EXPERIMENTAL STUDY OF ANTIMONY ADSORPTION ON MAGNETITE IN AQUEOUS SOLUTIONS

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Abstract

This paper presents the results of an experimental test for non-radioactive antimony removal from aqueous solutions using magnetite (Fe_3O_4) powder. Antimony (Sb) solubility in water was tested in autoclave using primary heat transport conditions. Solution obtained from the autoclave was sent to Inductively Coupled Plasma Optic Emission Spectrometry (ICP-OES) for quantitative analysis of Sb and a part of it was used for the adsorption tests. Furthermore, it was studied how pH influences antimony adsorption onto magnetite surface. After adsorption, solutions were filtered on Cellulose Mixed Ester membrane to remove magnetite powder and then the aqueous solutions were sent to ICP-OES to determine the Sb concentration. Forwards, magnetite powder from the filters were examined by optical microscopy. The experimental tests have shown that antimony adsorption on magnetite is decreasing at high pH of solution.

Keywords: *Antimony removal, Magnetite powder, pH influence, Cellulose mixed ester membrane*

Introduction

In nuclear power plants corrosion and activation of structural material and its re-deposition on out of core surface is of significance as far as structural integrity and radiation exposure to the workers are concerned. Component integrity and radiation dose to employees are two important factors for safe and economic operation of a nuclear power plant.

Problem of radiation exposure due to activated antimony (Sb) has arisen in some of the nuclear power plants. In the Pressurized Heavy Water Reactors (PHWRs) coolant pumps of the primary heat transport (PHT) system operate at high pressure and temperature. Pump seals and bearings of the pump contain antimony-impregnated graphite. Due to these aggressive conditions, traces of Sb come into the PHT system by erosion/corrosion either in ionic or submicron particulate form.

A schematic circuit of Sb activation and re-deposition mechanism in PHWRs is presented in Fig. 1. Under the reducing conditions of PHT and radiation-induced reduction, Sb ionic form can be reduced to lower oxidation state or to metallic nanoparticles. Thus, circulation and/or deposition of Sb on zircaloy surfaces inside the core of the nuclear reactor take place. Neutron flux present in the reactor core activates Sb^{121} and Sb^{123} to radioactive isotopes Sb^{122} and Sb^{124}, respectively, by neutron and γ reaction. Part of this activated Sb^{122} and Sb^{124} gets released and are deposited on the magnetite-coated carbon steel (CS) surface outside the core or on steam generator tube surfaces due to various mechanisms like surface charges, ion exchange and physical sorption. The release of Sb activities from reactor core occurs during the draining of steam generator and the header-level control operation carried out at the time of reactor shutdown. This might be due to the possibility of Sb(III) oxidation to Sb(V) by air ingress in the system [1].

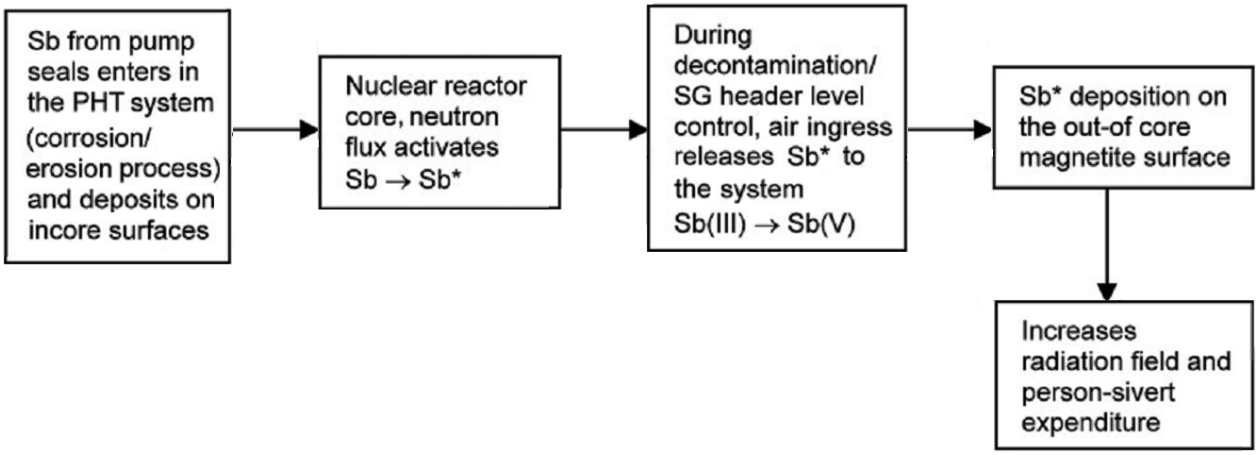


Fig. 1 Schematic of Sb activation and re-deposition mechanism in PHWRs. [1]

Standard water treatment systems (demineralizers, chemical additives, and ion selective media) are effective for the removal of radio-cobalt but generally inefficient for the removal of radioactive antimony [2, 3]. The difficulty of antimony removal stems from its complicated chemistry: antimony can exist in solution in two oxidation states (+3, +5) and in several species (e.g. $Sb(OH)_6^-$, $Sb(OH)_3$, $Sb(OH)_4^+$), depending on the pH and redox conditions.

However, chronic build-up of radio-antimony fields on out-of-core surfaces is limited due the short half-lives of Sb^{122} ($t_{1/2}$ = 2.7 days) and Sb^{124} ($t_{1/2}$ = 60 days), and the limited production rate of Sb^{125} in the absence of fuel defects [4].

Experimental work

The present work studied adsorption of non-radioactive antimony on magnetite powder (Fe_3O_4) from aqueous solutions in various pH and temperature conditions. Moreover, antimony dissolution in a LiOH solution was investigated in autoclave using primary heat transport condition.

Fig. 2 presents an autoclave that has been used to dissolve a small quantity of metallic Sb and to obtain the same species of antimony that can be found in primary heat transport system circuit from a CANDU NPP.



Fig. 2. PROLABO autoclaves

To prevent oxidation of Sb(III) to Sb(V) in autoclave, it has been performed a degasification procedure. It is known that air ingress in the system in the shutdown period of the reactor may leads to Sb(V) state. Fig. 3 shows the antimony species that can be formed depending on the pH and antimony oxidation states. Reduction and oxidation mechanism is given, as follows:

$$Sb(OH)_3 \underset{H_2}{\overset{O_2}{\rightleftarrows}} Sb(OH)_6^-$$

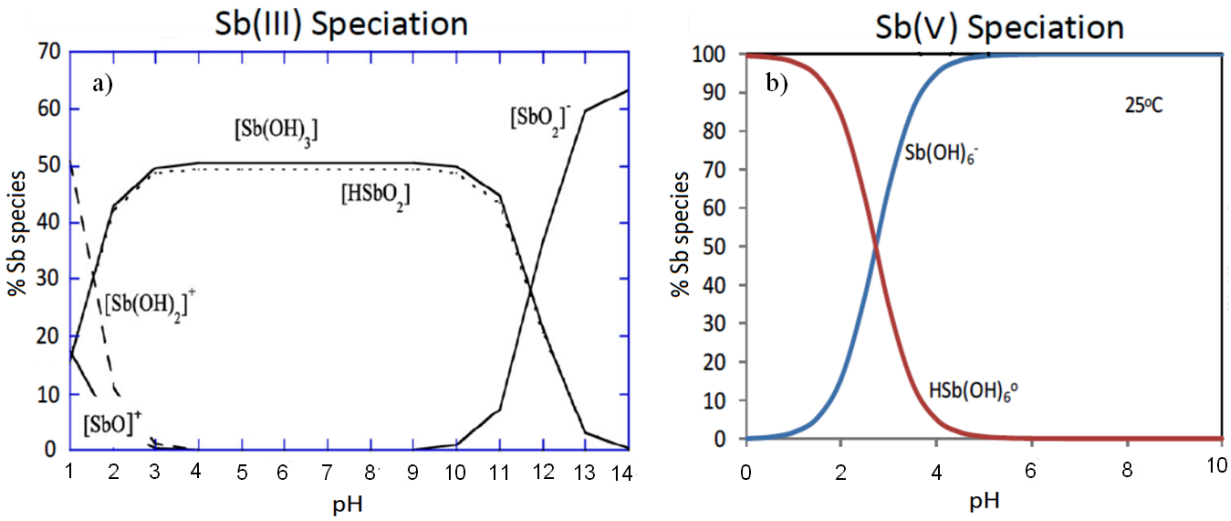


Fig. 3. Distribution of dissolved species of a) Sb(III) and b) Sb(V) at 25 °C as a function of pH [5]

After dissolving a part of the metallic antimony in the autoclave at temperature and pressure, a solution with unknown antimony concentration was obtain.

The quantity of antimony dissolved in the liquid was determined using an Inductively Coupled Plasma Optic Emission Spectrometer (ICP-OES). The solution obtained from autoclave was used for the adsorption tests and it was preserved into a box with an inert argon environment (see Fig. 4) in order to prevent oxidation to Sb(V).

However, during solution transportation from autoclave to the inert box it is possible that a part of Sb(III) may be oxidized to Sb(V) due to air ingress.

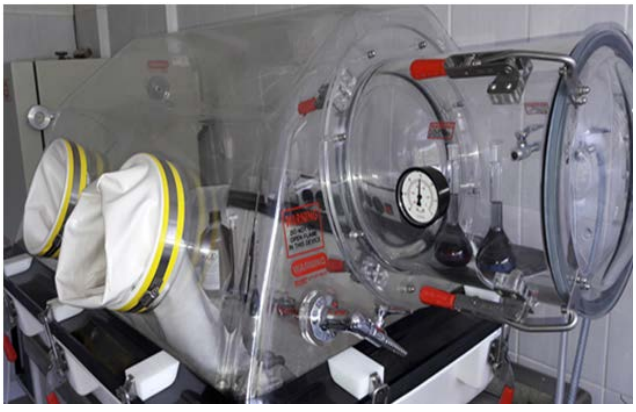


Fig. 4. Box with Argon environment

For the adsorption tests of antimony have been prepared several solutions which were kept in different pH, temperature and atmospheric conditions. The working steps for antimony adsorption test on magnetite powder (Fe_3O_4) from aqueous solutions are summarized in Fig. 5.

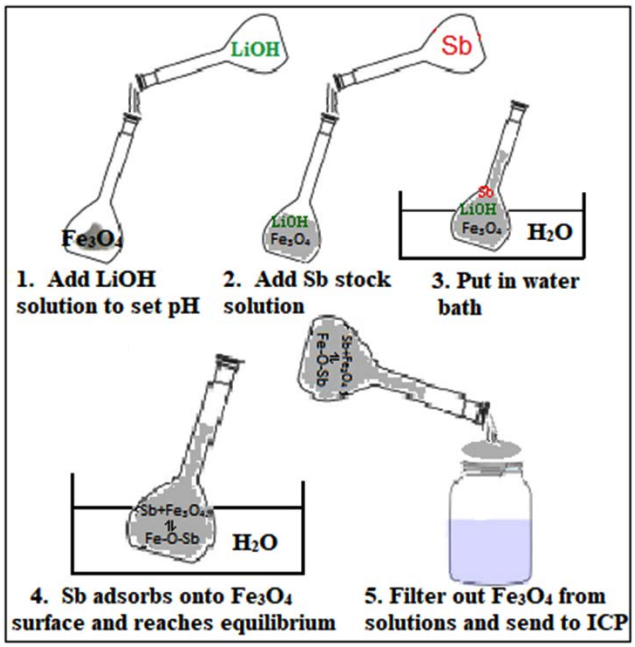


Fig. 5. Working steps for laboratory tests

Therefore, in several volumetric flasks a magnetite powder has been placed and the pH was set at 6, 10.5 and 12, respectively. A known quantity of antimony solution obtained in autoclave was added in the volumetric flasks, and then some flasks were placed to react in a water bath at 85 °C and others were kept in atmospheric condition at 25 °C. A third set of samples were placed in a box with Argon at 25 °C.

After the reaction took place, all the samples were filtered (see Fig. 6) on cellulose mixed ester filter paper to remove magnetite powder and the antimony adsorbed on the oxide (see Fig. 7).



Fig. 6. Filtered solutions on CME filter paper



Fig. 7. Magnetite powder from filter papers

Filtered solutions were sent to ICP-OES (Fig. 8) for quantitative analysis of antimony and the powder from the filter papers was examined using an Olympus GX 71 light microscope.



Fig. 8. Picture of the ICP-OES equipment

Results and discussion

Metallic antimony powder placed at temperature and pressure in autoclave, using primary heat transport conditions, in order to obtain a stock solution with similar species, was not dissolved entirely after 72 hours of testing.

Antimony stock solution used in the adsorption tests was first analysed to ICP-OES and the analysis report showed that only a part of Sb was dissolved in the solution. If the metallic antimony had undergone a complete dissolution in autoclave, the concentration of antimony in the solution should have been of 10 mg/l, and not only 3 mg/l, which was obtained.

The results of quantitative analyses after antimony adsorption tests on magnetite powder in different conditions are presented in Table 1.

Table 1. Experimental test results

Sample No.	Temperature [°C]	pH	Initial quantity of Sb (ppb)	Quantity of Fe_3O_4 [g]	Final quantity of Sb [ppb]	Atmospheric condition
1	25	6	90	0.1	sld*	Argon
2	25	10.5	90		23	Argon
3	25	12.0	90		21	Argon
4	25	10.5	90		28	Air
5	85	6	90		sld	Air
6	85	10.5	90		23	Air
7	85	12	90		26	Air
8-blank	25	-	90		86	Air

** sld = under detection limit*

According to the ICP-OES analysis report, in samples 1 (pH = 6, T = 25 °C, Argon atmosphere) and 5 (pH = 6, T = 85 °C, air atmosphere), the antimony concentration dropped below the detection limit of the device after the test, evidence of its retention on magnetite. In the case of samples 2 (pH = 10.5, T = 25 °C) and 3 (pH = 12, T = 25 °C), which were tested in Argon atmosphere, the antimony concentrations after the test were 23 ppb and 21 ppb, respectively. Furthermore, for the samples 4 (pH = 10.5; T = 25 °C), 6 (pH = 10.5; T = 85 °C) and 7 (pH = 12; T = 85 °C), tested in air, the final antimony concentrations in the solutions were 28 ppb, 23 ppb and 26 ppb, respectively. In all 7 samples, the initial antimony concentration was 90 ppb.

It was observed that the samples tested in alkaline conditions also showed antimony adsorption on magnetite, but not as effective as in the case of those with pH = 6. Neither the temperature nor reaction atmosphere (Argon or air) shows a significant influence regarding the adsorption efficiency of antimony on magnetite. However, it is possible that the antimony stock solution has absorbed some atmospheric oxygen when it was transferred from the autoclave to the inert box. This may have led to a partial oxidation of the antimony from Sb^{+3} to Sb^{+5}.

A control sample, which was also subject to the same filtration process but without the magnetite powder, was prepared. According to ICP-OES analysis report, the antimony concentration in the control sample after filtration was 86 ppb, from an initial concentration of 90 ppb. The difference between the initial concentration and the final one was very small, and may be due to the retention of a small antimony quantity on the filter paper, but most likely it can be attributed to the standard deviation of the measurement method.

Fig. 9 presents the microscopic aspect of the magnetite powder from the cellulose mixed ester filter paper for the sample 1. In this case, the solution was allowed to react at T = 25 °C and pH = 6 in Argon atmosphere. The particle size of the filtered magnetite is smaller than 5 µm.

The black Fe_3O_4 deposits on a filter paper, after filtering the solution 3, are shown in Fig. 10. The magnetite particle size can be determined much easier in the areas on the filter paper where micro-particles do not agglomerate to form successive layers. This time, the pH value at which the reaction took place, in the case of sample 3, was 12 and the temperature was 25 °C. Also, to prevent a possible antimony oxidation, an Argon atmosphere was used.

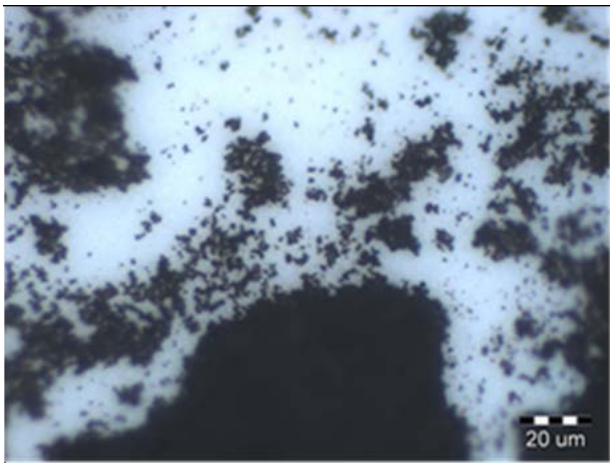


Fig. 9. Fe_3O_4 deposits on a filter paper from sample 1

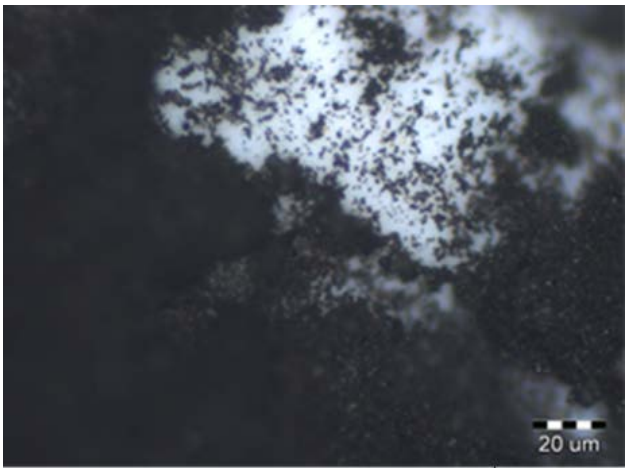


Fig. 10. Fe_3O_4 deposits on a filter paper from sample 3

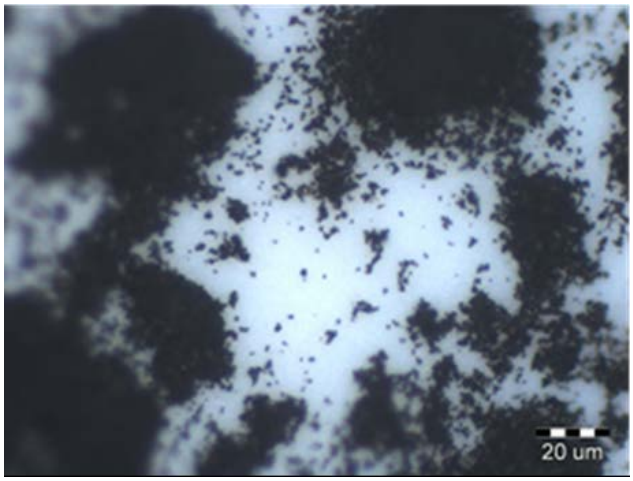


Fig. 11. Fe_3O_4 deposits on a filter paper from sample 5

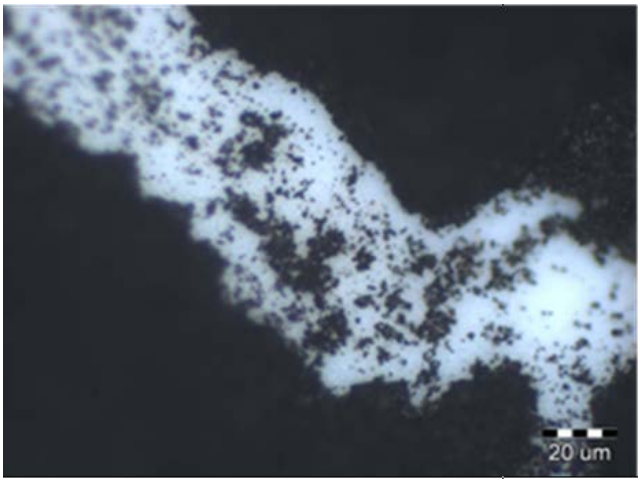


Fig. 12. Fe_3O_4 deposits on a filter paper from sample 7

Figs. 11 and 12 show the micrographs with magnetite deposits on the CME filters that came from sample 5 and sample 7, respectively. Both samples were tested in air at T = 85 °C, but at different pH values. For sample 5, the pH was set at 6, and for the solution 7, the pH was 12.

The deposits on the filter papers from all the tested samples show a very fine black magnetite powder with a particle size less than 5 µm.

Although in a few samples, the magnetite was able to absorb the antimony species introduced into the solution, the optical micrographs did not show significant difference between them. This is because the concentration of antimony used for adsorption on metal powder is extremely low and cannot make visible changes.

Conclusions

Magnetite powder can be used for antimony removal from aqueous solutions in some specific conditions. The adsorption experiments showed that antimony adsorption on magnetite is decreasing when the pH of the solution increases.

Because Sb concentration used in the test was very low (ppb), future works will focus on tests performed at higher concentrations.

Filter paper micrographs for all tested samples did not present significant changes and particle size of the magnetite powder was under 5 µm.

Temperature did not affect the adsorption mechanism of antimony on the oxide powder. Also, no significant change was observed when the samples were tested in two different conditions, with air and Argon. However, a slight oxidation to Sb(V) of the stock solution during transportation from autoclave to the box with inert atmosphere may occurred.

References

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