



# Investigations into high temperature separation of antimony from metal oxide varistors



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## ABSTRACT

Very little research has been done into methods for recycling antimony from end of life products. This study investigates separation of antimony from metal oxide varistors (MOVs), where antimony is present between 3 and 5 wt%. In MOVs, antimony is found in spinel ( $Zn_{2.33}Sb_{0.67}O_4$ ,  $Zn_7Sb_2O_{12}$ ) and pyrochlore ( $Zn_2Bi_3Sb_3O_{14}$ ) compounds. Due to the low concentration of antimony in MOVs, a leaching pretreatment using dilute sulfuric acid was performed where antimony remained in an insoluble solid. The leaching pretreatment resulted in a more than fivefold increase in the antimony concentration. In order to separate antimony from the MOV leaching residue, it was subjected to a simple thermal treatment and carbothermal reduction at temperatures of 500–1300 °C. Results showed that 80% of antimony can be separated from the leach residue by heat treatment at 1100 °C, while 85% of antimony can be separated from the leach residue at 1100 °C using carbothermal reduction. Once separated, antimony can be recovered from the gaseous phase due to its volatile nature. Results show that antimony recycling from MOVs is a promising source of secondary antimony.

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## 1. Introduction

Antimony is a strategic and critical metal due to its supply, availability and increased use in consumer goods (CRM-EU, 2010). Antimony is listed as a critical metal for the European Union (CRM-EU, 2010) as well as a strategic metal for the United States Department of Defense (NDS, 2009). The European Union is entirely dependent on imports of antimony, though total EU consumption in 2007 (792 tonnes) only accounted for 0.5% of global production (CRM-EU, 2010). It is predicted that, apart from antimony, a national security emergency in the US would entail a severe shortage of just three other metals (NDS, 2009). In 2013 the US imported 25,000 metric tonnes of antimony ores and concentrates, oxides and metal for consumption (Guberman, 2014). In total, 85% of the antimony used in the US was imported, predominantly from the People's Republic of China (74%), Mexico (10%) and India (7%). In 2008 a total of 187,000 tonnes of antimony was produced, 91% of which was produced in China. It is predicted that there will be a large deficit of antimony by 2020 (CRM-EU, 2014), and antimony will reach its peak production by 2018 (Sverdrup et al., 2017). The

amount of extractable antimony remaining is 1.8 million tonnes (Carlin, 2013), while the amount extracted up to 2012 was 6.7 million tonnes (Sverdrup et al., 2017), which means that only 21% of antimony remains for extraction. However, the recoverable amount of antimony is 7 million tonnes, not including undiscovered extractable antimony (Sverdrup et al., 2017).

Antimony is typically present in small amounts in industrial and commercial products, thus making recycling difficult (Graedel and Reck, 2014). Conventional recycling routes are typically not applicable for rare metals such as antimony if no prior pretreatment step(s) are performed (Rombach and Friedrich, 2014). Pretreatment is performed in order to increase the antimony concentration or to allow for proper separation of metals in further hydro- or pyrometallurgical recycling steps. Antimony recycling in the USA is currently limited to recycling of lead-acid batteries where the secondary antimony is put back into the construction of new lead-acid batteries. In the Netherlands about 375 tonnes of antimony is recycled per year while annual consumption is approximately 1300 tonnes (van Velzen et al., 1998).

Over 50% of antimony used is as a flame retardant (Kirk-Othmer, 1992) in, for instance, plastics, curtains, etc. Many items containing antimony end up as municipal solid waste (MSW) having an

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antimony concentration of 0.026–0.11 wt% (Van Gerven et al., 2005) or 0.001–0.006 wt% (Paoletti et al., 2001). The low antimony concentration means that designing a recycling route from an MSW waste stream can be difficult and cost ineffective (Rombach and Friedrich, 2014). Metal oxide varistors (MOVs) contain between 3 and 5 wt% antimony, which, with the exception of lead acid batteries, is one of the highest concentrations in consumer goods.

The focus of this research was on characterisation of MOVs before and after pre-treatment, along with determination of the concentration of antimony in the material and identification of antimony species formed during thermal treatment. To increase the antimony concentration, the MOV was pulverised and leached in a pre-treatment step resulting in a fivefold increase in antimony concentration. The leach residue was subjected to a simple heat treatment and carbothermal analysis in nitrogen atmosphere. Findings suggest that heating the MOV leaching residue and separation of antimony below 1000 °C was not possible. However, carbothermal reduction of the MOV leaching residue showed it was possible to separate antimony at temperatures near 900 °C. Antimony separated from the MOV residue can be recovered through condensation from the gaseous state.

There are several studies on the refining of main metals from raw materials and recycling sources. According to the report on the environmental benefits of recycling (Grimes et al., 2008), Al, Cu, Pb, Ni, Sn, and Zn, recycling processes require about a quarter of the energy of primary processing, and also minimise CO<sub>2</sub> emissions. Although we could not produce any data about antimony refining from primary and secondary sources, we can infer that Sb recycling has a smaller carbon footprint and needs less energy comparing the production from primary sources. High temperature industrial processes operate furnaces or kilns at temperatures greater than 500 °C and are considered energy intensive. However, using energy efficient equipment on an industrial scale can reduce energy consumption. This research constituted a lab scale feasibility study conducted in order to determine whether secondary antimony could be recovered from used MOVs.

There are 5 million more tonnes of antimony available from recoverable sources such as waste than are available for extraction (Sverdrup et al., 2017). It is therefore necessary to develop new methods to recover antimony from items which contain it. Other than recycling and then reusing antimony from lead acid batteries, no antimony is currently recycled. This research focused on a specific type of antimony containing waste and showed that the antimony concentration could be increased via leaching pretreatment. It was also shown that the concentrated antimony could be separated and concentrated from the flues after a simple and carbothermal heat treatment. Due to environmental concerns most research is focused on antimony stabilisation in waste. However, this investigation focused on recovery of antimony using its thermochemical properties.

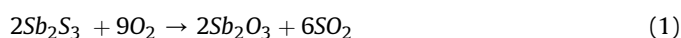
## 2. Background

In general, the MOV contains three phases: (I) bulk zinc oxide phase accounting for nearly 90% of the MOV, (II) bismuth oxide phase, and (III) antimony containing phase. Cobalt, manganese, and nickel impurities are also present in the MOV at less than 1 wt% each. Previous research has shown that leaching pulverised MOVs with a pH 3 sulfuric acid solution resulted in the bulk zinc oxide phase being separated from the bismuth oxide and antimony containing phases (Gutknecht et al., 2015). The leachate containing mainly zinc can be purified and used for zinc electro-winning. The insoluble leaching residue containing mainly bismuth oxide and antimony compounds (Zn<sub>7</sub>Sb<sub>2</sub>O<sub>12</sub>, Zn<sub>2.33</sub>Sb<sub>0.67</sub>O<sub>4</sub>, and Zn<sub>2</sub>Bi<sub>3</sub>Sb<sub>3</sub>O<sub>14</sub>) can be a source of secondary antimony. The impurity

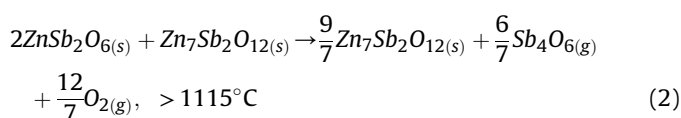
metals were distributed between the leachate and residue.

The MOV residue showed an increase in antimony concentration by a factor of 5–18 wt%. (Gutknecht et al., 2015). Characterisation of the residue revealed antimony to be contained within several compounds: spinel (Zn<sub>7</sub>Sb<sub>2</sub>O<sub>12</sub>, Zn<sub>2.33</sub>Sb<sub>0.67</sub>O<sub>4</sub>) and pyrochlore (Zn<sub>2</sub>Bi<sub>3</sub>Sb<sub>3</sub>O<sub>14</sub>). Since the antimony was not released from these compounds in fairly severe acid leaching, it was decided to investigate high temperature treatment routes, such as heating in an inert atmosphere (simple heat treatment) and reducing conditions (carbothermal reduction) to determine the temperature range needed for separation of antimony from the spinel/pyrochlore phases found in the leached MOV residue.

Low grade stibnite (Sb<sub>2</sub>S<sub>3</sub>) ores, containing less than 25 wt% antimony, typically produce antimony oxide by volatilisation (Anderson, 2012). Stibnite is converted to antimony oxide at 1000 °C and the gaseous antimony trioxide is condensed and collected (Anderson, 2012). The reaction is given in Eq. (1).



Since the antimony concentration is less than 25 wt% in the MOV leach residue, high temperature oxidation was considered to be a suitable process for recovery of antimony. Previous work has shown that temperatures higher than 1350 °C are needed to decompose  $\alpha$ -Zn<sub>7</sub>Sb<sub>2</sub>O<sub>12</sub> to ZnO while releasing Sb<sub>4</sub>O<sub>6</sub>(g) and O<sub>2</sub>(g) (Filipek and Dąbrowska, 2008). When heated in argon, samples with ZnO and  $\beta$ -Zn<sub>7</sub>Sb<sub>2</sub>O<sub>12</sub> remain in the solid state until approximately 1115 °C when Zn<sub>7</sub>Sb<sub>2</sub>O<sub>12</sub> starts to decompose according to the reaction given in Eq. (2) (Filipek and Dąbrowska, 2009).

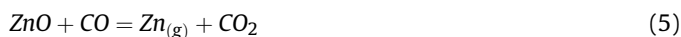


Work by (Filipek and Dąbrowska, 2008) suggests that the breakdown of the spinel phase occurs at temperatures above 1115 °C in argon, which would then be the temperature at which it might be possible to recover antimony as Sb<sub>4</sub>O<sub>6</sub>(g).

Carbothermal reduction could be an alternative separation method for antimony. In carbothermal reduction, carbon acts as a reducing agent. When carbon is present with the metal oxide two reactions take place simultaneously, as given by Eqs (3) and (4) (Rosenqvist, 1974).



One example where these reactions are utilised is in high temperature zinc production, where carbon is added to zinc oxide causing carbothermal reduction of zinc according to the reaction given in Eq. (4) (Truesdale and Waring, 1941). Equation (5) is thermodynamically favourable at temperatures above 907 °C (Roine, 2003) and has been proven to work in zinc production (Gordon et al., 2003).



Antimony oxides can be reduced with charcoal in a reverberatory furnace at temperatures near 1200 °C, however there is significant loss of antimony due to volatilisation during this process (Anderson, 2012). Antimony reduction proceeds according to Eqs. (6) and (7).

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