Chapter 3

STUDIES ON ANTIMONY DISSOLUTION IN ORGANIC ACIDS AND ITS DEPOSITION ON CARBON STEEL AND MAGNETITE SURFACES

3.1 Introduction

During the full PHT system chemical decontamination in PHWRs, occasionally very low decontamination factors (DFs) were achieved. The cause of low DF in some PHWRs was attributed to mobilization of activated antimony ($^{122,124}\text{Sb}$) isotopes from the core and their deposition on the out-of-core surfaces during chemical decontamination. In order to inhibit the antimony problem during chemical decontamination, the dissolution and deposition behavior of antimony in Nitrilo Tri Acetic Acid (NTA) based chemical decontamination formulations were studied.

3.2 Dissolution Behavior of Antimony

Antimony belongs to group (V) elements in the periodic table and is classified as a metalloid. Hence, it exhibits properties that are different from transition elements. It exhibits multivalency (0, +3 and +5) and it’s dissolved species in aqueous medium (> pH 2.5) is anionic in nature. Under the reducing condition prevailing in the primary coolant system of pressurized heavy water reactors (PHWRs), inactive antimony is deposited on the core zircaloy surface and become radioactive through neutron activation. The exact valence state of antimony on core zircaloy surfaces is not known though the high temperature (300°C) Pourbaix diagram [1] of antimony indicated the existence of antimony in 3+ state. During the chemical decontamination process, antimony is released
into the decontamination formulation which is transported to other parts of the PHT system. Hence, the dissolution of different antimony species was carried out under chemical decontamination conditions to find the possible valence state of Sb released during chemical decontamination. The soluble antimony species were used for subsequent deposition studies. The dissolution behavior of antimony in elemental form and antimony in oxide / compound forms viz. Sb₂O₃, antimonates was studied in NAC media at 85°C and under reducing conditions. Dissolution experiment for Sb₂O₃ showed complete dissolution of the oxide within 1 hour (Fig. 3.1). The Fig. 3.1 indicates that Sb(III) can be dissolved even in mild organic acids under reducing conditions. Further studies indicated that Sb(V) as a potassium antimonate hexahydroxide is highly soluble in the acid media (Fig. 3.2) in fact first sampling (at 15 minutes) itself completely dissolved. However, Sb in its elemental form could not be dissolved in simple acid media; it required the presence of an oxidizing agent such as dissolved oxygen to bring the antimony into solution as shown in Fig. 3.3.

![Fig. 3.1: Dissolution kinetics of Sb(III) (antimony trioxide) in NAC formulation at 85°C.](image-url)
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Fig. 3.2: Dissolution kinetics of Sb(V) (potassium antimonate hexahydroxide) in NAC formulation at 85°C.

It is justifiably presumed that antimony in the core surfaces exists in Sb(III) form because of the reducing conditions prevailing in the coolant. The above dissolution studies indicated that an organic acid can mobilize the antimony from the core zircaloy surfaces and can keep it in solution. As the possible soluble oxidation states are Sb(III)
and Sb(V) in the formulation under chemical decontamination condition, thus further studies were carried out with these soluble species.

Fig. 3.4: UV-Vis absorption spectra of (a) Pure Sb(III), (b) Sb(III) exposed for 2 hours under reducing conditions, and (c) Sb(III) exposed for 24 hours under reducing conditions.

Fig. 3.5: UV-Vis absorption spectra of (a) Pure Sb(V) and (b) Sb(V) exposed for 24 hours under reducing conditions.
3.3 Stable Speciation of Sb in Chemical Decontamination Solution

It is observed from dissolution studies that Sb(III) and Sb(V) are soluble species under chemical decontamination condition. It is necessary to know the stability of these species in the decontamination condition. Under oxidizing to slightly reducing conditions, the hydrolytic species Sb(OH)$_6^{2-}$ [Sb(V)] is the dominant antimony aqueous species for pH values greater than approximately 2.5. While at moderately reducing conditions, the speciation is dominated by the Sb(OH)$_3^-$ [Sb(III)] at pH values from 2 to 12 [2].

Stability of Sb(III) and Sb(V) under chemical decontamination (pH 2.7) was verified by the UV - spectrometer. In this method, Pyrogalol red was used as a complexing agent for Sb species at pH 2.0 maintained with HCl-KCl buffer [3]. The Sb solution in association with the complexant showed a peak at 540nm with Sb(III) and at 505nm with Sb(V) as shown in Fig. 3.4(a) and 3.5(a) respectively. These two peaks are taken as the standards for Sb(III) and Sb(V) respectively. Here, concentration of pure Sb(III) and Sb(V) were different compared to exposed samples thus the intensities were different. The peak positions are indicated by the dashed lines in these figures. Sb(III) and Sb(V) were separately exposed for 24 hours under chemical decontamination medium that is in acidic and reducing condition at 85°C. UV- spectrum for both cases Sb(III) and Sb(V) are shown in Fig 3.4(c) and Fig. 3.5(b) respectively. A. Abbaspour and M. Najafi observed $\lambda_{max}$ for Sb(V) and Sb(III) at 500nm and 550nm respectively [3]. Both Sb(III) and Sb(V) did not change their oxidation states. The observed metastability of Sb(V) and Sb(III) in chemical decontamination medium, might be due to slow rates of
redox reactions [2]. Thus, antimony deposition studies were carried out in these oxidation states only.

![Graph A](image1)

![Graph B](image2)

**Fig. 3.6:** Sb(V) deposition behavior on the carbon steel surface area in NAC formulation at 85°C. A. Sb in solution (a) 11 cm², (b) 33 cm² CS surface area. B. Fe dissolution (a) 11 cm², (b) 33 cm² CS surface area.

### 3.4 Deposition Behavior of Antimony

Antimony radioactivity was observed dominantly on Fe₃O₄ coated carbon steel (CS) during chemical decontamination [4, 5]. As Sb(III) and Sb(V) are the possible oxidation states in the formulation under chemical decontamination, their deposition behavior was studied. During the process of deposition of antimony, dissolution of ferrite
oxide / (carbon steel) metal also takes place due to the presence of acidic organic formulation and high temperature. Hence, in all deposition experiments, iron concentration was also measured along with Sb concentration for better understanding of the process.

### 3.4.1 Deposition Behavior of Sb(V) on Carbon Steel Surface

Antimony(V) deposition experiments were performed with potassium antimonates in NAC formulation on the CS surface at 85°C. Antimony(V) concentration was not reduced in the solution. Even with the variation in the CS surface area (Fig. 3.6) and in Sb(V) concentration (Fig. 3.7), there was no reduction in the Sb(V) concentration. The deposition experiments indicated Sb(V) has poor ability to deposit on the CS surface. Even though there was Fe dissolution and release it did not reduce Sb(V) and/or promote it’s deposition.

![Figure 3.7](image)

**Fig. 3.7:** Sb(V) deposition behavior on the carbon steel surface with variation in Sb concentration (a) 5ppm, (b) 20ppm in NAC formulation at 85°C.
Fig. 3.8: Sb(III) deposition behavior on the carbon steel surface area (a) 11cm$^2$, (b) 33cm$^2$ in NAC formulation at 85°C.

Fig. 3.9: Sb(III) deposition kinetics on carbon steel surface area 11cm$^2$ in the NAC formulation at 85°C.
3.4.2 Sb(III) Deposition Studies on Carbon Steel Surface

3.4.2.1 Deposition Behavior of Sb(III) on Carbon Steel Surface

Antimony(III) deposition experiments were performed with Sb$_2$O$_3$ in NAC formulation on the CS surface at 85°C. Deposition of Sb(III) on CS was observed from the solution analysis as shown in Fig. 3.8. The deposition rate was increased with the increase in the surface area of CS (Fig. 3.8). A logarithmic plot of concentration of Sb in solution with time for 5ppm Sb(III) and on 11cm$^2$ polished CS surface, showed the deposition of Sb(III) followed first order reaction kinetics with Sb(III) concentration as shown in Fig. 3.9.

The effect of variation of Sb(III) concentration on its deposition was also carried out as shown in Fig. 3.10. Antimony(III) deposition was slightly faster for 20 ppm Sb(III) in solution compared to 5 ppm (Fig. 3.10A). Iron dissolution from CS surface was more for 20ppm compared to 5ppm Sb(III) in solution and upto 4 hours of experiments iron dissolution rate was 34ppm/h. with 20ppm of Sb(III) while 27ppm/h. with 5ppm of Sb(III). However Fe dissolution rate reduced with time due to Fe$^{2+}$ ion build up in solution and reduction in acidity of the medium from pH 2.7 to 5.5. Some oxyanions viz. chromite, molybdate etc. shows inhibition on iron dissolution from the steel surface in acid solution [6]. As Sb(III) is also an oxyanion in aqueous solution, some inhibition was expected. However, the result was contrary to the expectation namely there was enhanced corrosion of CS with an increase in Sb(III) concentration. This observation is directly related to the deposition mechanism of Sb in an acid medium and is explained later.
Fig. 3.10: Effect of Sb(III) concentration variation on A. Sb(III) deposition behavior on carbon steel surface (a) 5ppm, (b) 20 ppm; B. Iron dissolution behavior (a) 5ppm, (b) 20 ppm

In an iron pre-saturated system also, Sb(III) deposition behavior was studied as shown in Fig. 3.11. In this experiment, iron saturation was achieved by dipping similar surface area of CS in the formulation for around 18 hours prior to start the deposition experiment. Although the saturation deposition amount was almost same for both cases, Sb(III) deposition was observed at a slower rate compared to the fresh one.
formulation (Fig. 3.11A). Slight iron dissolution was also observed even in iron saturated case (Fig. 3.11B). It appears Sb(III) deposition promotes iron dissolution.

Fig. 3.11: Effect of iron saturation system A. Sb(III) deposition behavior on the CS surface (a) Fresh NAC formulation, (b) Fe Saturated NAC formulation; B. Iron dissolution behavior (a) Fresh NAC formulation, (b) Fe Saturated NAC formulation.

The above observation of more iron dissolution with Sb deposition suggests that though Sb(III) is an oxyanion, its deposition mechanism on CS surface may not be like other oxyanions. Deposition of Sb(III) doesn’t inhibit the iron dissolution, on the
contrary, it promotes the iron dissolution. There is need for understanding the mechanism of Sb(III) deposition on the CS surface to prevent its deposition on CS surface.

3.4.2.2 Characterization of Deposited Material on Carbon Steel Surface

CS coupons exposed to Sb(III) containing NAC solution were characterized by SEM, XRD and XPS to understand the Sb(III) deposition mechanism on its surface. Exposed CS coupons, named as Sb-CS, were observed to hold loosely bound particles on its surface. An ultrasonic treatment was used for removing these loosely bound adsorbed particulates from the surface. Thus, it helps to distinguish between loosely deposited/precipitated substance and the adherent layer that is chemically bound to the surface. Here, loosely adhered layer abbreviated as ‘LAL’ and the surface layer on CS left after the ultrasonic treatment is termed as ‘Inner Layer’ and abbreviated as ‘IL’.

It was presumed that the characterization of LAL would depict the information about the deposited layer and the IL would give the information about the initial interaction of Sb with CS surface. It was observed that ultrasonic treatment detached the LAL completely from the CS surface. In Fig. 3.12, the SEM pictures of CS sample exposed to a solution containing Sb(III) before and after ultrasonic cleaning are given. Loosely bound deposited material was found to be present on the surface as seen from SEM picture in Fig. 3.12(a) and was found to be removed in ultrasonically cleaned sample shown in Fig. 3.12(b). EDX of loosely bound deposited material on CS sample showed around 9% Sb and the remaining was Fe. On the contrary, the EDX of ultrasonically cleaned CS sample showed the presence of only Fe. The observation supports the presumption that the ultrasonic cleaning method can be used to separate the
two layers from the CS surface. It further confirms that Sb deposition occurs on the loosely bound iron oxide layer only and does not have access through the pores to the inner layer over carbon steel. When plain CS is exposed to NAC formulation for Sb and subjected to the ultrasonic cleaning it resolved in IL and LAL. Upon analysis of LAL it showed the presence of only Fe as Fe hydrous oxide. IL is also hydrous oxide in native but was more tenacious. This layer reflects the primary interaction of Fe$^{2+}$ with locally exchanged OH$^{-}$ concentration (because H$^{+}$ is reduced to H$_{2}$ on surface).

Fig. 3.12: SEM picture of carbon steel coupons exposed to organic acid and 10 ppm Sb at 85°C under reducing condition; (a) before ultrasonic cleaning and (b) after ultrasonic cleaning.

3.4.2.2a XPS Analysis of Sb-Deposited Samples

As a reference sample for XPS analysis, a polished CS coupon was treated in NAC formulation (containing no Sb) under de-aerated condition at 85°C. The powder materials deposited on CS sample was taken for XPS analysis. Fe 2p photoelectron peaks (Fig. 3.13(a)) from the powder material showed a small amount of elemental Fe along with the presence of Fe$^{3+}$/Fe$^{2+}$ peak at 710.5 eV [7].
The Sb(III) adsorbed CS coupon was prepared by exposing the coupon in NAC with Sb(III) solution for 12 hours. LAL powder from this sample was taken for XPS analysis. It is known that the interaction of organic acid with CS surface forms H₂ and ferrous compound. The evolution of hydrogen from CS surface increased the availability of OH⁻ ions near the surface which promoted the formation of a Fe-hydroxide layer on CS surface. Fe 2p binding energy showed that Fe was in Fe²⁺ and Fe³⁺ which was difficult to resolve by XPS technique due to the spectrum background and overlap of satellite peaks. The Fe⁰ signal in the Fe2p spectrum (Fig. 3.13(b)) was assumed to be due to iron particles detached from the CS surface during ultrasonic removal of the deposits. Fe 2p peak recorded from the LAL sample was also seen to contain Fe⁰ along with Fe²⁺ and Fe³⁺ states (Fig. 3.13(b)).

**Fig. 3.13:** Fe 2p X-ray photoelectron spectra recorded from (a) powder deposited on carbon steel in the absence of Sb(III) in solution and (b) in the presence of Sb(III) in solution (sample LAL).
In addition to the Fe 2p peak analysis, it is important to analyze photoelectron peaks from antimony in the samples for a complete understanding of the mechanism. Antimony 3d photoelectron spectrum which is the most sensitive XPS spectrum from Sb was recorded for XPS analysis. In Fig. 3.14, the XPS of Sb 3d levels obtained from different specimens along with the standard samples are shown. In Fig. 3.14(a) showed the photoelectron spectrum from elemental Sb containing native oxide. The Sb 3d$_{5/2}$ peaks at 527.8 eV and 3d$_{3/2}$ at 536.9 eV were well matched with pure antimony [8]. Other two peaks at higher energy (Fig. 3.14(a)) were associated with the native oxide of antimony. The XPS peaks of Sb 3d$_{5/2}$ and 3d$_{3/2}$ from standard Sb(III) and Sb(V) are shown in Fig. 3.14(b) and 3.14(c) with binding energy values 529.8 eV and 539.2 eV. It
was evident from the figures that though the photoelectron peaks of elemental Sb and oxidized Sb was well resolved, there was almost no difference in the peak binding energy between Sb$_2$O$_3$ and Sb$_2$O$_5$. XPS analysis of Sb 3d$_{3/2}$ peak of LAL (Fig. 3.14(d)) showed the presence of oxidized Sb (III or V or both) along with a small quantity of elemental Sb (arrow in Fig. 3.14).

Analysis of the Sb 3d photoelectron spectrum is not straightforward due to two reasons. Firstly, the O1s (around 530 eV) spectrum overlaps with the Sb 3d$_{5/2}$ spectrum which is the most intense photoelectron peak from Sb. Secondly, the chemical shift of Sb(III) and Sb(V) is almost same and difficult to resolve through normal XPS instrument. An attempt was made to measure the Auger parameters from the standards of Sb(III) and Sb(V), but even then the difference was not sufficient to identify the chemical states.

Near Fermi level spectrum (valence band spectrum) was taken to identify the chemical state of Sb deposited on CS. In Fig. 3.15, the valence band spectra of the sample and the standards were presented. It was observed that valance band spectra of Sb(V) and Sb(III) were different [9,10]. The valence band photoelectron spectrum of Sb$_2$O$_3$ (Fig. 3.15(b) with circles) showed peaks at around 4.0 eV, 8.0 eV and 12.0 eV which were matched with the literature value [9,10]. The peaks at 4.0 eV and 12.0 eV, had contributed from the lone pair electrons (5s) in Sb$_2$O$_3$ and hence were characteristic of Sb(III) chemical state. Another peak of Sb(III) compound at around 8.0eV was a result of hybridization of O-2p with 5p/5s electrons of Sb.

While in the case of Sb(V) system, lone pair electrons in 5s were not available due to complete removal of these electrons in the oxidation process. As a result, the peaks associated with 5s electrons (marked in Fig. 3.15(b)) were decreased in Sb$_2$O$_5$. Indium
foil was used for fixing some powder samples before taking XPS spectra. The peak observed at 12 eV (3.15 d) was attributable to In 4d$_{3/2}$ and is due to the use of indium foil. In case of Sb$_2$O$_5$ the hybridization band was observed at around 6 eV [10]. So the peak at around 4 eV was observed to be very sensitive to oxidation and can be considered important for identifying the chemical state of Sb. For further confirmation pure Sb$_2$O$_3$ was oxidized and the valence band spectrum was recorded. In Fig. 3.15(c), the peak at 4 eV decreased indicating oxidation of Sb(III) to Sb(V). In Fig. 3.15(a), the valence band spectrum from Sb-CS sample was shown where a distinct peak was observed at around 4.0 eV. This confirmed the presence of Sb(III) in the deposited materials (LAL) on the CS surface. The spectrum (Fig. 3.15(a)) contained a shoulder near the Fermi level which showed the presence of elemental Sb or elemental Fe in the sample (LAL). A continuum background in the range of around 6-7 eV (Fig. 3.15(a)) was observed in the Sb deposited CS sample which was due to the presence of the Fe 3d-O2p hybridization band [11] from other Fe-oxides in the sample.

Fig. 3.15: X-ray photoelectron valence band spectra recorded from (a) Sb-CS, (b) Sb$_2$O$_3$, (c) Sb$_2$O$_3$-oxidized (d) Sb$_2$O$_5$. 
3.4.2.2b Identification of Sb-Fe-O Compound

The XPS characterization of the LAL and the Sb-CS samples showed the presence of Fe in 2+ and 3+ states and Sb was in 3+ states along with a small amount of elemental Sb and Fe. The quantification of these elements in the powder was done with the photoelectron peak area of these elements and the corresponding sensitivity values [12]. The peak area for Sb 3d_{5/2} peak was found overlapping with O1s peak which prohibits getting the peak area of Sb 3d_{5/2} correctly. Thus, the Sb 3d_{3/2} peak area was used for quantification instead of Sb 3d_{5/2} peak area [8]. It is to be mentioned here that the area of pure elemental peak of Fe and Sb were subtracted while finding the atomic concentration of Sb(III) and \( \text{Fe}^{3+}/\text{Fe}^{2+} \) in the sample. In Table 1, the atomic concentration of the oxide developed on CS surface is presented. It appears from the XPS analysis that Fe and Sb form a mixed oxide which is close to the stoichiometric oxide like FeSb\(_2\)O\(_4\). However the higher amount of O in the sample might be accounted for by the presence of adsorbed oxygen and oxygen associated with Fe in different compounds.

### Table-3.1: Quantification of Sb, Fe and O in the samples from photoelectron spectra.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fe (at %)</th>
<th>Sb (at %)</th>
<th>O (at %)</th>
<th>Formula obtained</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sb-CS</td>
<td>13</td>
<td>25</td>
<td>62</td>
<td>FeSb(<em>{1.9})O(</em>{4.8})</td>
</tr>
<tr>
<td>LAL</td>
<td>12.5</td>
<td>23.5</td>
<td>64</td>
<td>FeSb(<em>{1.9})O(</em>{5.1})</td>
</tr>
</tbody>
</table>

3.4.2.2c XRD Analysis of Sb Adsorbed Carbon Steel Samples

XRD analysis of Sb-CS and LAL samples were taken and their XRD patterns were presented in Fig. 3.16. The diffraction patterns of LAL sample showed the presence of elemental Sb [13] and small amount of FeOOH (Fig. 3.16(a)) [14]. In Fig. 3.16(b), the diffraction pattern of Sb-CS sample showed Sb\(^0\) and Fe\(^0\) which originated from the CS
substrate. These results were quite different from the XPS observations where Sb was observed in 3+ state dominantly.

![X-ray diffraction patterns](image)

**Fig. 3.16:** X-ray diffraction patterns obtained from (a) LAL and (b) Sb-CS samples.

Apparently, there is a possibility for Sb surface oxidation during the transfer of the sample in an XPS analysis chamber. But this probability could be ruled out because the sample was cooled down to room temperature under reducing conditions and the exposure time to atmosphere was around 10 minutes prior to the XPS analysis. It is also known that antimony does not react with air at room temperature. So the presence of Sb(III) observed in XPS analysis was not the result of any surface oxidation of Sb\(^6\). Antimony compound detected in XPS analysis might be amorphous, which remained undetected by the XRD technique. Another possibility was that the powder was
composed of Sb\textsuperscript{o} crystallites as the core and Fe-Sb-O compound as the shells of grains. The XPS technique being a surface analytical technique gave dominantly shell information while XRD gave the core information.

### 3.4.2.3 Mechanism of Sb(III) Deposition on Carbon Steel Surface

Presence of amorphous FeSb\textsubscript{2}O\textsubscript{4} compound along with Sb\textsuperscript{o} on the CS surface indicated that the reaction between Sb(III) and the CS surface is complex under chemical decontamination. It appears as if two separate processes are involved in the Sb(III) deposition on the CS surface. Figure 3.17 shows the schematic diagram of possible Sb(III) deposition mechanism on the CS surface.

![Fig. 3.17: Schematic presentation showing the mechanism of sorption of Sb(III) on the carbon steel surface in NAC solution.](image)

In one process, Sb\textsuperscript{o} was formed due to red-ox reaction occurring on the CS surface under chemical decontamination. From standard reduction potential considerations, Sb(III) was expected to be reduced to Sb\textsuperscript{o} by iron metal under acidic condition. The anodic reaction was the dissolution of Fe\textsuperscript{o} into the solution.

\[
\text{Fe}^0 \rightarrow \text{Fe}^{2+} + 2\text{e}^- \quad \text{(3.1)}
\]
The counter cathodic reactions under reducing conditions were,

\[ 2H^+ + 2e^- \rightarrow H_2 \quad \ldots \quad (3.2) \]
\[ Sb^{3+} + 3e^- \rightarrow Sb^0 \quad \ldots \quad (3.3) \]

In another process Sb(III) adsorbed through surface complexation as Fe-O-Sb and subsequently as amorphous FeSb$_2$O$_4$ surface precipitation [15,16]. The diffraction analysis of the LAL sample showed the presence of FeOOH in the NAC formulation at 85°C. This indicated that the –OH functional group was developed on the CS surface in NAC solution. It was observed that the surface of FeOOH is positively charged at lower pH as its pH$_{ZPC}$ is around 7.3 [17] resulting in a very high adsorption of oxyanions at lower pH under the Coulombic attraction [18]. As Sb(III) is an oxyanion, was also absorbed on the CS surface at pH 2.7 [17]. Antimony(III) species in solution got attached on the CS surface through forming a bond with one of the bridging oxygen of the functional group (-OH) available on the CS surface. The stability of the adsorbed complex was further enhanced by forming a hydrogen bond which created a six member ring on the CS surface [17]. This led to the formation of Fe-O-Sb complex and is known as the adsorbed complex on the CS surface. In fact, XPS of IL sample showed a small amount of only Sb(III) at the interface of the CS surface also supported such Fe-O-Sb surface complexation. Attached Sb(III) on CS surface was assumed to be strongly bonded complex as a monolayer of Fe-O-Sb complex on CS surface. The monolayer of adsorbed Fe-O-Sb complex has further undergone adsorption of Fe ions and Sb(III) available around the surface in the decontamination formulation. This process involved the onset of formation of the amorphous FeSb$_2$O$_4$ compound as surface precipitation [19].
3.4.3 Sb(III) Deposition on Magnetite Surface

As CS surface develops Fe₃O₄ oxide during the normal operation of PHWR reactors, Sb(III) adsorption studies were carried on Fe₃O₄ surface also. Adsorption studies were carried out on Fe₃O₄ powder and Fe₃O₄ coated CS surface. In the real power plant, Sb(III) is exposed to the huge surface area of Fe₃O₄ under dynamic condition. But in laboratory scale, experiments were performed on a limited surface area of Fe₃O₄ coated specimens. Experiments were performed on Fe₃O₄ powder also where the surface area was several times more compared to coated coupons.

3.4.3.1 Sb(III) Adsorption Behavior on Magnetite Powder

Antimony adsorption experiments on Fe₃O₄ powder were performed at ambient temperature and at 85°C in NAC formulation. In these experiments Fe₃O₄ powder surface area was more than 6000cm² (obtained from BET analysis) and volume of the NAC formulation was kept at 250 ml in reducing conditions. In an ambient temperature experiment, adsorption of Sb(III) was saturated within 30 minutes of exposure (Fig. 3.18A(a)) and iron dissolution was also saturated (Fig. 3.18B(a)) within the same duration. But in 85°C and NAC formulation, though adsorption of Sb(III) was saturated within 30 minutes but after ~5 hours of experiment, Sb(III) was released into the solution (Fig. 3.18A(a)). Iron dissolution in this experiment occurred at a much faster rate initially and saturated at a higher value (Fig. 3.18B(b)).

Another experiment was also performed at 85°C but in iron saturated NAC formulation. The adsorption of Sb in saturated iron environment was achieved by keeping 14 cm² CS surface for 18 hours in the NAC formulation at 85°C prior to the addition of
Sb(III) and Fe$_3$O$_4$ powder at 85°C. The Sb(III) adsorption kinetics became very slow and it took around 15 hours for reaching saturation adsorption on Fe$_3$O$_4$ powder. It was observed that there was no desorption of Sb(III) at 85°C as shown in Fig. 3.18A(c). The complementary result of Fe dissolution from Fe$_3$O$_4$ did not vary with time throughout the experiment as shown in Fig. 3.18B(c).

**Fig. 3.18:** Sb(III) adsorption behavior A. (a) NAC formulation at room temperature, (b) NAC formulation at 85°C, (c) NAC formulation with iron saturation at 85°C; Iron dissolution behavior B. (a) NAC formulation at room temperature, (b) NAC formulation at 85°C, (c) NAC formulation with iron saturation at 85°C.
Fig. 3.19: FT-IR data about (a) untreated Fe$_3$O$_4$, (b) Tartaric Acid treated Fe$_3$O$_4$, (c) Tartaric Acid and Sb(III) treated Fe$_3$O$_4$.

3.4.3.2 Mechanism of Sb(III) Adsorption on Magnetite Powder

An oxide like Fe$_3$O$_4$, in contact with an aqueous solution will hydrate; in other words it will acquire –OH functional groups on its surface [20]. The –OH groups can be acquired from the atmospheric moisture also. These surface hydroxyl functional groups (denoted as S-OH) give FTIR peak at around 3200 cm$^{-1}$ along with H$_2$O vibration at around 3450 cm$^{-1}$ as shown in Fig. 3.19(a) [21]. Here, FTIR data are shown for dissolution of Fe$_3$O$_4$ and deposition of Sb(III) on Fe$_3$O$_4$ in tartaric acid due to unavailability of data with NAC formulation. It is presumed that SOH group interaction will be independent of the organic acid used for dissolution. Dissolution of Fe$_3$O$_4$ in tartaric acid generates new surfaces and retains SOH group on the Fe$_3$O$_4$ surface as shown in Fig. 3.19(b). SOH groups become protonized in an acidic solution (SOH + H$^+$ → SOH$_2^-$) [22]. These protonized SOH groups attract negatively charged oxyanions viz. Sb(III) under the influence of coulombic attraction in acidic solution. The protonized
SOH groups make primary surface complex with oxyanions due to condensation or deprotonation reactions [23]. As this protonized SOH groups make surface complex with oxyanions viz. Sb(III), OH stretch (3200 cm\(^{-1}\)) vanishes after Sb adsorption as shown in FT-IR plot in Fig. 3.19(c). This indicates that the Sb(III) adsorption occurs via inner-sphere surface interaction with the formation of Fe-O-Sb [24].

**Fig. 3.20:** XPS data of Fe\(_3\)O\(_4\) exposed to Citric Acid (a) Sb 3d\(_{3/2}\), (b) Fe 2p, (c) deconvoultion of C 1s, and (d) C1s peak after exposure at room temperature and at 85°C exposed.

Further surface characterization was carried out using XPS. The XPS analysis of Fe\(_3\)O\(_4\) powder was shown in Fig. 3.20 which was exposed to Sb(III) containing citric acid
under chemical decontamination conditions. XPS peak of Sb 3d_{3/2} (Fig. 3.20(a)) showed the presence of Sb in +3 states only and no peak related to elemental Sb was seen. Fe2p3/2 peak was found at 711.0 eV (Fig. 3.20(b)) corresponding to Fe^{3+} state of iron [25]. As elemental Sb was not observed in the XPS spectrum, it was concluded that adsorption was not driven by a redox reaction unlike in the case of Sb(III) adsorption on the CS surface under similar conditions. As XPS data showed the adsorption of Sb(III), so it might be due to the formation of a surface complex of Fe-O-Sb on Fe_3O_4 powder in acid medium similar to CS case. But, absence of Sb⁰ on the magnetite surface after the adsorption indicated the lack of red-ox reaction for surface precipitation in the magnetite case.

3.4.3.3 Desorption Mechanism of Adsorbed Sb(III) on Magnetite Powder in NAC Formulation

Several adsorption studies are available on Fe_3O_4 in the pH range of 4-10 at ambient temperature and pressure where the surface adsorption phenomena are dominant [9-11]. But in chemical decontamination, the pH of the solution is 2.7, temperature is around 85°C, and presence of organic complexing acids in reducing medium makes the system different from the usual adsorption studies. The primary difference is the iron dissolution of Fe_3O_4 is very less in the pH range of 4-10 at ambient temperature while the dissolution of Fe_3O_4 is very fast at lower pH (<4) and at higher temperature affecting the adsorption behavior.

Dissolution of Fe from Fe_3O_4 was due to two different mechanisms; (A) Fe^{2+}/Fe^{3+} ions released from the bare surface of Fe_3O_4 form complexes with chelating ligands (viz.
NTA) in solution; simultaneously O$^{2-}$ ions react with H$^{+}$ in the medium causing further leaching of metal ions from the solid, and (B) the chelating species are chemically bound to the lattice iron and then the complexes of iron-chelating species are released into solution followed by O$^{2-}$ neutralization by H$^{+}$. Interaction of organic acid with Fe$_3$O$_4$ was observed in XPS as shown in Fig. 3.20. Carbon 1s peak acquired from Fe$_3$O$_4$ powder exposed in organic acid, showed the presence of COO$^{-}$ at 288.5 eV and or C–OH groups at 286.0 eV peaks, shown in Fig. 3.20(c) [26]. Interaction of organic acid with Fe$_3$O$_4$ increased with temperature as shown in Fig. 3.20(d) where the peak intensity related to COOH increased. Out of the two mechanisms, the one that prevails depending on the conditions of the system and the nature of the chelating agent [27]. Usually, dissolution of oxide occurs predominantly through the mechanism (A) and the mechanism (B) is rather less probable due to the difficulties involved in bond breaking under this condition. Presence of organic acids on Fe$_3$O$_4$ powder (in XPS analysis) supported the dissolution of the Fe$_3$O$_4$ powder with (B) mechanism also. Dissolution of Fe$_3$O$_4$ in the NAC formulation at 85$^\circ$C was continued till the equilibrium though the rate of Fe dissolution was less after 30 minutes as shown in Fig. 3.18B(b). The solution pH rose from 2.7 to 4.0 within 30 minutes. This implies that the mechanism (A), that involves H$^{+}$ ions directly, is dominantly present at the beginning of the dissolution process and the reduction in the concentration of H$^{+}$ after 30 minutes induced a shift in mechanism to (B).

As soon as Fe$_3$O$_4$ came in contact with NAC formulation, reduction in size and increase in surface of Fe$_3$O$_4$ were observed due to Fe dissolution. As SOH groups are on surface thus it amplifies due to increase in Fe$_3$O$_4$ surface. This resulted in the reduction in size and increase in surface of Fe$_3$O$_4$ powder. Protonation of these SOH groups attracted
Sb(III) oxyanions and got adsorbed through the mechanism mentioned above. Due to fast dissolution of Fe at RT and 85°C within 30 minutes of experiments (Fig. 3.18B(a)&(b)), the new SOH group was generated on the magnetite surface which caused fast adsorption of Sb(III) (Fig. 3.18A(a)&(b)). But in the case of iron saturated NAC formulation at 85°C, further dissolution of iron was not much (Fig. 3.18B(c)). As generation of new SOH groups on Fe₃O₄ surface was less, adsorption of Sb(III) was slow and it took around 15 hours for complete adsorption in iron saturated case (Fig. 3.18A(c)).

**Fig. 3.21:** Schematic diagram of Sb(III) desorption process from magnetite surface.

Desorption of Sb(III) occurred only for fresh NAC formulation at 85°C experiment where Fe release was observed even after 30 minutes although at a slower rate. So, the release of Fe from Fe₃O₄ surface after complete adsorption of Sb(III) played a role in the desorption of Sb(III) from Fe₃O₄ surface. In the presence of NAC formulation after ~5 hours, Sb(III) release occurred at 85°C. The released Sb(III) was not in the form of oxyanion. It was present as ligand-Fe-O-Sb complex as shown in Fig. 3.21. In this complex form adsorption of Sb(III) is not possible on magnetite.
3.4.3.4 Interaction of Sb(III) with NAC Formulation

So far we have discussed the interaction of Sb(III) with Fe$_3$O$_4$ surface (i.e. adsorption) and interaction of NAC solution with Fe$_3$O$_4$ surface (i.e. dissolution of iron). Similarly interaction of Sb(III) with NAC formulation is also possible. NAC formulation is a combination of organic acids and these organic acids hold carboxylic and/or hydroxyl functional groups. Marie Tella, et. al. [28] explained that in the presence of poly-functional carboxylic and hydroxyl-carboxylic acids, Sb(III) forms stable 1:1 and 1:2 complexes in a wide range of pH of natural water (3<pH<9). The adjacent set of functional groups of organic acids is used to form a five-membered bidendate chelate with Sb(III). The possibility of complexation of Sb by organic acid keeps Sb(III) in solution. The complexation behavior of Sb(III) with organic acids has been discussed in detail in chapter V.

![Fig. 3.22: Schematic diagram of Sb(III) adsorption on magnetite in organic acids.](image)

3.4.3.5 Overall Interaction of Sb(III) with Magnetite Powder in NAC Formulation

As discussed so far, the interaction of Sb(III) with the magnetite surface in NAC medium is very complex. A schematic diagram is shown in Fig. 3.22 which presented all
possible phenomena that occurs during Fe₃O₄ dissolution in organic acids in the presence of dissolved Sb(III) at 85° C under reducing conditions. The schematic diagram shows the occurrence of both mechanisms of Fe₃O₄ dissolution. In mechanism (A), iron is released in the form of Fe²⁺/Fe³⁺ into the solution and subsequently forms complexes with chelating ligands in solution as indicated in the schematic diagram. In mechanism (B), initially chelating ligands interact with Fe through –OH groups on Fe₃O₄ surface and then the complexes of iron-chelating species are released into solution followed by O²⁻ neutralization by H⁺. Dissolution of iron increases the surface of Fe₃O₄ and hence more SOH groups are available for Sb(III) adsorption. Antimony(III) in solution can adsorb on the Fe₃O₄ surface via surface complexation or be in solution in complex form with organic complexant.

3.4.3.6 Behavior of Sb(III) Deposition on Magnetite Coated Carbon Steel Surface

Antimony(III) adsorption studies were carried out on thick (~30μ) Fe₃O₄ coated CS with a surface area of 15cm² obtained from power plant using 900ml of NAC solutions. Two different experiments were performed, the fresh NAC formulation was used in one experiment while 150ppm Fe loaded NAC formulation was used in another experiment. In both experiments, Sb(III) adsorption saturation was observed at around 30% of total Sb(III) in solution as shown in Fig. 3.23A. Iron dissolution was also saturated as shown in Fig. 3.23B. The adsorption and dissolution behavior can be compared directly with the case of magnetite powder shown in Fig. 3.18A. It appears that thick Fe₃O₄ coated CS coupons behave like Fe₃O₄ powder. The coating of these coupon remained adherent before and after exposure.
Fig. 3.23: Sb(III) adsorption behavior on thick magnetite coated CS area 15cm² in NAC formulation at 85°C A. (a) Without Fe powder addition, (b) With 150ppm Fe addition; Iron dissolution behavior B. (a) Without Fe powder addition, (b) With 150ppm Fe powder addition.

Antimony(III) adsorption experiment was also performed with thin (~0.8μ) Fe₃O₄ coated CS with surface area 6.2cm² using of 250ml of NAC solution. The Fe₃O₄ coating over the CS was developed in a pre-conditioned autoclave by keeping the coupons for 13days in LiOH (pH at room temperature) at 265°C. The autoclave solution was de-aerated by purging argon gas before heating and 25ppm of hydrazine was added to take
Fig. 3.24: Sb(III) adsorption behavior on thin magnetite coated CS area 6.2cm² in NAC formulation at 85°C (a) Sb(III) adsorption fraction, (b) Iron dissolution behavior.

care of remaining oxygen. Saturation adsorption of Sb(III) was not observed as shown in Fig 3.24 and iron release was continued throughout the experiment. The observation was very much different from the Fe₃O₄ powder case (Fig. 3.18A). In fact, the Sb(III) adsorption on thin Fe₃O₄ coated CS is almost linear with time and quite similar to that observed on the CS surface (Fig. 3.8). The delayed or slow adsorption of Sb on CS with a thin magnetite film is because of the hindrance caused by Fe₃O₄ where Sb adsorption is
by a different mechanism. However upon removal of magnetite film, the Sb adsorption pattern is similar to that on CS metal. The thin Fe$_3$O$_4$ coating on CS was adherent before exposure and the micrograph of the coating is shown in Fig. 3.25(a). The SEM taken after exposing the coated specimen in the NAC, the layer became loosely attached as shown in Fig. 3.25(b) and it was similar to the plain CS coupon exposed in NAC as shown in Fig. 3.25(c).

![Fig. 3.25: SEM picture of (a) Thin magnetite coated CS coupons, (b) Thin magnetite coated CS coupons exposed to NAC and Sb$_2$O$_3$ at 85°C under deoxygenated condition, and (c) Plain CS coupons exposed to NAC and Sb$_2$O$_3$ at 85°C under reducing condition.](image)

3.5 Summary

Dissolution studies showed only Sb(III) and Sb(V) species are soluble in a NAC solution under chemical decontamination condition. Both Sb(III) and Sb(V) species are stable under the decontamination condition due to slow rates of redox reactions between them.

Sb(V) does not adsorb on the CS surface (without oxide) in the decontamination condition while Sb(III) is adsorbed on the CS surface with first order reaction kinetics. XRD and XPS analyses showed Sb(III) migrated to the surface of the CS and formed bonds with O site of Fe-OH, resulting in the formation of a layer of Fe-O-Sb complex on
the surface. It was assumed that subsequently further adsorption of Fe\(^{2+}\) and Sb(III) on the layer initiated the formation of surface precipitation of amorphous FeSb\(_2\)O\(_4\) compound. Simultaneously, the red-ox reactions at the surface resulted in formation of Sb\(^\circ\).

Surface hydroxyl functional groups play a vital role in the adsorption of Sb(III) on Fe\(_3\)O\(_4\) surface. These SOH groups become protonized in acidic solution and attracts Sb(III) oxyanions Coulombically. Antimony(III) oxyanions make primary surface complex due to condensation or deprotonation reactions.

Desorption of adsorbed Sb(III) occurred from Fe\(_3\)O\(_4\) surface in the NAC formulation at 85\(^\circ\)C after ~5 hours. The continuous release of Fe from Fe\(_3\)O\(_4\) surface even after complete adsorption of Sb(III), plays a role in the desorption of Sb(III) from Fe\(_3\)O\(_4\) surface. The released Sb(III) was not absorbed back on the Fe\(_3\)O\(_4\) surface because it is released from the surface as ligand-Fe-O-Sb complex rather than as free Sb (III) oxyanion.

Sb(III) adsorption on thick Fe\(_3\)O\(_4\) coated CS surface is like Sb(III) adsorption on Fe\(_3\)O\(_4\) powder while with thin Fe\(_3\)O\(_4\) coated CS surface like Sb(III) adsorption on CS surface.

### 3.6 References


