Evaluation of Thermodynamic and Metallurgical Limits for Pure Sb_2O_3 Vaporization from Lead Drosses

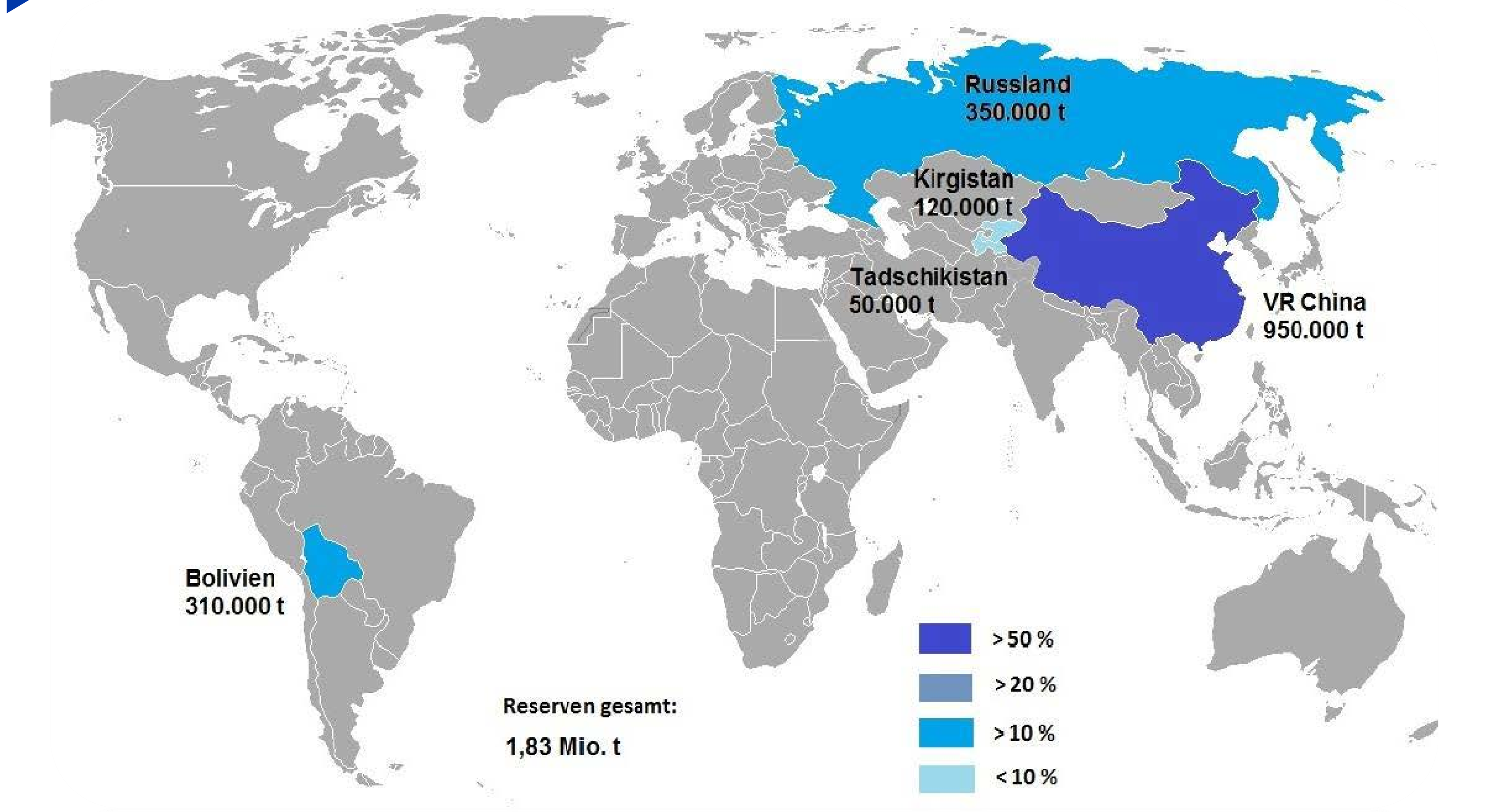

Figure 1: Global Sb-reserves

The use of antimony as flame retardant in plastic products nowadays plays a major role in the antimony processing industry with antimony accounting for over 70 % of today´s worldwide antimony consumption [1]. China holds a nearly monopolistic market position. As the Chinese strictly control export rates, they apply strong pressure to the market leading to an uncertain situation regarding the Sb-price as well as the availability of antimony for 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. Aim of the project is to develop a process for antimony trioxide winning directly from Sb-bearing residues. The product has to meet the strict regulations of plastic industry (Fig. 2) to be applicable in this sector.

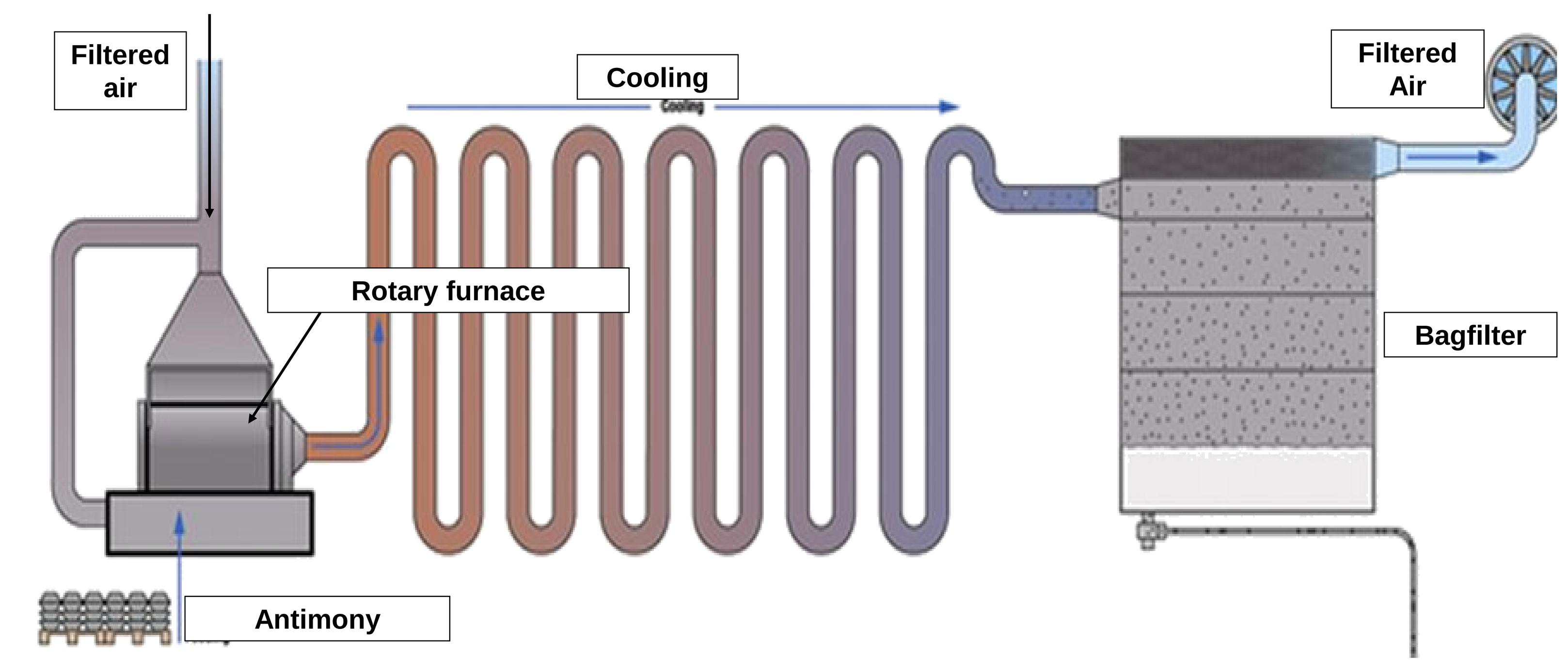

Figure 2: Conventional production of antimony trioxide from Sb-metal

Sb_2O_3 [Wt.-%]	PbO [ppm]	As_2O_3 [ppm]	Fe [ppm]	Grain size [µm]
> 98	< 2500	< 1000	< 30	0,2 - 44

The Sb-bearing drosses originate from pyrometallurgical lead refining. After decopperization, tin, antimony and arsenic are removed by oxidation via air injection (Softening: Fig. 3). Selectivity of this process is considered low due to high oxygen partial pressures leading to lead losses and simultaneous oxidation of named impurities. Via exact oxygen control which is also part of this project, drosses mainly consisting of PbO und Sb_2O_3 can be produced. However kinetic disadvantages can not be overcome. More distinctive separation of the impurity oxides in this process step leads to better fuming conditions in the following process step. Antimony rich drosses from industrial lead refining usually contain ~ 30 Wt.-% of antimony and ~ 60 Wt.-% of lead in oxide form.

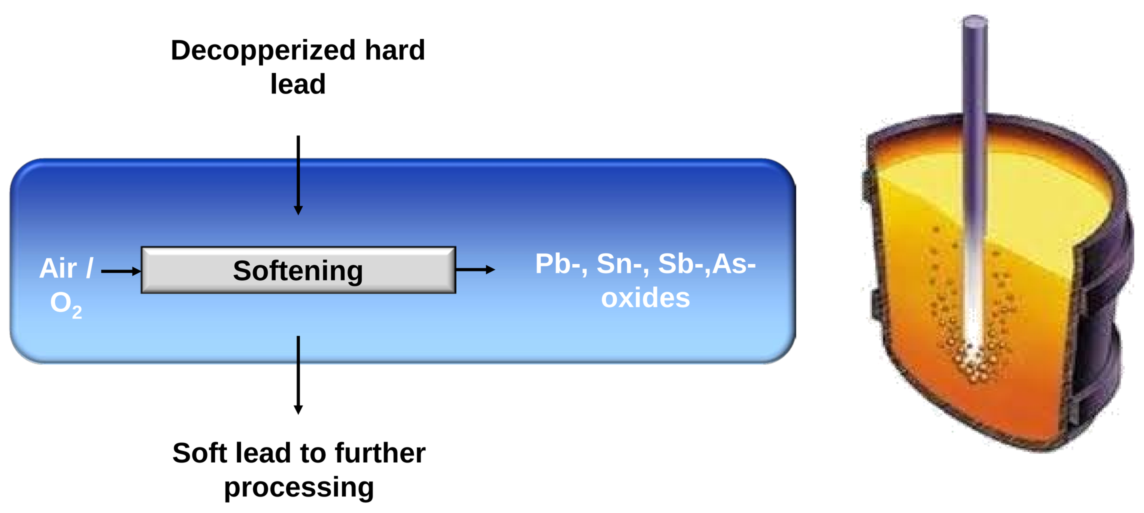

Figure 3: Origin of Sb-bearing drosses in lead raffination

Sb_2O_3 [Wt.-%]	PbO [Wt.-%]	ZnO [Wt.-%]	SnO_2 [Wt.-%]	As_2O_3 [Wt.-%]
30 - 35	60 - 65	< 1	< 0,5	< 0,2

Thermochemical boundaries for fuming of qualified antimony white from drosses are evaluated in the forefront of experimental investigations through detailed thermochemical modelling in the Sb_2O_3-PbO system. Initially activities and vapor pressures are calculated from literature data. Then partial pressures are calculated at given temperatures and compositions.. From these values a partial pressure ratio of Sb_2O_3 to PbO is determined. This also describes the molar Sb_2O_3 to PbO ratio in the condensate quality as fuming from the surface happens in this ratio. Process boundaries can be set via comparison to the required condensate composition. Figure 4 shows that unconditioned drosses do not fit these boundaries. Preconditioning of the drosses before fuming therefore is inevitable.

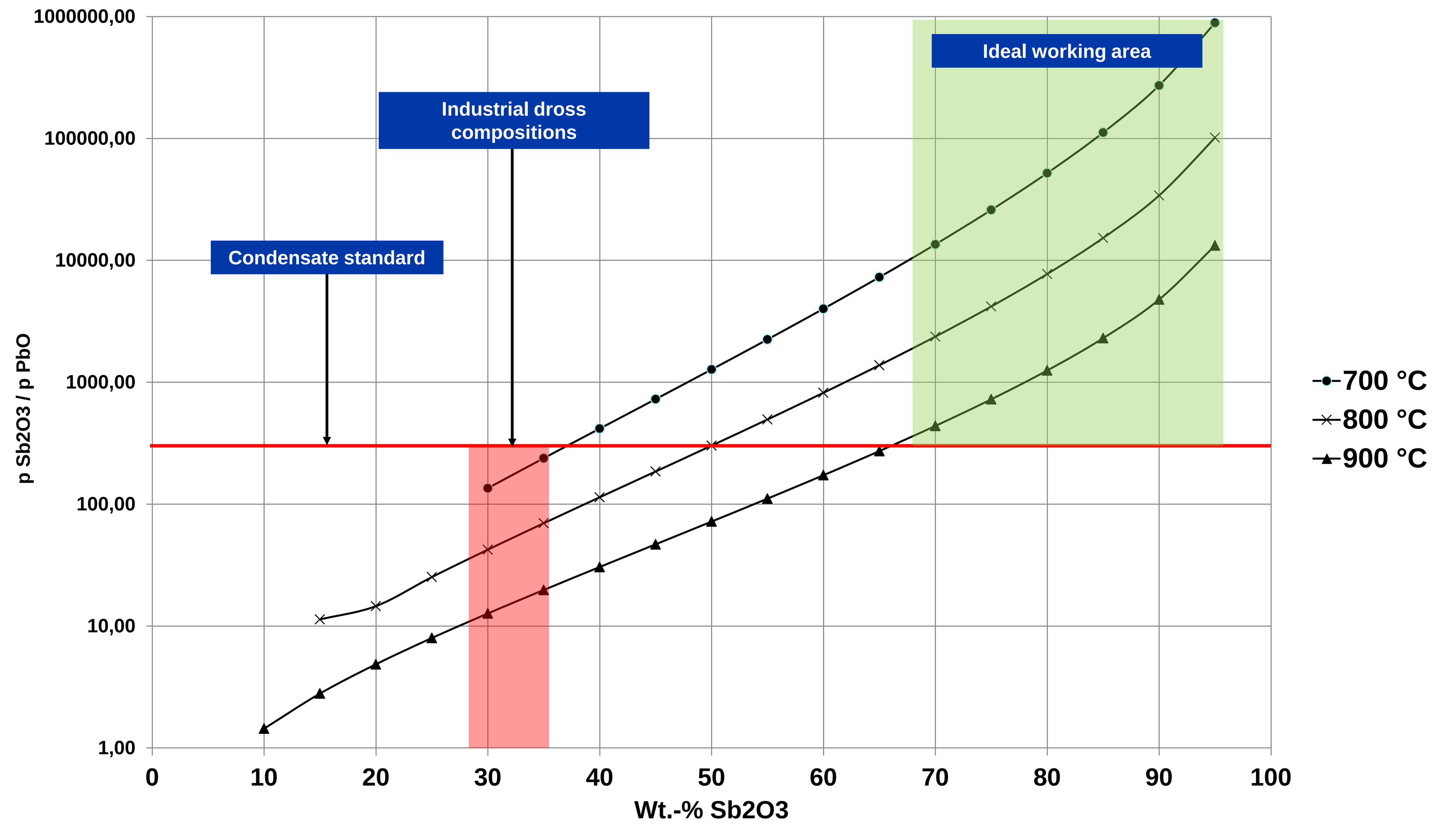

Figure 4: Calculated vapor pressure ratios as function of temperature and dross composition

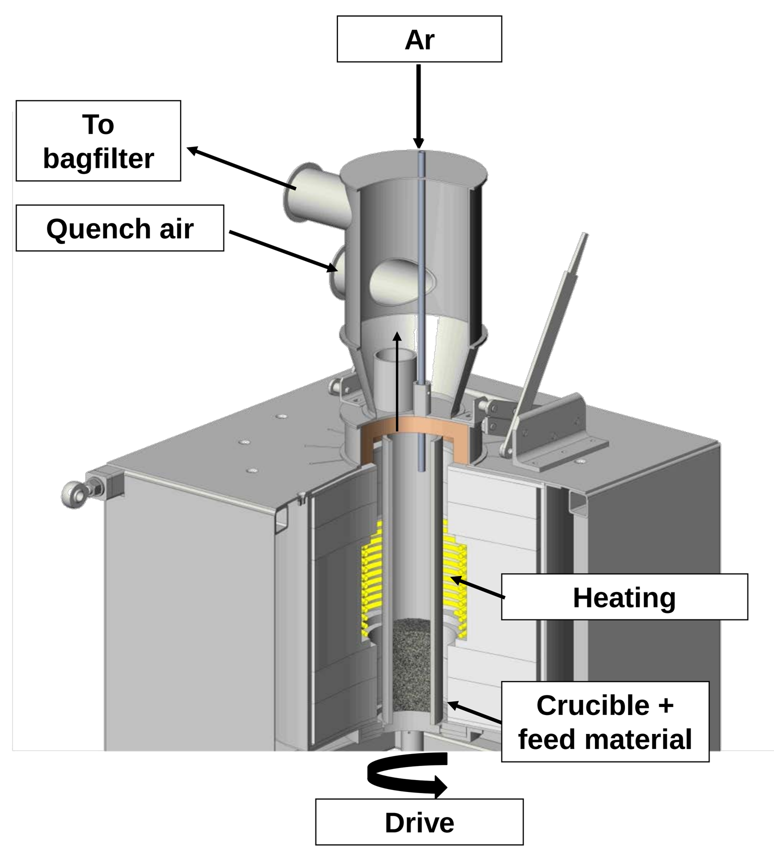

Figure 5: Fuming reactor at IME

Figure 6: Fuming trial (lid open)

Preconditioning of the drosses is achieved by selective carbothermic reduction of lead oxide. Within the project, optimal reduction parameters have been modelled and experimentally validated. Drosses are successfully enriched to 75 Wt.-% Sb_2O_3 by preconditioning and thus fit the defined working area. Lead yields in the preconditioning step are 90 %. Higher dross enrichment is possible by changes in reduction parameters but will result in higher antimony losses to the metal phase.

After preconditioning achievable condensate qualities are evaluated in an IME designed fuming reactor (Fig. 5). The lab scale activities within the project identified temperature and slag composition as major factors for condensate quality. Figure 6 shows best and worst case lab scale results fumed from industrial slags in comparison to the standard. Lead oxide content remains problematic in these condensates due to complex dross systems.

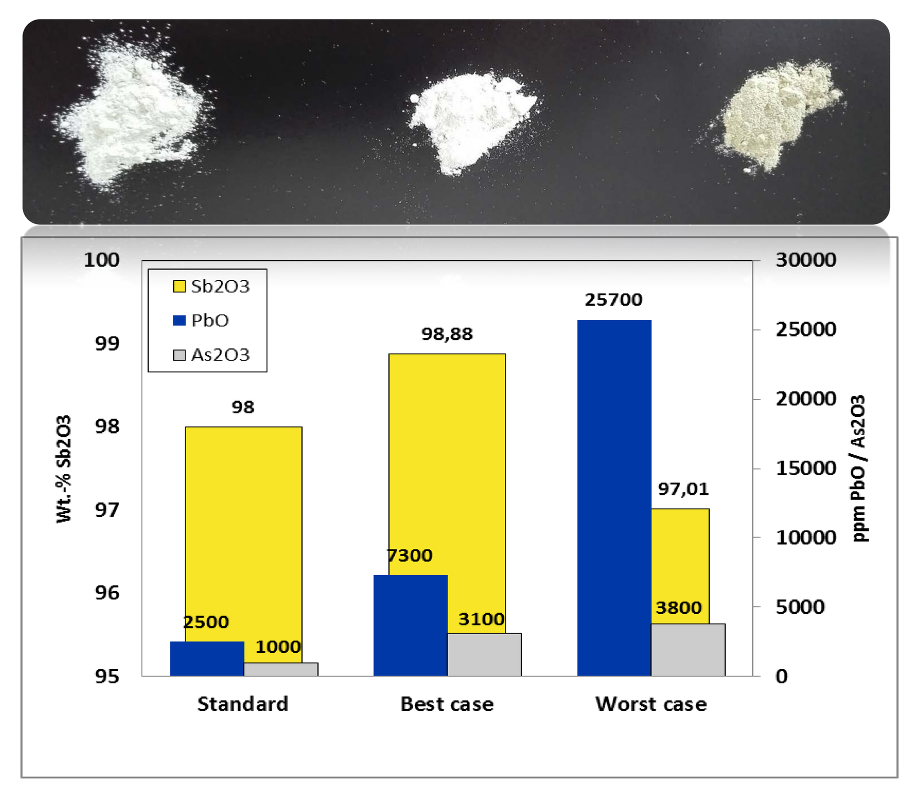

Figure 7: s-AmOx condensates in different qualities

Experiments with synthetic drosses describe vapor pressure behavior in the binary PbO- Sb_2O_3 system without the effects of accompanying oxides. Figure 8 shows experimental results in comparison to the calculations. The experiments clearly show similar vapor pressure behavior with slight absolute offset. However they also confirm the possibility to fume qualified Sb_2O_3 from the binary system with minimal changes of the dross requirements.

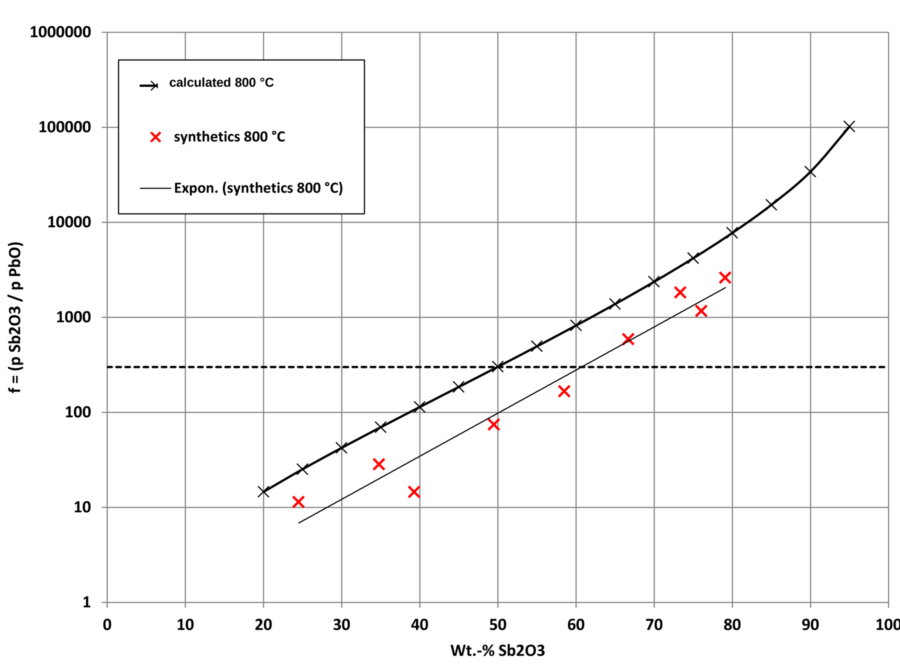

Figure 8: Experimental vapor pressure ratio at 800° C as function of dross composition

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[1] Anderson CG (2012) The metallurgy of antimony. Chem. Erde, 72:3-8

[2] Roskill Information Services Ltd (2011) Study of the antimony market. Roskill, London

[3] European Commission (2015) Report on Critical raw materials for the EU 2014. European Union

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