
ANTIMONY REMOVAL FROM AQUEOUS SOLUTIONS USING ZIRCONIUM HYDROXIDE

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ABSTRACT

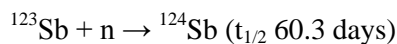
In this paper it is presented an experimental test for non-radioactive antimony removal from aqueous solutions using zirconium hydroxide powder. Also, it was studied how the temperature and pH influences antimony adsorption onto zirconium hydroxide surface. After the adsorption, solutions were filtered on Cellulose Mixed Ester Membrane with 0.2 μm pore size to remove the zirconium powder and then the aqueous solutions were sent to Inductively Coupled Plasma Optic Emission Spectrometry (ICP-OES) for quantitative analysis of Sb. Zirconium hydroxide powders were examined by optical microscopy. For the solutions that were tested at pH 4.5 and 10.2 the antimony concentration dropped below the detection limit of ICP-OES device, proof of antimony adsorption on zirconium hydroxide. Also, for the other tested solutions which had pH=12 the antimony concentration reduced with 77% and 80%. The temperature had no influence upon adsorption mechanism.

Key words: antimony removal, zirconium hydroxide, pH influence

Introduction

Radiation field builds up in the nuclear coolant systems of nuclear reactors and causes exposure of personnel to radiation. Efforts are being made world over to reduce the radiation field that builds up in the reactor coolant systems. Deposition of radioactive contaminants takes place due to the transportation of corrosion products into and out of the reactor core. These corrosion products are made radioactive by the neutron flux present in the core [1].

Antimony present in some of the fuel surfaces and pump seals in the heat transport system gets released due to mechanical wear. As the antimony chemistry is quite complex, its removal from coolant becomes very difficult. Majority of the inventory of antimony resides in the core on zircaloy-4 surface during regular operation of the reactor. During shutdown and start-up, there is sharp release of antimony activity. It is known that there is oxygen excursion in the coolant along with temperature fluctuations during these periods. The radioactive antimony (^{122}Sb , ^{124}Sb) so released from the core gets easily deposited on out-of-core surfaces if not removed effectively by specific ion exchangers [1]. ^{122}Sb and ^{124}Sb are two multi gamma emitters with radioactive half-life of 2.7 days and 60.2 days respectively. Thanks to its short radioactive half-life, ^{122}Sb has a low impact on health physics, but it allows to determinate antimony sources [2]. ^{124}Sb have relatively long half live and the γ -rays emitted by them are having energy sufficient to penetrate the thickness of pipes to cause exposure of personnel manning the power plant to radiation. This radio-active isotope is formed by the following nuclear reaction involving neutron (n) and the parent inactive isotope present in the corrosion products:



Sb source that gave rise to the high radio-antimony fields was site specific: Sb-impregnated carbon primary HTS pump seals and bearings. Antimony-impregnated carbon typically contains between 10-30% Sb, and wear and/or dissolution of this material introduces Sb into the HTS coolant. Antimony-impregnated carbon seals and bearings have been the cause of many of the reported Sb activity problems in PWRs worldwide [3].

Radioactive antimony ($^{124,125}\text{Sb}$) exist in many Pressurized Water Reactor (PWR), Pressurized Heavy Water Reactor (PHWR) and Boiling Water Reactor (BWR) water circuits and waste streams in activity concentrations comparable to that of radio-cobalt ($^{57,60}\text{Co}$). 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. The difficulty of antimony removal stems from its complicated chemistry: antimony can exist in solution in two oxidation states (+3, +5) and in several hydroxyl species (e.g. $\text{Sb}(\text{OH})_6^-$, $\text{Sb}(\text{OH})_3$, $\text{Sb}(\text{OH})_4^+$), depending on the pH and redox conditions [4, 5]. Efforts are being made to minimize the radiation field in the reactor coolant systems of nuclear power plants by careful selection of materials or by reduction the antimony concentration from the HTS using special water treatment systems.

Experimental

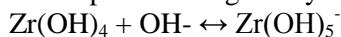
In this paper it is presented an experimental test for non-radioactive antimony removal from aqueous solutions using zirconium hydroxide powder.

Point of zero charge and adsorption mechanism

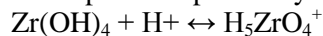
Point of zero charge (PZC) of a suspended particle in a medium is the pH of the medium at which particle surface charge (zeta potential) is zero. It gives an idea about the surface charge of a particle in a particular medium and hence its interaction with other charged surfaces. The PZC value of zirconium hydroxide will help us to understand in what way antimony it can be adsorbed on the reactor internal surfaces.

In **Figure 1** it is presented the attraction and repulsion mechanism of antimony hydroxide anion onto zirconium hydroxide as a function of PZC. If pH is below the PZC of $\text{Zr}(\text{OH})_4$, then the hydroxide is positively charged, and it takes place the attraction of particles with opposite charge. When the pH is above PZC of $\text{Zr}(\text{OH})_4$, then hydroxide charge changes from plus to minus and repulsion between particles occurs. With increasing pH, the $\text{Zr}(\text{OH})_4$ charge changes from positive to negative by deprotonation of M-OH functional group.

pH > PZC a species is negatively charged



pH < PZC a species is positively charged



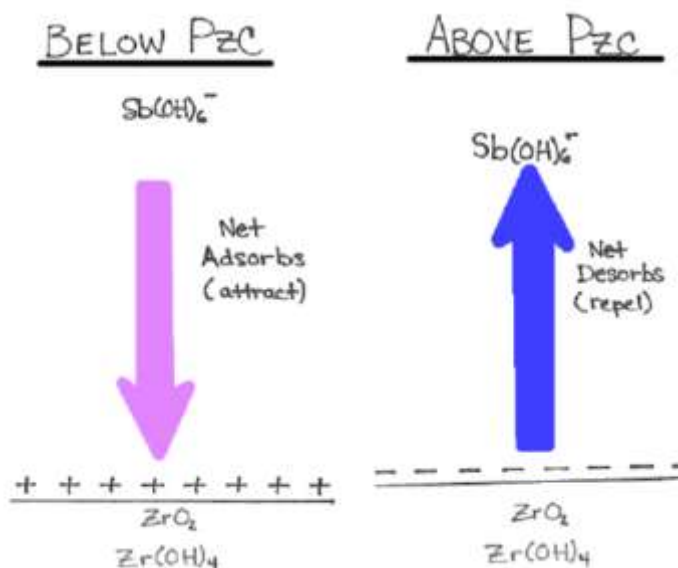


Fig. 1 The effect of PZC of $Zr(OH)_4$ on $Sb(OH)_6^-$ adsorption [6]

In the pH range of 2 to 11, Sb (III) should form a neutral complex, $Sb(OH)_3$ (as shown in **Figure 2**).

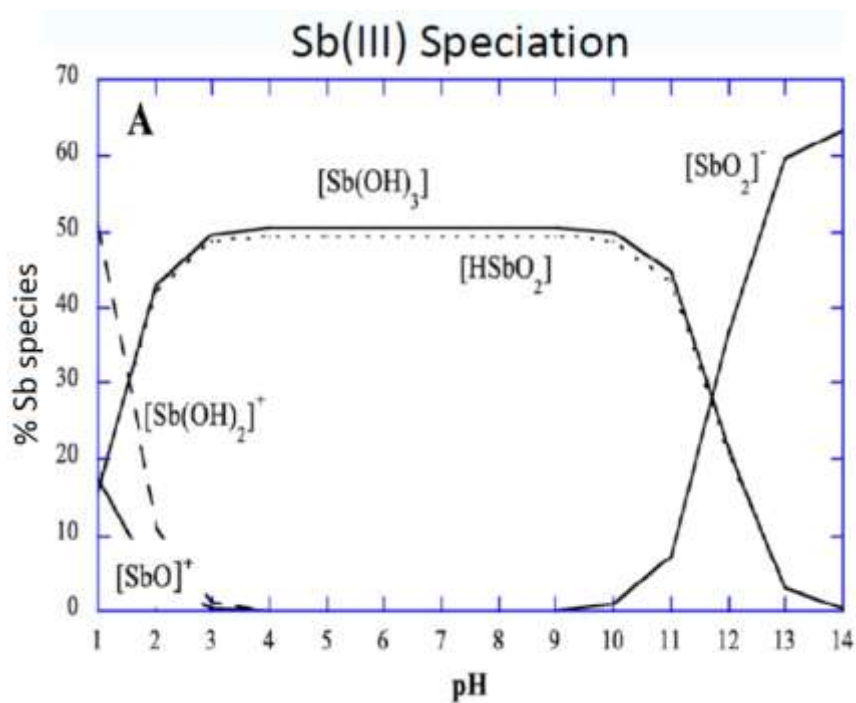
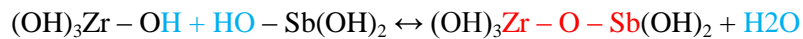


Fig. 2 Distribution of dissolved species of Sb(III) at 25 °C as a function of pH [6]

For $Sb(OH)_3$ adsorption and desorption are in equilibrium with each other:



In the pH range of 2 to 10, Sb (V) should exist as a negatively charged complex, $Sb(OH)_6^-$ (Figure 3).

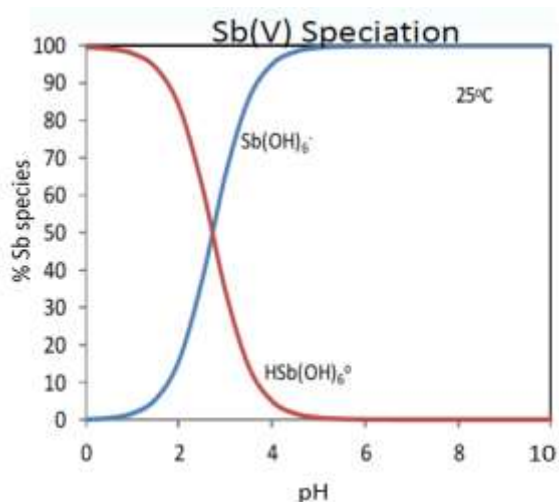
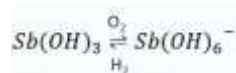


Fig. 3 Distribution of dissolved species of Sb(III) at 25 °C as a function of pH [6]

Reduction and oxidation mechanism is as follows:



Test description

For adsorption test of antimony onto zirconium hydroxide powder have been prepared seven solutions which were kept in different pH and temperature conditions. Working procedure is presented in Figure 4 and consisted in several steps.

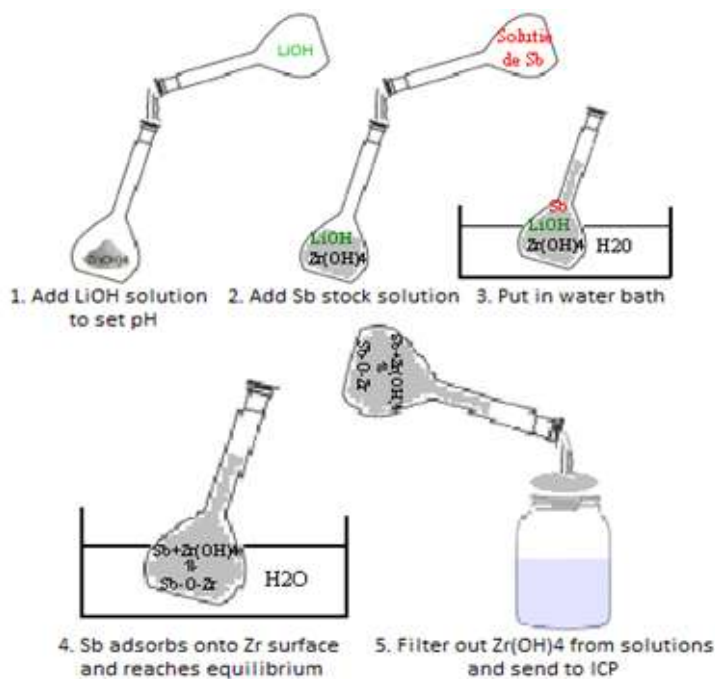


Fig. 4 Working steps for laboratory test

1. Was placed into several volumetric flasks a quantity of zirconium hydroxide and then the pH was set at 4.5, 10.2 and 12 using a solution with LiOH.
2. Further was added an antimony solution, obtained by dissolving a metallic antimony powder in autoclave.
3. After that, some of the volumetric flasks were placed in a water bath at 85 °C and others were kept at room temperature.
4. The solutions were kept in different condition for several hours to see the influence of temperature on the adsorption mechanism.
5. Forwards, the solutions were filtered (as is shown in **Figure 5**) on Cellulose Mixed Ester filter paper with porosity of 0.2 μm to remove $\text{Zr}(\text{OH})_4$ insoluble and the antimony adsorbed on the hydroxide.



Fig. 5 Solution filtering on filter paper with porosity of 0.2 μm

6. Filtered solutions were sent to ICP-OES (**Figure 6**) for quantitative analysis of antimony and the powders from the filter papers were examined using an Olympus GX 71 light microscope.



Fig. 6 Images of ICP-OES equipment

Results and discussion

Figure 7 presents the microscopic aspect of the zirconium hydroxide powders from the CME filter paper for the solutions tested at the same temperature (85 °C) but in different pH conditions: 4.5, 10.2 and 12.

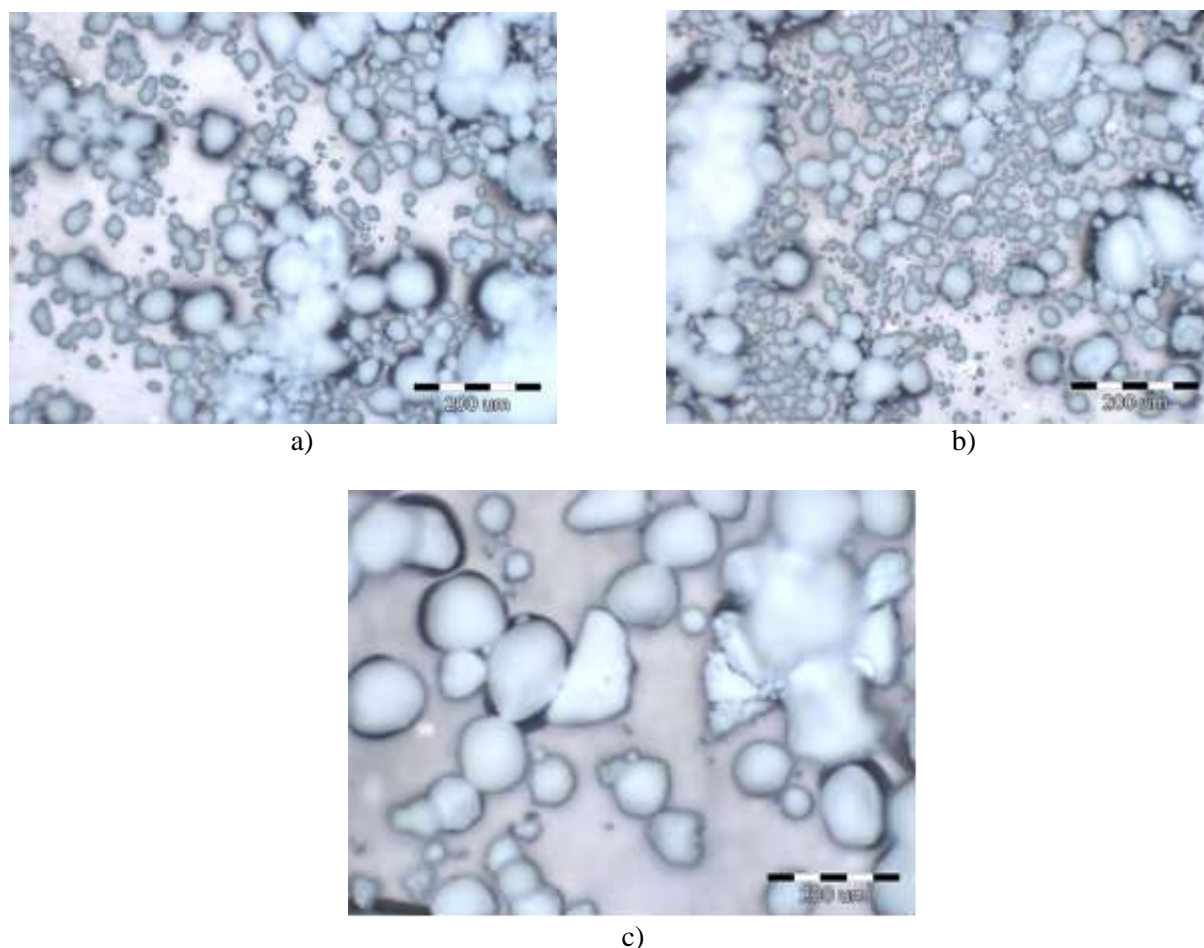


Fig. 7 $Zr(OH)_4$ deposits from the paper filters of the solutions tested at 85 °C and
a) pH = 4.5 b) pH = 10.2 c) pH = 12

According to ICP-OES analysis report, the concentration of antimony from the tested samples, both at room temperature or at 85 °C and in acidic or weakly alkaline condition, dropped below the detection limit of the ICP-OES devices. For the samples tested in alkaline conditions at 20 °C and 85 °C the concentration of antimony dropped with 80% respectively 77%.

Conclusions

- Antimony is insoluble in aqueous solution at normal temperature and pressure.
- The temperature had no significant influence regarding antimony adsorption mechanism onto zirconium hydroxide.
- ICP-OES analysis showed that the concentration of antimony dropped below the detection limit of the device for the solutions that were tested at pH 4.5 and 10.2, proof of antimony adsorption on zirconium hydroxide.
- Micrographs of CME filters for the samples that we had had in work don't show notable differences.

References

- [1] S. Velmurugan, “Water Chemistry in Nuclear Reactor” IANCAS, No. 43, Vol. VII (2), April 2008
- [2] A. Rocher, J.L. Bretelle, “Impact of Main Radiological Pollutants on Contamination Risks (ALARA) Optimisation of Physico Chemical Environment and Retention Technics during Operation and Shutdown”; Report Electricité de France/GPR, 2003
- [3] H. Stockert, H. Emmert, K. Seifert, “Entfernung von Antimon aus dem Primarkreis von DWR-Anlagen und Ergebnisse aus der Durchführung beim Kernkraftwerk Philippsburg-2”, VGB Kraftwerstechnik 67, 288.
- [4] Electric Power Research Institute, Analysis of Advanced Liquid Waste Minimization Techniques at a PWR, TR-109444, 1998.
- [5] R. Harjula, A. Paajanen, R. Koivula, E. Tusa and R. Kvarnström, “Removal of Antimony-124 from PWR Coolant Water”, Proceedings of Waste Management 2009 Conference, March 1 – 5, 2009, Phoenix, AZ.
- [6] S. Qiu, M. Zhou, “Antimony Adsorption on Zirconium Hydroxide in Aqueous Solutions”, Deep River Science Academy-Poster, AECL