Treatment of Intermediate level liquid waste of reprocessing origin-PREFRE, Tarapur

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Abstract

Industrial scale treatment of alkaline intermediate level liquid waste stored in waste tanks at PREFRE, Tarapur has been carried out successfully, utilizing an indigenously developed process, involving ion exchange removal of $^{137}$Cs and $^{90}$Sr, followed by combined chemical treatment of the down-stream effluent. More than 250 M$^3$ of the waste was decontaminated and discharged. This achievement has paved the way for creating adequate tank space, as a result of which the operation of PREFRE could be carried out uninterruptedly. A brief description of the process and highlights of the achievement are summarized in this paper.

Keywords: Intermediate level waste, decontamination, ion exchange, chemical treatment.

Introduction

Intermediate level liquid waste (ILW) generated from reprocessing plants is made alkaline by the addition of Na$_2$CO$_3$ and NaOH and stored in underground carbon steel tanks. This waste is characterized by high salt loads and high gross $\beta$ activity, mainly due to the presence of $^{137}$Cs and traces of $^{90}$Sr, $^{106}$Ru etc. This alkaline ILW is treated by adopting an indigenously developed ion exchange based process, utilizing in-house synthesized, Cs-selective, Resorcinol Formaldehyde Polycondensate Resin (RFPR), followed by a commercially available Sr selective Iminodiacetic Acid Resin (IDAR). Industrial scale application of the process has been successfully demonstrated earlier, at Trombay [1-3], wherein large volumes of ILW originating from reprocessing of research reactor spent fuel have been decontaminated. Operation was made easily mobile, by installing the whole ion exchange facility on a 40 Te trailer, which could be taken to the waste tank for treatment.

Excellent decontamination performance of the process and confidence gained during treatment of the ILW, encouraged us in setting up the facility for treatment of alkaline ILW, stored in underground tanks at PREFRE Tarapur plant. This plant is under continuous operation since commissioning, for reprocessing of spent fuels irradiated in power reactors. Unlike processing of ILW at Trombay, adaptation of the process for treatment of the ILW of PREFRE reprocessing plant origin, posed major challenges, mainly due to the presence of some trace quantities of chemical and radiochemical constituents in the waste.
Notably, the presence of traces of dissolved organics, generated from degradation of tri-butyl phosphate (TBP), interfered significantly in the decontamination of the waste. Further, presence of substantial amounts of $^{106}$Ru and $^{99}$Tc activity in the down-stream of ion exchange process entailed development of efficient processes, to bring down the activity level below discharge limits. Although it is known that $^{99}$Tc in reprocessing waste is present mostly as $\text{TcO}_4^-$ anion, presence of the radioelement in ILW was found for the first time in India. Apart from the chemistry aspects, implementation of the process within a very short time period was another challenge to engineers, as it involved shifting and refurbishment of the mobile facility, installation and its commissioning. All the challenges were met easily and more than 250 M$^3$ of the ILW including 200 M$^3$ of Tank-6 and 50 M$^3$ of Tank-5 waste was decontaminated, thereby creating adequate tank space and ensuring sustainability of PREFRE operation. A summary of the treatment campaign including a brief description of the processes used for treatment, are highlighted in the following sections.

### Characteristics of waste

Detailed characterization of WTF-06 and WTF-05 waste of PREFRE Tarapur was done, prior to the treatment campaign. Further, radiochemical characterization with respect to the minor constituents was obtained, by analyzing the samples generated after removal of major radionuclides, $^{137}$Cs by ion exchange. A typical characteristic of both the tank’s contents before and after ion exchange treatment, is shown in Table 1. It can be seen that, both the wastes are similar with respect to their chemical and radiochemical constituents although their concentrations vary widely. The total dissolved solids are mainly due to the presence of NaNO$_3$ and Na$_2$CO$_3$. The salient features of both wastes include: presence of dissolved organics, significantly higher amounts of $^{106}$Ru and $^{99}$Tc activity and $^{137}$Cs being the major radionuclide. In comparison to WTF-06, the WTF-05 waste contained about 2.5 times higher $^{137}$Cs and, more importantly, about 35 times higher $^{106}$Ru activity.

### Removal of $^{137}$Cs and $^{90}$Sr by Ion exchange

A thumbnail view of the ion exchange system is shown in Fig.1. The waste was pumped at a flow rate of 400 L/h to the system, which comprised of a pre-filter (F1), three ion-exchange columns (two of them are loaded with RF resin for Cs-removal and one with imino diacetic acid resin for Sr-removal), each of 100 liters capacity in series and a resin trap. The ion exchange columns are installed on a self shielded cubicle. This was further enclosed by a

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### Table 1: Characteristics of ILW before and after ion exchange treatment

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Before IX treatment</th>
<th>After IX treatment</th>
<th>Before IX treatment</th>
<th>After IX treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>12.8</td>
<td>12.8</td>
<td>12.5</td>
<td>12.7</td>
</tr>
<tr>
<td>TDS, g/L</td>
<td>140</td>
<td>140</td>
<td>180</td>
<td>180</td>
</tr>
<tr>
<td>Total P as TBP, g/L</td>
<td>1.8</td>
<td>1.8</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Gross â, mCi/L</td>
<td>21.5</td>
<td>0.17</td>
<td>54.6</td>
<td>0.34</td>
</tr>
<tr>
<td>$^{137}$Cs, ””</td>
<td>21.1</td>
<td>0.10</td>
<td>48.8</td>
<td>0.02</td>
</tr>
<tr>
<td>$^{90}$Sr, ””</td>
<td>$2.0 \times 10^{-3}$</td>
<td>$1.4 \times 10^{-3}$</td>
<td>$2.0 \times 10^{-3}$</td>
<td>$2.0 \times 10^{-3}$</td>
</tr>
<tr>
<td>$^{106}$Ru, ””</td>
<td>$5.2 \times 10^{-3}$</td>
<td>$5.2 \times 10^{-3}$</td>
<td>0.18-0.10</td>
<td>0.18-0.05</td>
</tr>
<tr>
<td>$^{99}$Tc, ””</td>
<td>$5.1 \times 10^{-2}$</td>
<td>$5.1 \times 10^{-2}$</td>
<td>0.10</td>
<td>0.09</td>
</tr>
</tbody>
</table>
bigger cubicle within which all the piping, valves, instrument gadgets have been installed. The whole facility is installed on a 40 Te trailer. The treated effluent was collected in a monitoring tank. At the end of loading run, only lead RF column was eluated and then flow path between the two RF columns was interchanged for the next cycle to use the regenerated column as guard column, in every cycle. About 25-35 M³ of waste was treated in each cycle. The performance of the ion exchange column was found to be almost invariant throughout the campaign and thus a typical profile of the treated effluent is shown in Table 1. This treated effluent from monitoring tank was routed to the LWTP for further treatment as described below.

Decontamination of down-stream of ion exchange by chemical treatment

The down-stream of ion exchange is highly alkaline and mainly ¹⁰⁶Ru and ⁹⁹Tc rich. Decontamination of the down-stream of ion exchange process was done at LWTP, by adopting waste-specific chemical treatment formulations. Two processes have been used, for treatment of effluents generated during the campaign. Evaluation of processes and optimization of process parameters have been discussed in detail, in our earlier communications [4-5].

In summary, all the processes involve adjustment of pH to 2 by addition of acid, followed by addition of coagulant and adjustment of final pH to 7-8. The initial adjustment of effluent pH <2 was necessitated for destruction of carbonate, which interferes significantly in ¹⁰⁶Ru decontamination. For adjustment of pH of the effluents, instead of using HNO₃, the acidic ILW generated from evaporation of high level waste in Advanced Vitrification System (AVS) was used. The AVS waste was an acidic (4M) effluent, containing about 0.1 mCi/L of ¹³⁷Cs and traces of ¹⁰⁶Ru activity. After pH adjustment, the effluent was treated by a two-step chemical treatment, involving precipitation of ferrous hydroxide in the presence of sulphite, FeS, copper ferrocyanide and barium sulphate. After the two-step treatment using the same formulation, the gross beta activity of the supernatant was reduced to 1 x 10⁻³ mCi/L and therefore it was discharged after suitable dilution. The organics present in the waste were found to be separated in the form of an oily layer, at laboratory scale trials and in the form of a yellow layer at plant scale. A file photograph of the layer can be seen in Fig. 2. Interference of the presence of organics on Ru decontamination was overcome by using higher dosing of coagulants. The sludge generated from precipitation was conditioned, cemented and disposed off as solid waste.

In the case of WTF-05 effluent, the Fe(OH)₂-based precipitation process, was found to be ineffective mainly...
due to the presence of higher concentration of $^{106}$Ru activity and high organic interference. An improved process was adopted for decontamination of the effluent. In this process, the organics, mainly dibutyl phosphate, were separated by the addition of Fe$^{3+}$ in pH 2 solution for its precipitation as Fe-DBP complex. Then precipitation of CoS along with FeS, copper ferrocyanide and barium sulphate, was carried out. After Step-I treatment in the first trial (batch size: 12 M$^3$), the reduction of gross beta activity from 0.34 mCi/L to 7.2 x 10$^{-3}$ mCi/L was achieved. Since only $^{106}$Ru activity remained, Step-II treatment was therefore carried out, by adding 1000 ppm of Fe$^{2+}$ as Fe(OH)$_2$ and a decontaminated effluent containing $< 1.7 \times 10^{-3}$ mCi/L was obtained. During 2nd trial, Fe(OH)$_2$ precipitation (500 ppm Fe$^{2+}$) was included along with CoS and FeS precipitation in the 1st Step which resulted in a decontaminated effluent containing $< 2.7 \times 10^{-3}$ mCi/L. The effluent was then discharged after suitable dilution.

**Executive summary of the campaign**

About 200 M$^3$ of WTF-06 and 50 M$^3$ of WTF-05 waste was treated successfully in the first phase of the campaign. Waste specific chemical treatment processes have been used, for decontamination of the down-stream effluent in a cost-effective manner. The highly $^{99}$Tc and $^{106}$Ru-rich effluent, generated from treatment of WTF-05, was also treated successfully. Experience gained in this campaign will be utilized in future treatment efforts.

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**References**