Process for $^{99}$Tc Removal from Intermediate Level Waste of Reprocessing Origin by in-situ formed Corrosion Product of Mild Steel Wool

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A novel process has been developed for removal of Technetium ($^{99}$Tc) from intermediate liquid waste (ILW) by making use of in-situ formed corrosion products of mild steel. The process has been demonstrated with the actual ILW at NRB, Tarapur. A healthy decontamination factor of 2000 was also demonstrated in the process.

Introduction
Technetium ($^{99}$Tc) arising from spent fuel reprocessing is a major radiation concern owing to a combination of high thermal fission yield (6%), long half life ($2.13 \times 10^7$ y), high environmental mobility in oxidized pertechnetate form, combined with radioactivity as a $\beta$ – emitter [1]. Further, $^{99}$Tc presents a challenge to conventional high temperature vitrification in a borosilicate glass matrix owing to its volatility at glass synthesis temperatures.

Thus, efforts are underway to capture and sequestrate $^{99}$Tc using ion exchange resins (elutable and non-elutable), crown ethers or capture in mineral phases [2, 3]. Indeed, it is known that $^{99}$Tc can be sequestrated into various mineral phases including perovskites, rutile, sodalite, trevorite etc [2]. However, the preparation of most of these phases requires high temperature conditions with specialized equipment such as hot isostatic pressing (HIP).

Efforts to utilize goethite/magnetite to capture $^{99}$Tc from Sanford Low Activity Waste (LAW) were carried out on bench scale by co-precipitating goethite in the LAW solutions. While Tc capture using goethite was demonstrated in these studies, the ferrihydrite precursor for goethite formation was synthesized ex-situ under anoxic conditions [4]. Synthesis, and particularly storage, of ferrihydrite is challenging due to its instability and its conversion to Fe$_2$O$_3$ upon exposure to air oxygen [4]. It has also been demonstrated that ex-situ synthesized Fe$_2$O$_3$ does not show Tc uptake.

It is clear from the literature that mineralization of Tc in Fe-oxides/oxyhydroxides is well known. Indeed, such take-up has been the subject of several papers and reports listed in the references [1 – 3]. Also, well known is that mild steel can corrode in aqueous environment to produce iron oxides/oxyhydroxide phases. In the process developed, we exploit corrosion of mild steel to produce the iron oxide/oxyhydroxide phases required for Tc sequestration, while avoiding ex-situ synthesis of ferrihydrite under demanding anoxic conditions [5].

This paper highlights the process development studies and the results of $^{99}$Tc removal with actual Intermediate Level Waste (ILW).

Experimental Techniques
The experimental set-up used for Tc removal studies is presented in Fig. 1.

Fig. 1: Lab scale experimental set-up for Tc removal from ILW
The lab scale studies consist of a batch reactor containing MS wool, into which the waste was introduced \( (V/m = 100) \). Continuous air bubbling was provided for nearly four hours, and thereafter the solution was left standing overnight. Subsequently, the supernatant was analyzed radiometrically for \( \text{Tc} \). Process optimization with respect to \( V/m \) ratio, effect of starting \( \text{pH} \) and effect of anions and nitrates in the ILW were studied and the results are used to arrive at optimum process conditions for \( \text{Tc} \) removal.

Scale-up studies were then carried out at HIRUP, BARC with simulated waste solutions on a 25 lit. scale using \(^{99m}\text{Tc}\) milked from a moly-cow sourced from BRIT, Mumbai. Finally, the process was demonstrated on a 40 lit. scale at NRB Tarapur.

**Results and Discussions**

In the present process, corrosion of mild steel results in the formation of corrosion products, which then pick up \(^{99m}\text{Tc}\) from the ILW solution. Therefore, it is necessary to optimize process conditions for in-situ formation of corrosion product and \( \text{Tc} \) trapping. One of the main process conditions is the \( \text{pH} \) of the starting solution. Fig. 2 shows the effect of different starting \( \text{pH} \) on \( \text{Tc} \) removal performance.

In the case of waste with a \( \text{pH} \) of 2, an over 99.6% removal of Technetium was observed within the first 2 hours of initiation. During corrosion, release of \( \text{Fe}^{2+} \) ions from the surface of the corroding steel leads to a concomitant release of \( \text{OH}^- \) ions which cause an increase in the solution \( \text{pH} \) from 2 to 6 resulting in the formation of a reddish-brown corrosion product that settles at the bottom. Notably, most of the original activity of the ILW is concentrated in this phase. Since the corrosion product settles to the bottom, separation becomes quite simple.

Similar inactive studies were carried out to generate mineral phases for X-ray Powder Diffraction (XRD) analyses. From these studies, the dominant mineral phase is found to be Goethite \((\alpha-\text{FeOOH})\). It has been shown in the literature that three \( \text{Tc} \) (IV) can replace four \( \text{Fe} \) (III) in Goethite \((\text{FeOOH})\), while creating one \( \text{Fe} \) (III) vacancy as depicted in Figure 3. The \( \text{Tc} \) (IV) is formed from \( \text{Tc} \) (VII) by reduction due to \( \text{Fe} \) (II) according to the following reaction:

\[
\text{Tc} \text{ (VII)} + 3 \text{ Fe} \text{ (II)} \rightarrow 3 \text{ Fe} \text{ (III)} + \text{Tc} \text{ (IV)}
\]

Further, process parameters such as the \( V/m \) ratio, were also optimized on lab scale. It was found that the process is effective over a wide \( V/m \) range from 10 to 1000. As expected, process kinetics is significantly accelerated using lower \( V/m \). However, low \( V/m \) also results in a larger volume of secondary wastes. On the other hand, a higher \( V/m \) ratio reduces secondary waste volume at the expense of slower process kinetics, which is inadequate for plant scale treatment of large waste volumes. Therefore, a \( V/m \) of 100 has been selected for further processes.

Bench scale trials at 25 lit. scale using \(^{99m}\text{Tc}\) were carried out with various simulated waste solutions containing differing concentrations of \( \text{NaNO}_3 \). One study was also carried out with sea water spiked with \(^{99m}\text{Tc}\) to simulate accidental scenario. In all the cases, excellent \( \text{Tc} \) removal was observed, confirming the efficacy of the process.

A process flow chart based upon above results has been finalized and is presented in Fig. 4.

A demonstration trial has been conducted at 40 lit. scale with actual ILW in NRB, Tarapur. ILW as generated is alkaline in nature, therefore pre-treatment by addition of \( \text{HNO}_3 \), was carried out to adjust \( \text{pH} \) to 2. About 400 g MS wool was used in
Radiochemical composition of the waste is shown in Table 2. The system was agitated continuously by air bubbling, at a flow rate of ~1 lpm, for 6 h, and left standing overnight. Samples were withdrawn at periodic intervals for radiochemical analysis. In the second experiment, same MS wool from the previous run was used. The objective of this experiment was to ensure the efficacy of MS wool in repeated experiments, in addition to verification of reproducibility of the results. Results of these experiments are summarized in Table 3.

It is evident from Table 3 that Tc DF of about 1700 was obtained during the first trial and the same MS wool is effective for the second experiment. Laboratory results show that the same wool can be used for more than five cycles. It is noteworthy that this process is useful for removal of $^{106}$Ru and $^{125}$Sb also, which are major activity contributors to LLW after $^{99}$Tc and $^{137}$Cs removal. This process generates a small volume of secondary sludge, typically in the order of magnitude which is smaller than the conventional processes.

The sludge is amenable to vitrification in suitably optimized glass matrices having a reducing melt environment. In such glasses, Tc retention approaching 70% is presently possible, compared to less than 20% upon direct vitrification of Tc bearing streams in conventional borosilicate glasses.

**Conclusions**

Tc removal by in-situ formed corrosion product of mild steel wool is an effective method to remove Tc from low and intermediate level wastes. The process generates low volume of secondary sludge, which can be immobilized in a suitable glass matrix. Further R&D is being pursued to process corrosion products and used MS wool into suitable wasteforms.

**References**