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Original Scientific Article

Treatment of Antimony-Rich Waste Streams

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Abstract: The use of antimony in various chemical industries represents a potential source of environmental pollution, that occurs by discharg of untreated wastewater generated in the watercourses. Another sources of this pollutants can be individual sources from improper recycling of products containing antimony as, for example, of old batteries containing antimony in the bars and in the electrolyte.
Here, it is suggested to extract antimony from waste water, with the possibility of application to different flows and concentrations of metals.

INTRODUCTION

Lead-acid batteries production and recycling plants are common sources of antimony in waste streams, because of its common usage as alloying element in lead grids. Antimony can also be found as an additive in car brake linings (in form of antimony(III) sulfide), in heads of safety matches, as a catalyst in some industrial processes (PET production) (Erosa 2008) and as a colorant for ceramics. In waste streams antimony can be found in many forms, including very toxic and corrosive fluorides and chlorides, in concentrations as high as 44 μg/l (PET production), which is well above maximum allowed concentration of 5 μg/l for drinking water. Extraction of antimony from waste streams (with 4 – 12 mass % of antimony) is cost effective, considering its price (10$ per kilogram). However, removal of antimony requires special conditions that can only be achieved in separate facility.

EXPERIMENTAL

Removal of antimony from waste water

Research and scientific approach to the problem of antimony in waste streams is rarely found in publications, partly because of its very low concentrations in most of industrial waste streams. Apart from sources mentioned above, antimony can be found in waste waters from glass production facilites (up to the 450 mg/l, depending on the technology), in streams from incineration plants (up to the 4 mg/l) and in waste waters from anode sludge treatment (up to the 500 mg/l) (Fujita 2006). In Germany, as well as in Bosnia and Herzegovina, upper limit of antimony that is alowed in waste waters infusing natural streams is 0.3 mg/l.

Due to the amphoteric nature of its ions, reactions of antimony in waste streams are pH dependent and are quite diverse. In general, in alkaline envirnoments antimony is mainly in the form of antimonite anions, while antimone cations are main form in acidic environments.

Behavior of antimony(III) and (V) in different pH is shown on Figures 1 and 2. Analysis of the influence of pH is important because its precise adjustment allows precipitation and extraction of all present forms of antimony. If pH value is below or above provided limits precipitation of antimony is hindered, with oxidation and reduction becoming major processes.

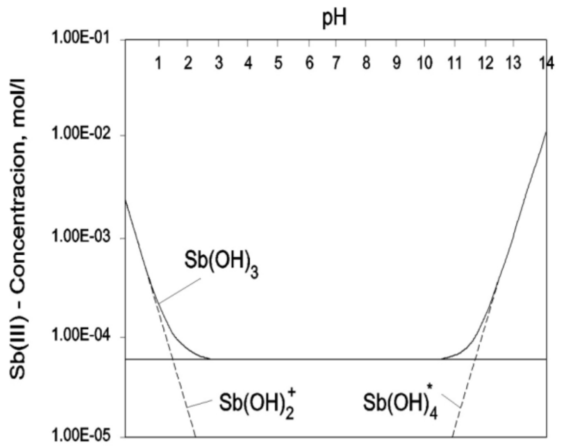

Figure 1: Solubility and concentration of antimony (III).

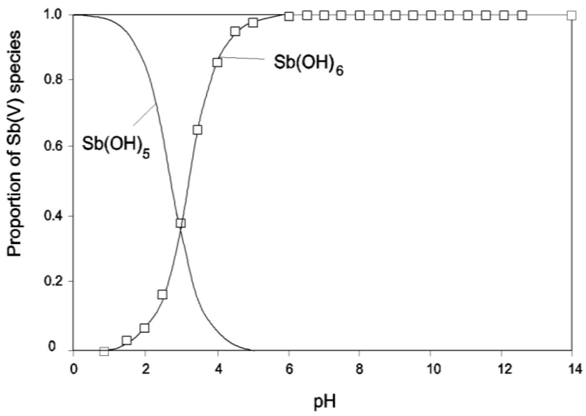

Figure 2: Solubility and concentration of antimony (V)

Main difficulites in the process of antimony removal arise from inability to accurately controll the pH value, by adding acid or base. Each sample that is to be treated must be tested separately and, on the basis of obtained results, sequence and quantities of required reagents has to be determined.

It has been found, in some experiments conducted in Japan, that the addition of adsorbent (eg. iron(III) chloride) can have significant influence on removal efficiency (Gannon 1986). In some research dealing with removal of antimony(III) oxide, published by Ganon and Wilson, significant improvement was attributed to the presence of calcium hydroxide rather than the chosen sequence of pH alteration. They also found that addition of aluminium hydroxide had no effect on the removal of antimony, while iron(III) salts significantly improved the process. Detailed insight into different aspects of the process can be found in works of Erosa (Erosa 2008). He showed that some methods that were succesfully used to remove antimony in one case can be absolutely inefficient in the other (eg. active charcoal is good adsorbent for antimony(V), but in some cases, as in pH range from 4 – 10, shows no effect).

Numerous researches showed that the addition of iron chloride leads to a very satisfying results, which is, for neutral and alkaline environment, shown on Figure 3.

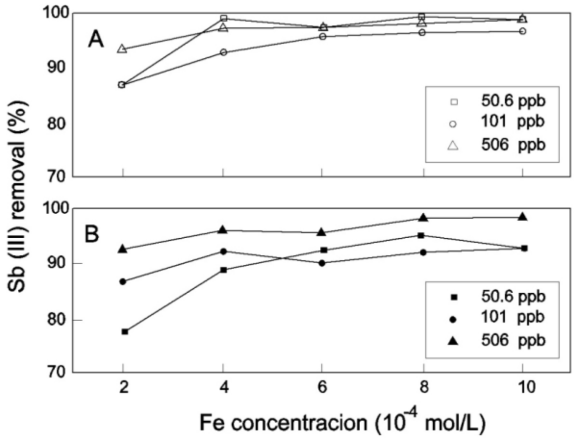

Figure 3: Extraction of antimony(III) compounds by adding iron(III) chloride: A. acidic environment (pH = 6 ± 0.2); B. weak alkaline (pH = 7.8 ± 0.2); temperature 25 ± 1 °C.

In the pH range between 6 – 8, efficiency of extraction is as high as 98%, regardless of initial concentrations.

Treatment of waste streams from battery-recycling plants

Recycling of used lead-acid batteries includes extraction of metallic components and their recycling, during which antimony(III) and (V) oxides can be found in waste gas. Waste gas is purged through waste water, which is than treated with iron(III) chloride and sodium hydroxide. Alkaline environment causes hydrolysis and preciptation of red-brown iron(III) hydroxide, antimony compounds adsorbs on the obtained precipitate, and are easily removed from the waste water.

Proposed technological process is based on classical flocculation-precipitation approach, the precise control of pH being the most important issue.

A typical scheme for the treatment of wastewater containing antimony is shown in Figure 4.

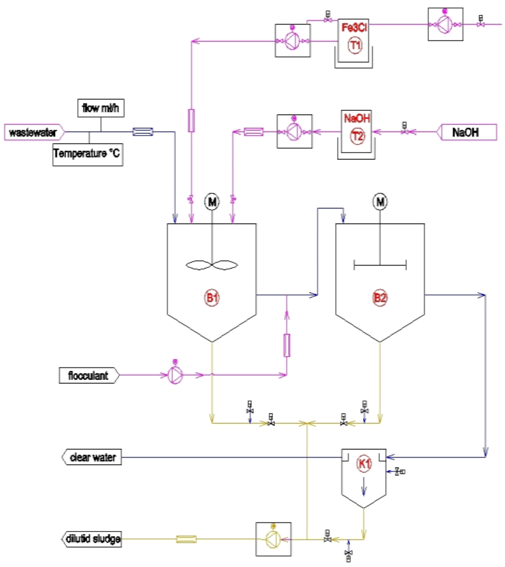

Figure 4: Schematic diagram of a typical antimony-containing wastewater treatment plant (Anlagenkonzept der HST 2012)

CONCLUSION

Antimony compounds are considered as potential polutants of drinking water and natural water streams. Some researchers compare its damaging effect to that of arsenic. Some research studies showed that iron(III) chloride can be used to reduce antimony levels to allowed limits. Described methods were succesfully used in large scale production plants. Considering that every waste water has distinctive properties, separate testings should be done, including on-site testings. For optimal process operation it is necessary to use precise measuring and automated process-controling technique, with well defined process conditions, which includes optimal pH values and time intervals for adding desired reactants. This represents the only way to enhance succesful and effective operation of industrial plant.

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Summary/Sažetak

Upotreba antimona u različitim hemijskim industrijama predstavlja i potencijalni izvor zagađenja životne sredine, ispuštanjem nastalih neprečišćenih otpadnih voda u vodotoke. Slijedeći izvor ovog zagadživača predstavljaju i pojedinačni izvori nastali nepropisnim recikliranjem proizvoda koji sadrže antimon kao naprimjer starih akumulatora koji sadrže antimon u rešetkama a i u elektrolitu. Ovdje je dat predlog za izdvajanje antimona iz otpadnih voda, sa mogućnošću primjene na različite protoke i koncentracije metala.