentioned project belonging into the substitution category. All the funded ventures are accompanied by the superordinate “MaRKT” project which aims to define every undertaking’s contribution towards resource efficiency as well as to help to spread the results in an attempt to increase benefit for society and industry.

Driving force for the realization of the project is the aforementioned situation on the antimony market dealing with volatile price developments and possible supply shortage for western industrial nations with antimony trioxide playing a major role for the antimony demanding 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. Due to the relatively high reworking costs part of the slags are either deposited or even sold back to China.

To address this issue an optimization of the lead refining process is one of the project’s aims. As the complex composition of the drosses containing SnO, Sb<sub>2</sub>O<sub>3</sub> and As<sub>2</sub>O<sub>3</sub> besides PbO is the responsible for the high reworking costs. An improved softening process is applied which allows sharper separation of the accompanying elements’ oxides into three different slags containing mainly one of the mentioned oxidic compounds besides PbO. Besides that the optimized process allows to minimize lead losses to the slags as it is based on a more selective approach than state-of-the art industrial softening processes.

In a second step the antimony rich dross from aforementioned process forms the charge material for a fuming process. The aspired process needs to separate antimony trioxide from the slag by volatilization. Due to low critical values for accompanying elements in the final product, fuming parameters have to be chosen very carefully. To achieve better product quality, not only the process window and design for volatilization is taken into account but different approaches on an upstream refining of the slag are examined.

Finally the fumed off product undergoes an in depth analysis where it has to meet the same requirements as antimony trioxide produced from primary antimony. Besides the chemical composition attributes which are important for the practical application are whiteness, grain size distribution opacity and tinting strength. To determine the mentioned attributes, portions of the secondary produced oxide are worked into samples of PVC and compared to its primary counterpart according to the mentioned parameters.



### 3 Methodology

Optimization of the lead softening step is carried out according to an approach published by Friedrich & Arnold in 2011. The method aims to achieve an improved selectivity during oxidation of the accompanying elements tin, arsenic and antimony from lead bullion in the softening step. 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 quaternary subsystems 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. [4]

The described study focuses on metal phase composition and oxidation kinetics. For the s-AmOx project emphasis lies on composition of the formed drosses as they represent the raw material for downstream processing. Lead bullion is softened under use of a rotary injection unit in a 450 kg scale with a defined mixture of nitrogen and oxygen (see figure 1). Metal samples are taken and analysed by spark emission spectroscopy. Drosses are removed every 30 minutes and analysed by XRF spectroscopy. In addition to these trials, best case parameters are tested in a pilot plant at one of the industrial partner's lead refinery.

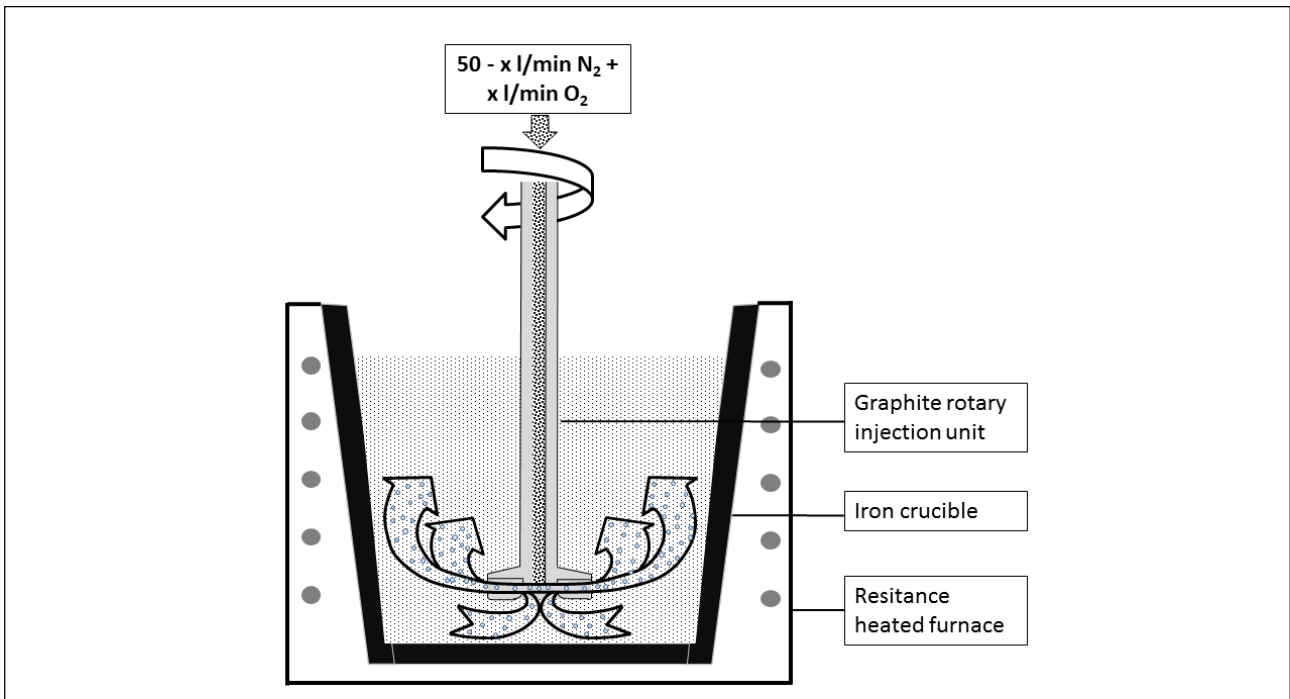


Figure 1: Setup used for selective oxidation trials



The Sb-rich drosses are used to produce antimony trioxide by fuming in a second step. Table 1 shows typical requirements for an industrial grade antimony white produced from primary antimony. Combined with the aforementioned optical criteria, these values are used as benchmark for the secondary oxides.

Table 1: Industrial grade antimony trioxide standards for the application in plastic products

Wt.-% Sb <sub>2</sub> O <sub>3</sub>	ppm Pb	ppm As	ppm Fe	Ø grain size [µm]
≥ 99,80	< 1000	< 750	< 30	1-10

In a first attempt to prove the principle of producing antimony white from mentioned drosses a laboratory scale tubular furnace (see figure 2) is used to volatilize the desired compound under different conditions without pre-treatment of the drosses. Condensates are analysed by ICP-OES. An improved laboratory scale trial setup is currently being built, featuring a small rotary drum furnace with attached bag filter (see figure 3) to produce larger samples. Furthermore the best case laboratory parameters for the fuming step will be reassessed in a pilot scale TBRC at one of the involved industrial partners.

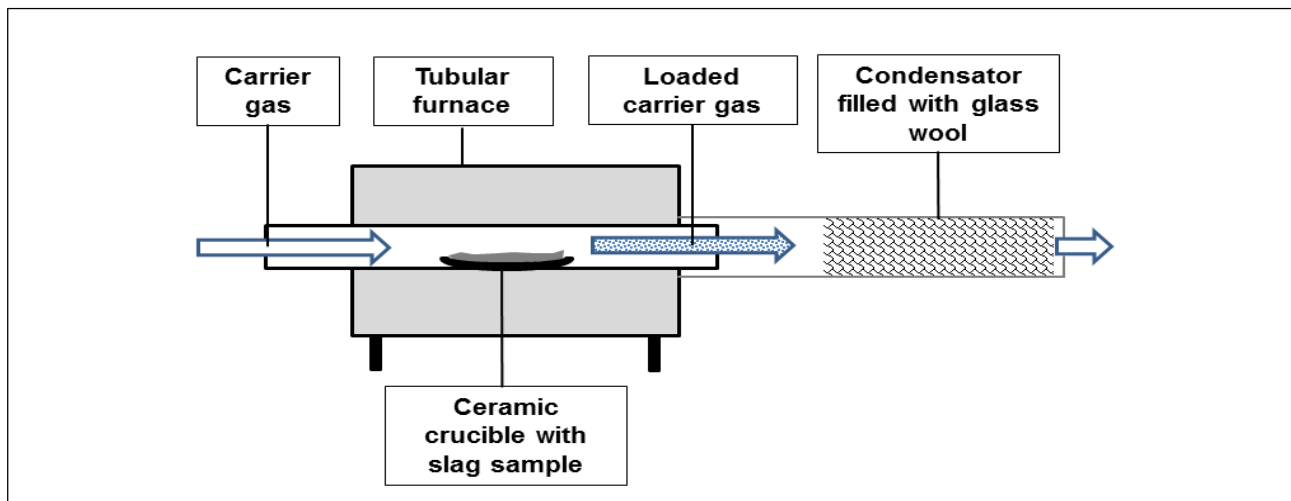


Figure 2: Setup used for fuming trials

Especially the requirements for lead and arsenic are critical for the process development. Despite pure lead oxide having a  $10^2$  to  $10^3$  times lower partial pressure than antimony trioxide depending on fuming temperature, lead content in the final product is one of the most critical factors due to high lead oxide activities in the slags. Arsenic contents hence activities in the slags are relatively low. Nevertheless As<sub>2</sub>O<sub>3</sub> contents in the condensate are critical due to its high vapor pressure. Therefore not only fuming from untreated slags is taken into consideration. Slag additives and partial reduction of lead from the slags are also investigated.

Fuming steps as well as the slag treatment possibilities are evaluated with the thermochemical simulation software FactSage 6.4™ in a first step. As the standard software does not include data for the investigated slag systems, a custom built database was developed in cooperation with *GTT-*



technologies. The database allows taking activities of the main components into account which are essential for optimization of the described processes.

## 4 Results

Results of the first laboratory scale trials for the first approach process route – selective oxidation and direct fuming from the formed slag - are pointed out. This series of trials intends to show proof of principle. Best case results indicate technical boundaries of the process without further modification.

From all the formed Sb-rich drosses – collected after selective removal of tin - antimony trioxide contents vary between 39,8 and 56,4 Wt.-%. This shows a significant increase in antimony content as industrial antimony rich drosses usually contain no more than 30 Wt.-% antimony trioxide depending on the lead bullion composition. Table 2 shows the complete slag analysis of the slag highest in antimony content, which can be seen as best case scenario.

Table 2: Composition of highest Sb-containing slag formed in the first trial series (XRF)

Wt.-% Sb <sub>2</sub> O <sub>3</sub>	Wt.-% PbO	Wt.-% SnO	Wt.-% As <sub>2</sub> O <sub>3</sub>
56,4	42,3	0,76	0,55

The high antimony content compared to relatively low Pb-content qualifies the slag as feed material for the downstream fuming process. Tin oxide content is mainly due to slag contamination with tin powder of the earlier selective tin oxidation as metal samples do not show tin oxidation in the sequence where shown slag is formed. Arsenic content is relatively high as it is regarded critical for the fuming step. Adjustment of the oxygen partial pressure to the declining Sb-content is crucial for the prevention of arsenic oxidation but practical realization is difficult due to the lack of online analysis.

The slag is fed to the fuming process carried out in the described setup without pretreatment (see figure 2). Of all the relevant fuming parameters only temperature has significant effect onto condensate composition in this setup. Antimony contents in the product vary between 98,6 and 99,6 Wt.-% Sb<sub>2</sub>O<sub>3</sub>. Product composition of the best case trial is pointed out in table 3.

Table 3: Composition of fumed secondary antimony trioxide (ICP)

Wt.-% Sb <sub>2</sub> O <sub>3</sub>	ppm Pb	ppm As	ppm Sn
99,574	4100	< 50	< 50

It can be seen that the fuming approach is successful in principle. However requirements of an industrial antimony trioxide can not be met yet due to the high lead content. Lead oxide activity in the slag has to be reduced in order to achieve lower lead oxide partial pressures during fuming. This can be done by either selective reduction of lead from the slag or addition of additives which lower lead



oxide activity relatively to antimony trioxide activity. Both possibilities are currently being investigated.

The first laboratory scale fuming setup needs to be altered due to different reasons. The condensation apparatus is not capable of catching the entire fumed product which hinders production of larger samples together with the limited feed of 10 g in the tubular furnace. The ceramic crucible itself is not moving during fuming which may lead to partial enrichment of lead oxide at the surface during the process. This might influence condensate quality as the locally increased lead oxide activity promotes lead oxide fuming. Due to these factors, the new setup shown in figure 3 is currently built. It allows production of larger antimony white samples at boundary conditions closer to actual processes.

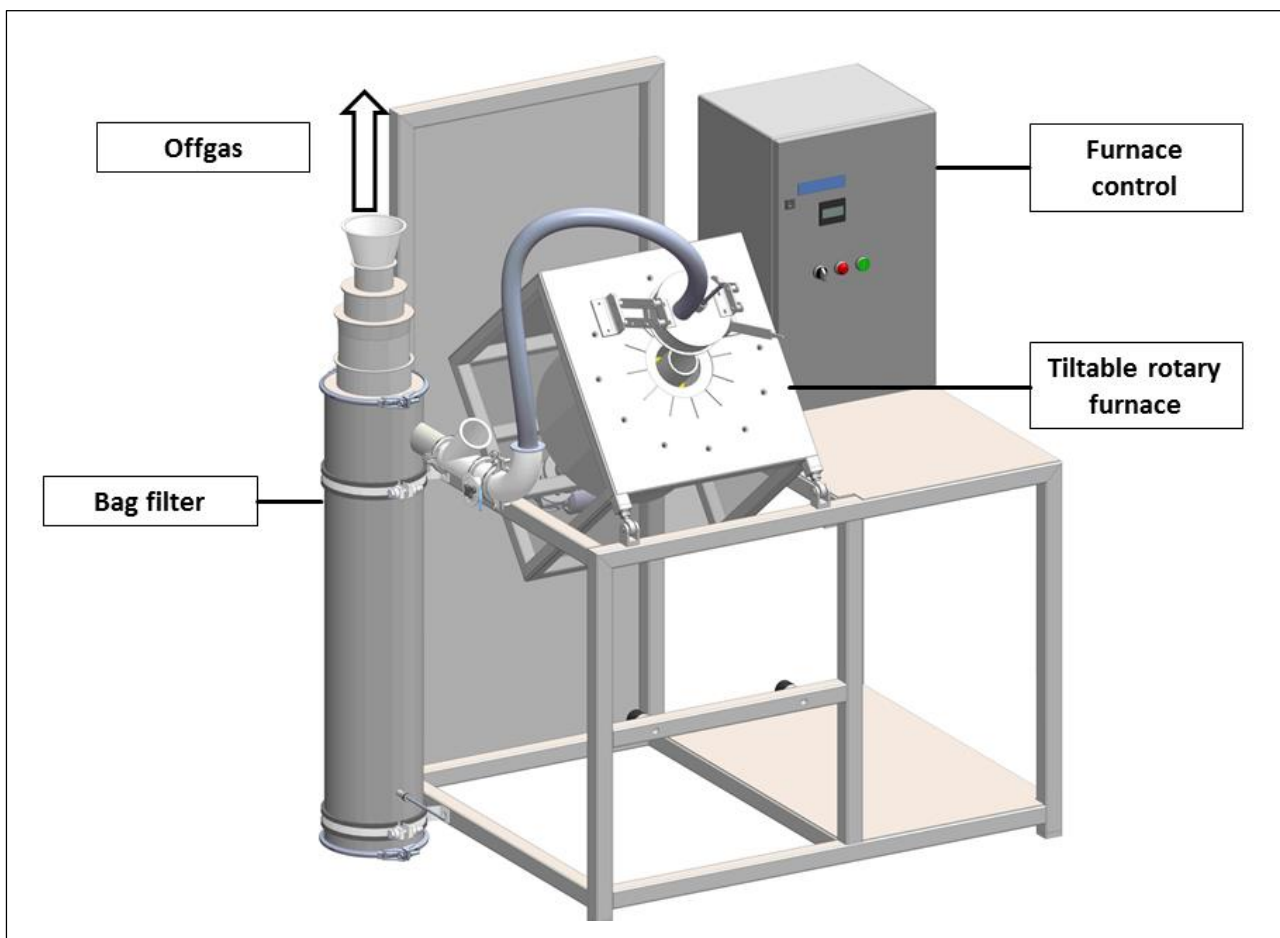


Figure 3: Improved setup for volatilization trials

## 5 Conclusion

Goal of the s-AmOx project is the industrial grade antimony trioxide production from antimony rich drosses formed during lead softening. The project's framework is based on a two stage metallurgical approach including highly selective oxidation of Sn, Sb and As from lead bullion followed by a slag fuming process. To point out the proof of principle, a first series of trials is executed and set as



benchmark for all following optimization steps. First results confirm the possibility to form drosses with more than 60 Wt.-%  $\text{Sb}_2\text{O}_3$  and low Sn and Arsenic contents by ultrasensitive oxidation. Those slags represent feed charge for the subsequent fuming step. However kinetic disadvantages occur due to lower oxygen partial pressure and can not be fully compensated by the use of a rotating gas injection unit. Aforementioned dross is then fumed in a tubular furnace under varying conditions to identify ideal fuming parameters. Secondary antimony white with more than 99,5 Wt.-%  $\text{Sb}_2\text{O}_3$  and less than 50 ppm As can be produced in this setup. However lead content remains critical and has to be lowered by further optimization of the process.

## Acknowledgement

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