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Removal of actinides and fission products activity from intermediate alkaline waste using inorganic exchangers

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Hydrated iron oxide or amorphous-$Fe_2O_3 \cdot 3.5\ H_2O$ (HFeO), hydrated titanium oxide (HTiO) and hydrated thorium oxide (HThO) were synthesized and their applicability for the decontamination of intermediate level liquid wastes (ILLW) was tested. The sorption of a few actinides like plutonium and americium on HFeO, ^{137}Cs and ^{106}Ru on HTiO and ^{90}Sr on HThO was investigated as a function of pH, time and loading capacity of the hydrous oxide with metal ions. The influence of the total dissolved salt content was also monitored. Some of these parameters influenced the sorption behavior significantly. The radiation stability of these inorganic sorbents were studied by irradiating them up to 48 Mrad. Adsorbed actinides and fission products were successfully eluted from HFeO and from the mix-bed of HTiO and HThO by 0.5M nitric acid.

Introduction

An efficient and economically viable waste disposal system is essential for safe and effective management of radioactive liquid wastes. The alkaline intermediate level liquid waste (ILLW) is generated from radiochemical operations in the nuclear fuel cycle. The waste contains non-negligible amounts of alpha-emitting radionuclides such as uranium, plutonium and americium. Fission products such as strontium (^{90}Sr), cesium (^{137}Cs) and ruthenium (^{106}Ru) associated with this waste, contribute significantly to beta- and gamma-activities (Table 1). Removal of actinides such as Pu, Am, and fission products like ^{137}Cs, ^{106}Ru and ^{90}Sr from the ILLW have been attempted by a combination of solvent extraction (SX) and ion-exchange (IX).[1] The particle hydrates[2] are gaining in importance as they are easy to prepare and stabile towards thermal, chemical and radiation effects. These properties make them viable materials for the separation of toxic metal ions in waste management.

Table 1. Typical chemical composition of ILLW solution

pH	9.4
Total alkalinity, N	0.29
^{134}Cs, mCi/l	0.0035
^{137}Cs, mCi/l	2.21
^{106}Ru, mCi/l	0.02
^{90}Sr, mCi/l	0.0044
Uranium, g/l	4.97
Plutonium, mg/l	0.86
Americium, mg/l	$1.2 \cdot 10^{-4}$
Dissolved solids, g/l	192.8
Na/Cs ratio	10^7

The hydrated iron oxide ($Fe_2O_3 \cdot 3.5\ H_2O$) or amorphous iron oxide {am-$Fe_2O_3 \cdot 3.5\ H_2O$ (HFeO)} have been reported to be a good adsorbent for Eu(III) and Co(II)[3] and Pu.[4] Mixture of hydrated thorium oxide (HThO) with other inorganic exchangers can be applied successfully in the preparation of inorganic ion exchange membrane,[5] and also for decontamination of ILLW from fission products.[6] Based on preliminary experiments, a comprehensive study was initiated to develop a scheme for removal of plutonium, americium and fission products using HFeO, HTiO and HThO alone as well as their mixtures.

In the present study we describe the preparation of HFeO, HTiO and HThO. Their adsorption-desorption and loading characteristics, the effect of high salt content and their stability towards radiation are also given.

We present the removal of Pu, Am and major fission products such as ^{137}Cs, ^{90}Sr and ^{106}Ru from ILLW using those inorganic exchangers.

Experimental

Reagents

Analytical grade $Fe(NO_3)_3$ and $TiCl_4$ were used to produce hydrated iron and titanium oxides, respectively. The crystalline thorium nitrate used for the synthesis of hydrated thorium oxide was procured from British Drug House (BDH). The radiochemical purity of Pu^{239} and Am^{241} tracers were proved by alpha-spectrometry while ^{137}Cs and ^{106}Ru tracers were tested by high energy photon spectrometry coupled with a 4K multichannel analyzer.

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Intermediate level liquid wastes (ILLW)

In the nuclear chemical facility, liquid aqueous acidic wastes are generated during the purification of U and Pu. These wastes contain substantial amount of actinides and fission products, and are evaporated for volume reduction using a 3-stage evaporation cycle. The concentrated solution obtained after the 3rd cycle of evaporation is neutralized with 8M sodium hydroxide upto pH~4, followed by the addition of 2M sodium carbonate till pH 9 to 10, to produce the ILLW which is finally stored in carbon steel tanks. The purpose of adjusting pH between 9 to 10 by sodium carbonate is to avoid the precipitation of uranium and plutonium. The typical composition of ILLW is presented in Table 1.

Preparation of simulated feed solution

Sorption measurements were carried out using real and simulated ILLW solution. Simulated ILLW solution was prepared by neutralization of a 3M HNO_3 solution, spiked with ^{238}U, ^{239}Pu, ^{241}Am, ^{137}Cs, ^{90}Sr and ^{106}Ru, using solid NaOH to reach pH~4. Then pH was adjusted to 9.2 by addition of solid Na_2CO_3. All pH adjustments during the sorption were made by diluted HNO_3 and NaOH solutions. The effect of concentration and loading capacity was examined using simulated ILLW solution.

Synthesis of hydrous iron oxide (HFeO)

Hydrous iron oxide was prepared by mixing ca. 400 cm^3 of 0.2M $Fe(NO_3)_3$ solution (pH~1.5), to 2000 cm^3 of 1M NH_4OH solution,[3] at a rate of 10 cm^3/min. The precipitate was removed by decantation, followed by filtration and finally it was washed with distilled water till it was free from alkalinity and kept for air drying at room temperature. The solid mass was immersed and crushed in distilled water and kept for drying overnight and then ground. A particle size of ca. 80–100 μm was separated by sieving (U.S. mesh) and this was conditioned with 10^{-3}M HCl to convert all adsorption sites in H^+ form. am-Fe_2O_3 was always stored over a saturated NH_4Cl solution in a desiccator.

Synthesis of hydrous titanium oxide (HTiO)

The synthesis of HTiO was carried out according to the procedure described by KASUGA et al.[7] Hydrous titanium oxide was precipitated by adding 1 mol/l NaOH solution into the diluted $TiCl_4$ solution under vigorous stirring. After 2 days, the precipitate was separated from the mother liquor by filtration, and then it was uniformly dispersed into an excess of distilled water. The fine white precipitate was filtered and dried at 70 °C under an infra red lamp, thus the precipitate got converted into grey lumps. The product was ground and sieved, then converted to the H^+-form with 0.05 mol/l HCl solution. After washing with distilled water to remove Cl^-, the exchanger was air dried at room temperature and stored in a desiccator.

Synthesis of hydrous thorium oxide (HThO)

Hydrous thorium oxide was synthesized according to the procedure described by MISHRA et al.[8] A 0.1M solution of $Th(NO_3)_4 \cdot 6H_2O$ in 1M HNO_3 was heated to about 70 °C. An excess of 1M NaOH solution was added slowly under constant stirring. A glossy white precipitate thus obtained was digested at 70 °C for 2 hours and stored for 2 days. The content was filtered and the precipitate was washed repeatedly with distilled water to remove alkalinity and then dried at 50 °C under an I.R. lamp. The dried mass was dipped in distilled water and crushed. The crushed particles were filtered and dried at room temperature (25 °C) and then sieved to get uniform size particles.

Sorption measurements

Weighted amounts of HFeO, i.e., ~0.05 g were taken with 3 ml of actual ILLW (pH~9.2) and equilibrated for 2 hours. The gross alpha-activity in the filtered solution was monitored by a ZnS (Ag) scintillation counter. Equal quantities of HTiO and HThO were mixed together, blended for homogeneity and used as a mixture for experiment. The adsorption of Cs, Sr and Ru was measured individually for HTiO and HThO, by taking 0.05 g of adsorbent (HTiO)/(HThO) in 1.5 ml of waste effluent obtained from HFeO+ILLW solution at pH 10 by stirring mechanically for 2 hours at room temperature (25–26 °C). Gamma- and beta-activities in the aqueous phase were analyzed using NaI(Tl) and plastic scintillation counters. Similarly, the adsorption of ^{137}Cs, ^{90}Sr and ^{106}Ru was measured using a mixture of HTiO and HThO exchangers. All the measurements were done at least in duplicate.

Plutonium and americium were separated from ILLW by HFeO. The effluent thus obtained was adjusted to pH 10, then equilibrated thrice. Each time fresh ion exchanger (mixture of HTiO and HThO) was used. After three contacts, the gamma- and beta-activities in the effluent obtained were measured using NaI (Tl) and plastic scintillation counter, respectively. The flow sheet is briefly summarized in Fig. 1.

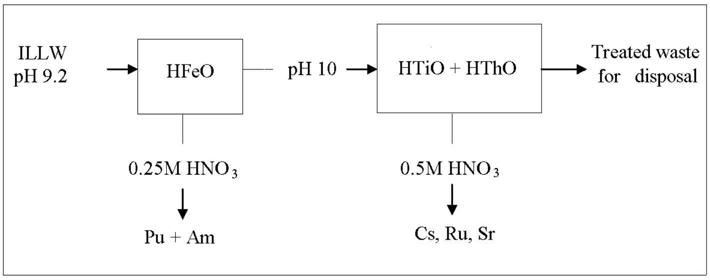


Fig. 1. Flow-sheet of the ILL waste treatment

Adsorption rate

The rate of sorption was evaluated by determining the extent of sorption with the equilibration time. Aqueous solutions containing traces of Pu, Am and fission products such as ^{137}Cs, ^{90}Sr and ^{106}Ru and 0.05 g of the ion-exchanger were equilibrated in closed test tubes. At regular time intervals, samples were pipetted from the liquid phase and the activity was measured. The percentage adsorption (Ad%) was calculated as:

$$Ad\% = (C_i - C_f)\cdot 100/C_i \qquad (1)$$

where C_i and C_f are the initial and final activities in the liquid phase, respectively. The particle size of exchangers was in the range of 80–100 mesh. All experiments were carried out at room temperature, except for the study of the temperature effect.

Radiation stability measurements

In order to see the radiation stability of the synthesized hydrous oxides, known amounts of HFeO, HTiO and HThO were exposed to γ-irradiation (2,425 Ci ^{60}Co) in presence of air at a dose rate of approximately 0.516 Mrad/h. After irradiation, the adsorption of Pu, Am, Cs and Sr was carried out under identical conditions.

Results and discussion

Characterization

The hydrated HFeO, HThO and HTiO were analyzed for crystal phase using a X-ray diffractometer (Model Kristalloflex-D-500). All the oxides air dried at 70 °C were amorphous in nature, as described in the literature.[3,8]

Effect of pH and the time dependence of adsorption

The pH of the sorptive solution is generally responsible for the surface electric charge of the sorbents affecting the ionic sorption on the metal oxide–solution interface. To assess the uptake process, the sorption of Pu, Am on HFeO, Sr on HThO, Ru and Cs on HTiO was examined in aqueous solutions of various pH (between 2 and 10). The results of U, Pu and Am on HFeO are presented in Fig. 2. The uptake increased with increasing pH as shown in the Table 2. On the other hand, adsorption of Pu and Am on HFeO exceeded well above 95% (Fig. 2) at pH~10. The uptake observed for uranium was maximum upto 32% and an apparent equilibrium was achieved within 120 minutes as shown in Fig. 3. Similarly, the percentage of fission products sorbed on HTiO and HThO was plotted as a function of time at pH~9.2 (Fig. 4). Sorption of ^{90}Sr and ^{106}Ru on HThO was reached a maximum of 99% for ^{90}Sr and 58% for ^{106}Ru in 120 minutes, however, for ^{137}Cs adsorption it was found to be around 18% on HThO.

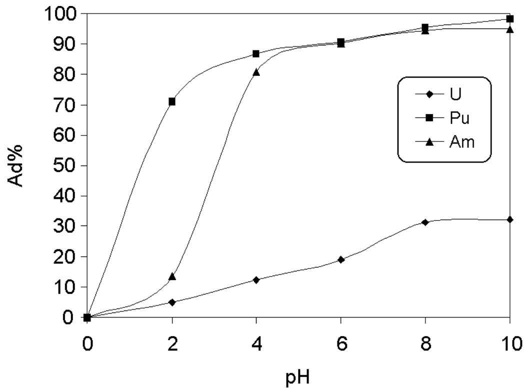


Fig. 2. Adsorption of U, Pu and Am on HFeO as a function of pH. Feed: simulated ILLW, weight of sorbent: ~0.05 g, equilibration time: 120 min., salt: 19%, U: $2.1\cdot10^{-2}$ mol/l, Pu: $3.58\cdot10^{-6}$ mol/l, Am: $4.97\cdot10^{-7}$ mol/l

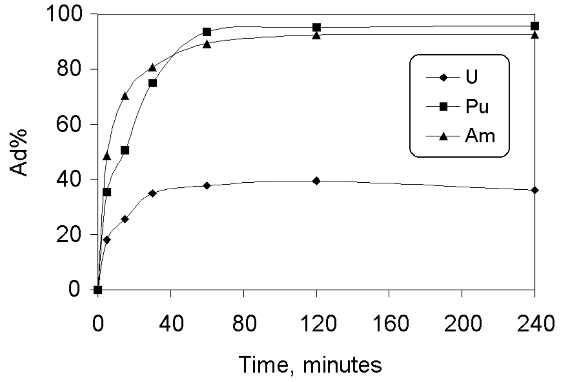


Fig. 3. Adsorption of U, Pu and Am on HFeO as a function of time. Feed: simulated ILLW, weight of sorbent: ~0.05 g, pH: ~10, salt: 19%, U: $2.1\cdot10^{-2}$ mol/l, Pu: $3.58\cdot10^{-6}$ mol/l, Am: $4.97\cdot10^{-7}$ mol/l

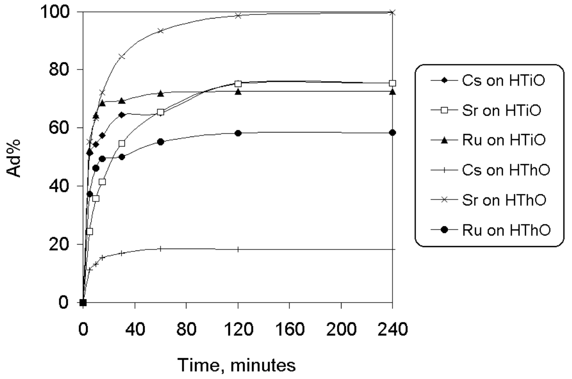


Fig. 4. Adsorption of fission products on different hydrous oxides as a function of time. Feed: simulated ILLW, weight of each sorbent: ~0.05 g, pH: ~10, salt: 19%, activity (mCi/l) ^{137}Cs: 0.14, ^{106}Ru: 0.17, ^{90}Sr: 0.16

Sorption for ^{90}Sr, ^{106}Ru and ^{137}Cs on HTiO was found to be around 70–75% at the same time. This indicates that although the apparent equilibrium is reached in 120 minutes the complete sorption of U, Pu, Am, Cs, Sr and Ru metal ions takes longer. The fast sorption may be due to the availability of active oxide sites. When these sites are occupied, the rate becomes slower and reaches a plateau. At a specific concentration of the adsorbate, an apparent equilibrium between the two phases is attained.

Influence of the salt content

The effect of salt content ($NaNO_3$) of the solution, on the adsorption behavior of Pu on HFeO, Cs on HTiO and Sr on HThO was studied between 8 and 260 g/kg of $NaNO_3$. Results from Fig. 5 indicate that the *Ad*% for Cs on HTiO decreases significantly as the salt content increases. However, the uptake of Pu on HFeO and Sr on HThO was not much affected at higher salt content (Figs 6 and 7). This may be due to the hindrance caused by the maximum hydrated Na$^+$ ions,[9,10,11] present in much larger quantities than the Cs$^+$ ions. This may shield the active sites of metal oxides and interferes with the approach of Cs$^+$ to the active sites. This results in decreased uptake of cesium with increasing salt content.

Table 2. Adsorption of Cs, Ru and Sr on inorganic ion-exchangers

pH	*Ad*%					
	HTiO			HThO		
	^{137}Cs	^{106}Ru	^{90}Sr	^{137}Cs	^{106}Ru	^{90}Sr
2	0.6	2.2	1.9	2.0	4.9	1.13
4	27.2	45.9	5.4	11.8	20.1	25.32
6	63.7	71.9	30.1	15.2	30.3	50.03
8	70.9	65.1	63.2	17.9	45.6	80.64
10	77.1	73.9	75.1	18.3	59.0	99.80

Feed: Simulated ILLW solution.*
Feed pH: 10.
Weight of exchangers: 0.05 g each (HTiO and HThO).
Equilibration time: 120 minutes.
* Initial activity: ^{137}Cs: 0.14; ^{106}Ru: 0.17; ^{90}Sr: 0.16 mCi/l.

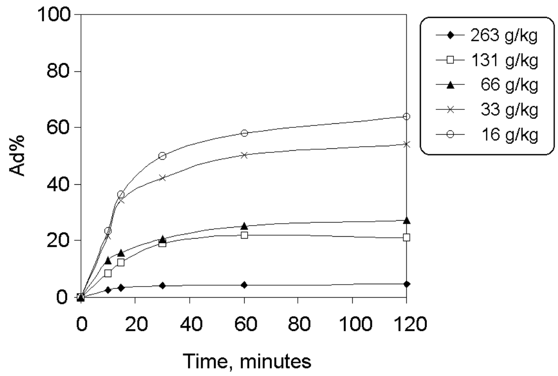


Fig. 5. Adsorption of ^{137}Cs on HTiO at various salt content. Feed: simulated ILLW, pH: ~10, weight of sorbent: ~0.05 g, ^{137}Cs: 0.14 mCi/l

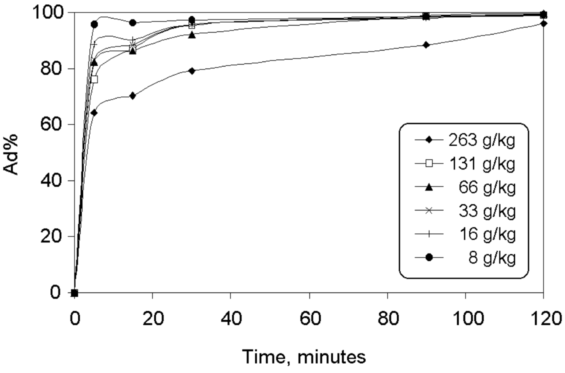


Fig. 6. Adsorption of Pu on HFeO at various salt content. Feed: simulated ILLW, pH: ~10, weight of sorbent: ~0.05 g, conc. of Pu in feed: $3.58\cdot10^{-6}$ mol/l

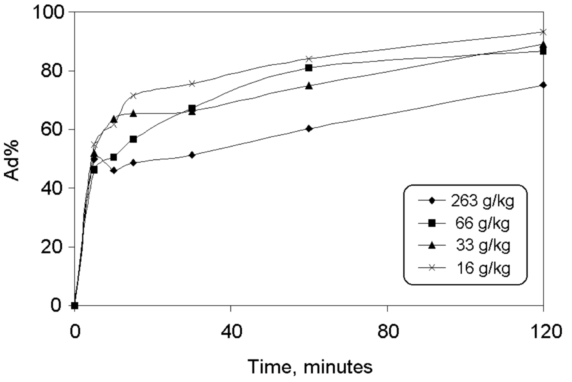


Fig. 7. Adsorption of ^{90}Sr on HThO at various salt content. Feed: simulated ILLW, pH: ~10, weight of sorbent: ~0.05 g, ^{90}Sr: 0.16 mCi/l

Effect of the metal ion concentration

The adsorption as a function of the concentration of the cations was studied. The results are presented in Figs 8 to 11. The concentrations of cations are varied over a wide range. It is seen that the percentage of cations adsorbed increases with decreasing cation concentration. This may be due to the availability of a higher number of active sites than required for the adsorption of all the available cations.

Plutonium loading of $2.86 \cdot 10^{-5}$ mol/g and americium loading of $2.86 \cdot 10^{-8}$ mol/g was achieved on HFeO, even though complete saturation could not be reached. At pH 10, the cesium loading on HTiO was $1.55 \cdot 10^{-3}$ mol/g. The strontium loading on HThO was found to be $2.23 \cdot 10^{-3}$ mol/g. In all cases, the loaded exchanger was washed with a pH 10 solution and then with distilled water followed by a wash with 0.01M HNO_3. Using 0.5M HNO_3, a quantitative desorption of the metal ions (>99%) was possible.

Effect of gamma-irradiation

The stability against radiation damage of HFeO, HThO and HTiO was evaluated. A weighed amount of metal oxide was exposed to a gamma-radiation of 48 Mrad. The adsorption of Pu and Am on HFeO, ^{137}Cs on HTiO and ^{90}Sr on HThO was determined under identical conditions as for the control sample. The K_d values obtained for the irradiated and control samples were similar, showing that the irradiation upto 48 Mrad has no influence on the adsorption characteristics of the metal oxides.

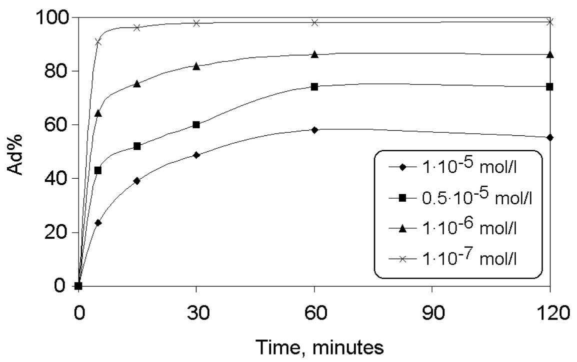


Fig. 8. Adsorption of Pu on HFeO at various concentrations. Feed: simulated ILLW, pH: ~10, weight of sorbent: ~0.05 g, salt: 19%

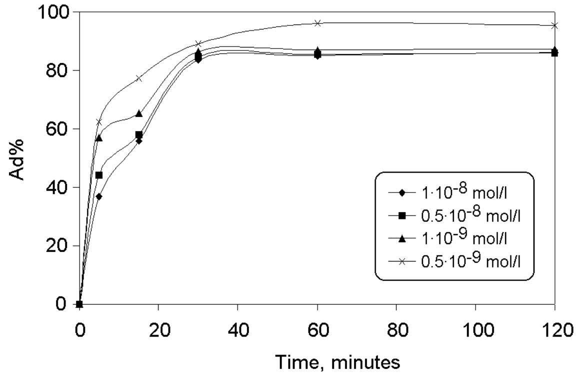


Fig. 9. Adsorption of Am on HFeO at various concentrations. Feed: simulated ILLW, pH: ~10, weight of sorbent: ~0.05 g, salt: 19%

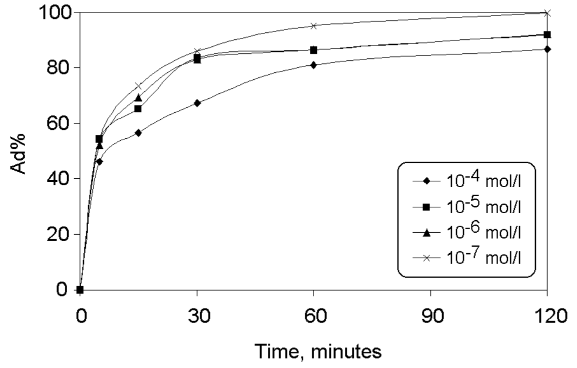


Fig. 10. Adsorption of Sr on HThO at various concentrations. Feed: simulated ILLW, pH: ~10, weight of sorbent: ~ 0.05 g, salt: 19%

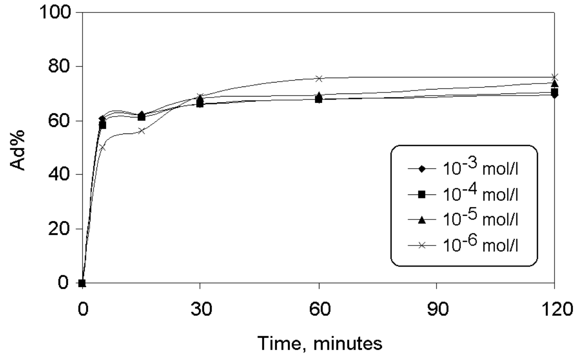


Fig. 11. Adsorption of Cs on HTiO at various concentrations. Feed: simulated ILLW, pH: ~10, weight of sorbent: ~0.05 g, salt: 19%

Adsorption mechanism

In hydrous metal oxides, both cation- and anion-exchange reactions can occur simultaneously,[12] as shown in Scheme 1.

MISHRA et al.[8] has demonstrated that at lower pH ranges anion exchange takes place and at higher pH range cation exchange reaction is preferred. Surface hydroxyl groups are responsible for the ion exchange properties of hydrous oxides. Table 2 presents the amount of tracers adsorbed on the synthesized metal oxides and shows that the amount adsorbed increases with increasing pH of the solution. MO^- is probably the adsorbent at higher pH. The negatively charged surface favors the cation exchange behavior. HEINONEN[13] described the cation uptake as an electrostatic attraction between the positively charged cations of strontium and the negatively charged surface of the hydrous titanium oxide. PARK[14,15] demonstrated that the hydrous oxides have a negative surface charge above pH 8. The exchange mechanism of hydrous inorganic exchangers can be presented as:

$$\begin{gathered} \text{M-OH} \Leftrightarrow \text{M-O}^- + \text{H}^+ \\ \text{M-O}^- + \text{B}^{n+} \Leftrightarrow \text{M-OB}^{(n-1)+} \end{gathered} \tag{2}$$

Significant absorption of Cs, Ru and Sr takes place only in alkaline medium of pH 8–12.

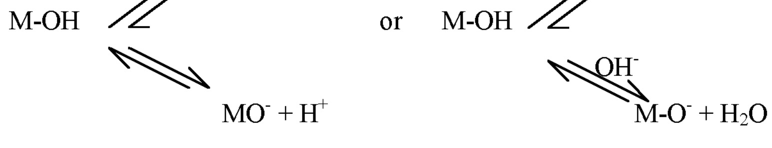
In carbonate medium, Pu and Am form carbonate complexes $Pu(CO_3)^{2+}$ [16] and $Am(CO_3)^+$,[7] respectively, and can be exchanged by hydrogen ions. At pH 4–6 uranium is present as $U_2O_5^{2+}$ and $U_3O_8^{2+}$,[18] which leads to cation exchange reactions. At higher pH U(VI) forms soluble neutral carbonate complexes, e.g., $Na_2UO_2(CO_3)_2$ [18] which are not adsorbed.

Cesium and strontium are present as Cs^+ and Sr^{2+} in ILLW. The hydration of Cs^+ is much less than Sr^{2+}. When spent fuel is dissolved in nitric acid, ruthenium forms a variety of complexes containing the nitrosyl ruthenium (Ru–NO) group, i.e., $[RuNO(NO_3)_x(NO_2)_y(OH)_z(H_2O)_{5\text{-}x\text{-}y\text{-}z}]^{3\text{-}x\text{-}y\text{-}z}$.[19]

These complexes are stable through various processing stages. The Ru complexes can be cationic, anionic or neutral, depending on the number and type of ligands attached to the Ru–NO group. When the acidic solution is neutralized, the nitrato or nitro groups attached to the Ru are removed by the hydroxide groups, converting the Ru either to a soluble cationic species or to colloidal Ru. This explains the presence of Ru in ILLW, which gets adsorbed on dissociated metal oxides.

Treatment of alkaline ILLW

Alkaline waste generated in the PUREX process was used for batch equilibration. Results are given in Table 3 and it is shown that high separation factors of the order of 10^4 were obtained for alpha emitting radionuclides such as Pu and Am from fission products, with HFeO. The effluent obtained was treated with a mixture of HTiO and HThO for the removal of fission products. Table 3 shows that more than 98% of the radioactive nuclides can be removed from alkaline ILLW.



Scheme 1. Cation- and anion-exchange reactions in hydrous metal oxides

Table 3. Sorption of activities due to actinides and fission products using HFeO and a mixture of HTiO and HThO

Activity	Kd, (HFeO)	Separation factor*	After 3 contact total,** *Ad*(%) (HTiO+HThO)
Gross-α	$4.59 \cdot 10^4$	–	98.2
Gross-β	2.61	$1.72 \cdot 10^4$	98.7
Gross-γ	1.71	$2.61 \cdot 10^4$	98.9
Uranium	9.40	$4.88 \cdot 10^3$	32.1

Feed ***: alkaline ILLW solution.
Equilibration time: 120 minutes.
pH: 10.
Weight of HFeO: 0.05 g.
Weight of the mixture: 0.1 g (HTiO+HThO).
* Separation factor obtained for α-emitters, with respect to other contaminants.
** Feed solution used after equilibration with HFeO.
*** Composition of feed solution given in Table 1.

Conclusions

Our results show that more than 98% of alpha-activity and fission product activity (gross gamma-activity 2.51 mCi/l and gross beta-activity 3.04 mCi/l) can be removed using HFeO and a mixture of HTiO and HThO in three contacts. The resulting waste is suitable for disposal. It is observed that HFeO can be used for the removal of Pu and Am, while the mixture of HTiO and HThO is suitable for the removal of Cs, Ru and Sr from alkaline intermediate level liquid wastes.

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