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Evaluation of Alternate Materials and Methods for Strontium and Alpha Removal from Savannah River Site High-Level Waste Solutions

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1.0 Summary

A literature survey indicated a number of alternate materials and methods for the removal of strontium and alpha-emitting radionuclides (actinides). We evaluated the use of alternate materials versus proposed flowsheets for salt processing at the Savannah River Site (SRS). From this evaluation we recommend the following materials for further testing to determine the rate and extent of removal; : (1) sodium nonatitanate, (2) SrTreat, (3) crystalline silicotitanate, (4) pharmacosiderites and (5) coprecipitation with $Sr^{2+}/Ca^{2+}/NaMnO_4$. We do not recommend testing of liquid/liquid extraction and polymer filtration methods at this time.

2.0 Introduction

The Savannah River Site selected an amorphous sodium titanate material, referred to as monosodium titanate (MST) to remove strontium from supernatant high-level wastes as part of the In-Tank Precipitation process. This material is of a class of hydrous metal oxides originally developed by R. Dosch and coworkers at the Sandia National Laboratory in the 1970s. These amorphous materials are prepared by a sol-gel process and feature a high surface area. Testing also indicated that these materials remove a number of other species from alkaline solution including the actinides.[2,]

Kilpatrick and Hobbs of the Savannah River Technology Center (SRTC) modified the synthesis of the MST, which provided a narrower particle size distribution and improvements in filtration and settling characteristics. WSRC

provided this information to a number of vendors to prepare commercial quantities of the MST for the ITP operation. Two vendors, Optima Chemical Company and Boulder Scientific successfully prepared materials that met purchase specifications for strontium removal capacity, particle size distribution, solids concentration and alcohol content.

Actinide removal characteristics of the MST came under increasing scrutiny in early 1990s to ensure that the MST would not sorb sufficient fissile isotopes from the waste to pose a nuclear criticality hazard.' Research also investigated whether the decontaminated liquid waste from the ITP process would meet Z-Area limits for total alpha activity. The SRTC conducted a number of tests to support these concerns. Results indicated that the MST effectively removes uranium and plutonium, but will not load sufficient quantities of fissile isotopes to pose a criticality concern.' None of this testing investigated the kinetics of the adsorption process.

The Salt Disposition Systems Engineering Team identified the adsorption kinetics of actinides and strontium onto MST as a technical risk for several of the processing alternatives selected for additional evaluation in Phase III of their effort. The Flow Sheet Team requested that the Savannah River Technology Center examine the adsorption kinetics of MST for several process alternatives. The Phase III studies examined the extent and rate of adsorption of strontium, uranium, neptunium and plutonium as a function of temperature, monosodium titanate concentration, and the concentrations of sodium and adsorbing species (Sr, Pu, Np and U). Additionally, comparison tests in the design of the experiments assessed the effects of mixing, sludge solids and the presence of sodium tetraphenylborate solids. Preliminary and final reports documented findings of the Phase III testing. Analysis of the Phase III testing indicated the need to perform additional kinetic testing with radioactive SRS tank waste and with simulants at lower ionic strength and MST concentrations.

Phase IV radioactive waste tests utilized a composite material prepared from archive samples from over twenty SRS tanks. Results indicated that the extent and rate of strontium, plutonium, neptunium and uranium removal with MST in radioactive waste agree with those previously measured with simulants. Additional tests with simulated waste solutions measured the extent and rate of strontium, plutonium, neptunium and uranium removal at 25 ° C in the presence of 0.2 and 0.4 g/L MST at 4.5 and 7.5 M sodium concentration.

Flowsheet calculations indicate that the rate of actinide removal is a key variable in sizing equipment for the salt processing alternatives. Filtration of MST and sludge mixtures exhibits reduced filtration fluxes compared to mixtures containing MST, sludge and tetraphenylborate solids. Production of clarified feed solution occurs in the current Alpha Sorption process about one-third of the time. This, combined with the low filtration fluxes, results in large equipment sizes for the Non-Eluatable Ion Exchange (N-IX), Caustic Side Solvent Extraction (CSSE) and Direct Grout (DG) processes, which are is much greater than that in the Small Tank Tetraphenylborate Precipitation (STTP) process. Thus, the Salt Disposition Systems Engineering Team requested that SRTC evaluate alternate materials or processes and determine if candidate materials and processes exist that may exhibit improved actinide removal kinetics and filtration characteristics compared to MST and thus merit testing.

3.0 Results and Discussion

Evaluation Criteria

We limited the scope of this evaluation to materials and processes that treat alkaline waste solutions. Thus, we did not consider options that acidify the waste in a pretreatment step. We selected candidates for testing as an alternate to monosodium titanate (MST) based on reported performance characteristics, technical maturity, impacts on current baseline flowsheets for the four Salt Disposition Alternatives and impacts on downstream facilities such as the Defense Waste Processing Facility (DWPF) and the Saltstone facility. We did not develop detailed flowsheets and mass balances with any of the materials. We also estimated required quantities based on amounts used in the literature to provide an order of magnitude assessment of possible impacts on downstream operations such as the DWPF and Saltstone.

Possible Materials and ProcessesRemoval Methods

The Department of Energy has funded a number of investigations during the last decade to evaluate and develop new

materials and materials and methods for the removal of strontium and, to a lesser extent, alpha-emitting radionuclides (i.e., actinides). Removal mMaterials and methods investigated include ion exchange, sorption, precipitation, coprecipitation, chelation or complexation and liquid/liquid extraction. With someFor some of the materialsmethods evaluated, the method for , removal may include more than one mechanism (e.g., both surface ion exchange and chemical sorption).

For this evaluation, we grouped all materials methods that utilize a preformed solid phase regardless of removal mechanism into a single category referred to as Solid Removal Agents. Monosodium titanate falls into this category. In principle, processes could use any of these materials in a batch reactor or continuous operation (e.g., packed column). Most of the available literature reports batch contact results. We discuss column results where available.

We also evaluated several alternate processes including precipitation/coprecipitation, liquid/liquid extraction and aqueous polymer filtration. Precipitation processes add a chemical reagent to the solution that causes a chemical transformation resulting in the formation of a solid phase due to solubility limitations. Note that certain aspects and implementation of a coprecipitation process resemble that of sorbents (e.g., sorption of a species onto freshly precipitated solids).

Liquid/liquid extraction techniques that separate metal ions from one liquid phase to another are well known. For example, irradiated fuel/target reprocessing operations use an extraction process that includes an organic extraction phase to separate uranium and plutonium from fission products. A more recent variation of liquid/liquid extraction for metal separation involves the use of high molecular weigh polymers that that produces two immiscible aqueous phases when added to a salt solution into which metal ions can partition.

Solid Removal Agents

This separation method involves contacting a preformed solid material (sorbent) with the waste. The radionuclide transports to the solid phase and sorbs, nucleates, complexes or exchanges with another ion on the agent. The process may add the agent to the solution in a batch mode and after some period of time separate the solids from the liquid by filtration. Alternatively, the material can be produced with physical characteristics that allow operation in a packed bed arrangement. The waste stream passes through the bed and the species transfer from solution upon contact with the solid removal agent. In this manner, the separation process operates in a continuous or semi-continuous mode.

Extensive literature reports strontium removal from alkaline salt solutions upon contact with many different sorbents. Materials include titanates, zirconates, silicates, germanates, calcium phosphate, hexacyanoferrates, hydrous manganese oxides and hydrous iron oxides. Other examples include the attachment of water-soluble complexants and chelants onto an insoluble polymer. Some applications have dispersed insoluble sorbents onto a variety of inert solids to enhance reactivity by improving the dispersion of the sorbent. These materials can exist as fine powders or engineered forms that allow for use in a packed bed mode for continuous operation.

One may also remove alpha-emitting radionuclides (i.e., we limit our interest to principally uranium, plutonium, neptunium and americium) from alkaline salt solutions by a number of materials including many of the same materials reported to remove strontium. Available data for comparison of removal capacity and rate prove far scarcer for the actinides than for strontium.

Table I provides a listing of the reported batch distribution constants (K_d) for strontium and actinides for a selected number of sorbents. The K_d value for each sorbent derives from equation 1. A high K_d indicates high removal of the sorbate from solution.

$$K_d = \frac{\{(C_o / C_t) - 1\} \times V}{m} \qquad (1)$$

where C_o is the initial sorbate concentration, C_t is the sorbate concentration at time t, V is the volume of treated solution and m is the weight mass of sorbent added.

The distribution constant will vary with the test conditions. Factors reported to influence K_ds include the sorbate concentration and speciation, pH, ionic strength, sodium concentration and concentration of other metal ions such as calcium and magnesium. Variability in the synthesis of the sorbent batches can prove important presumably due to variances in the particle size, surface area and surface activity of the sorbent. Consequently, direct comparison of the materials reported in Table I is difficult because of the wide range of test conditions. However, general trends among the sorbents tested at a particular condition can guide selection of candidates for further evaluation.

In the application of interest, testing indicated K_ds of $\geq 3 \times 10^4$ mL/g for strontium upon contact of between 0.2 and 0.4 g/L MST and concentrated alkaline salt solutions ranging from 5×10^{-8} to 1×10^{-6} molar in strontium. Other sorbents that exhibited high K_ds for strontium in alkaline salt solutions (see Table I) include several sodium titanate materials (sodium nonatitanate and SrTreat), titanosilicates (e.g., crystalline silicotitanate and the pharmacosiderite $Na_3HTi_4O_4(SiO_4)_3 \cdot nH_2O$), sodium zirconate, and a modified mica.

Researchers at Texas A&M University developed sodium nonatitanate ($Na_4Ti_9O_{20} \cdot nH_2O$) and Honeywell has attempted to commercialize production. The SrTreat is a sodium titanate produced by Selion OY (Finland) and available both as a powder and an engineered form for packed bed operation. Researchers at Sandia National Laboratory first prepared crystalline silicotitanate (CST). and UOP now offers the crystalline silicotitanate commercially both as a powder form (IONSIV® IE-910) and an engineered form (IONSIV® IE-911). The chemical compositions and structures of these materials are trade secrets.

Clearfield and coworkers report that titanosilicates (or silicotitanates) can have sorption affinities for both cesium and strontium. The ideal formula for sodium titanosilicate is $Na_2Ti_2O_3SiO_4 \cdot 2H_2O$. This material contains one-dimensional channels that are ideally suited for selective adsorption of Cs^+ ions. A related class of materials that exhibit a pharmacosiderite structure have the empirical formula, $M_3H(AO)_4(BO_4)_3 \cdot nH_2O$, where M=H, Na or , K, A=Ti or , Ge and B=Si or ,Ge, and exhibit a pharmacosiderite structure. Clearfield and coworkers report that these tunnel-type materials exhibit sorption affinities for both cesium and strontium.

Collins and coworkers at ORNL developed a method for making microspherical sorbents of hydrous titanium oxides and titanium monohydrogen phosphate. They also produced composites of the engineered forms homogeneously embedded with various amounts of sodium titanate powder. Strontium removal sorption data given in Table 1 shows both pure ST microspheres and hydrous titanium oxide microspheres (embedded with MST) worked as well as granular ST (of equal particle size (~0.5 mm in diameter). As an engineered form, the microspheres are structurally stronger that the granular forms and are less likely to degrade and or cause column plugging and provide good flow dynamics for use in columns. These materials would not be a good substitute for MST powder for batch treatment because of lower K_d values. The microsphere technology was patented and Eichrom Industries, Inc. obtained the license in 1997.

The engineered inorganic sorbents IONSIVÒ IE-911 (CST), Honeywell ST and SrTreat, are all commercially available and suitable for packed bed operation. Since Eichrome Industries, Inc. does not offer the microspheres commercially at this time, we do not recommend testing of the microsphere sorbents at this time. However, if degradation problems with the granular forms occur that cause column plugging, the use of the microsphere sorbents might become attractive and could be tested later.

Solid removal agents that featured lower distribution constants but were evaluated because of other potential advantages (e.g., improved filtration, packed bed operation, regenerable) included sorbent microspheres, coated and uncoated magnetic particles, iron oxide coated sand (IOCS) and polyacrylonitrile (PAN) embeddcoated with hydrous metal oxides and nickel ferrocyanide. The microsphere sorbents exhibit improved flow dynamics for packed bed operation. The magnetic materials offer the potential for improved solid/liquid separation compared to conventional filtration. The IOCS is a regenerable sorbent and exhibits good performance in a packed bed operation. The PAN materials also offer the potential for sorbate removal in a packed bed operation.

Testing at Argonne demonstrated the feasibility of removing strontium from alkaline salt solutions using coated and uncoated magnetite particles. However, the authors did not report filtration data for comparison with conventional filtration. The impact of sludge particles on the magnetic filter performance remains an unknown. For these reasons, we do not recommend testing of the magnetically assisted chemical separation technology for treating SRS high level wastes at this time.

Benjamin and coworkers reported strontium removal from simulated Hanford tank waste solutions in a packed column containing iron oxide coated sand (IOCS). Benjamin reported to the author that one can strip the IOCS of the strontium into a small volume and the IOCS regenerated for further use. Organic complexants decreased strontium decontamination factors. The study did not examine actinide removal.

The presence of aluminate in the tank wastes and silica in the IOCS may result in the formation of aluminosilicates that could foul the IOCS column. The unpublished results used a solution containing 0.23 molar aluminate. The workers did not observe formation of an aluminosilicate phase over the testing period, which featured 28 loading/regenerating cycles. The workers also did not report analysis of the solutions for changes in aluminum and silicon. The absence of aluminosilicate solids may reflect the low rate of aluminosilicate formation due to the low temperature or possibly the removal of aluminosilicate solids formed on the surface of the IOCS during regeneration with dilute nitric acid.

Based on the available data the use of IOCS for strontium and actinide removal has merit for the N-IX and CSSE flowsheets. Note however that the IOCS does not appear reasonable as a batch sorbent for the STTP flowsheet due to the handling considerations imposed by the sand particles and impacts on the DWPF. Use of IOCS as a batch sorbent would send significant quantities of silica to the DWPF. The large quantity of silica from the IOCS would require modification of the frit (i.e., to reduce silica content) and possibly result in an increased number of HLW glass canisters. Since CST offers the same potential of application in packed bed mode as IOCS, CST appears more attractive than IOCS. Also, CST offers the potential for removal of cesium,

Table I. Distribution Constants for Selected Solid Removal Agents

Sorbent[a]	[Na] (M)	Time[b] (h)	V/m[c] (mL/g)	$[Sr]_o$ (μg/L)	Sr K_d (mL/g)	Ac	[Ac] (μg/L)	Ac K_d (mL/g)	Ref.
CST	d	≥168	1000	nr	97300				25
Clinoptilite	d	≥168	1000	nr	90300				25
$KCoFe(CN)_6$	d	≥168	1000	nr	23500				25
Pharmacosiderite	d	≥168	1000	nr	644000				25
Pharmacosiderite	d	≥168	1000	nr	4770000				25
Sodium nonatitanate	d	≥168	1000	nr	48000				25
Sodium nonatitanate	d	≥168	1000	nr	1830000				25
SrTreat	d	≥168	1000	nr	91000				25
Modified Mica	d	≥168	1000	nr	139000				25
Sodium Zirconate	d	≥168	1000	nr	399000				25
SrTreat	0.2	72	100	nr	8820000	Pu	nr	6100	26
CST(IONSIV® IE-910 powder)	2.2	6	200	3	>9000	Am	30	12	27
Bone Char	2.2	6	200	3	>1100	Am	30	3084	27
Hydrous titanium oxide	2.2	6	200	3	>4200	Am	30	779	27
MST	4.5	4	2500	90	128000	Pu	64	26200	14
MST	4.5	4	5000	90	105000	Pu	64	22400	14
MST powder	4.9	24	200	1500	24200				28
MST PAN	4.9	24	200	1500	3070				28
IONSIV® IE-910 powder	4.9	24	200	1500	24900				28
IONSIV® IE-910 granular	4.9	24	200	1500	2400				28
ST granular (Allied-Signal)	4.9	24	200	1500	12600				21
ST microspheres	4.9	24	200	1500	14000				21
23% MST/HTiO microspheres	4.9	24	200	1500	17300				21
HTiO DuNord granular	4.9	24	200	1500	4300				21
Chabazite	5.0	≤24	200	nr	260				29
HTiSi	5.0	≤24	200	nr	44820				29
KTiGe	5.0	≤24	200	nr	1570				29
$KTiSi_{gel}$	5.0	≤24	200	nr	9100				29
$KTiSi_{sol}$	5.0	≤24	200	nr	20180				29
ST	5.0	≤24	200	nr	235120				29
MST	5.6	4	2500	87	128000	Pu	190	290000	30
MST	5.6	4	5000	87	105000	Pu	190	397000	30
MST	7.5	4	5000	106	278000	Pu	280	2000	14
MST	7.5	4	5000	41	72500	Pu	13.5	1300	14

[a] CST = crystalline silicotitanate. MST = monosodium titanate. TiHP = titanium monohydrogen phosphate. ST = sodium nonatitanate. HTiO = hydrous titanium oxide. HTiSi, KtiGe, $KTiSi_{gel}$, and $KTiSi_{sol}$ are mixed metal oxides of the type $M_3H(AO)_4(BO_4)_3 nH_2O$, where M=H, Na, K, A=Ti,Ge and B=Si,Ge) that have the pharmacosiderite structure.
[b] contact time upon addition of sorbent to test solution.
[c] ratio of test solution volume in milliliters to weight of sorbent in grams.
[d] Hanford K-Basins cooling water used to store spent nuclear fuels.
nr = not reported.

strontium and actinides in a single operation. Thus, we recommend testing of CST in preference to the IOCS.

For actinides, testing at SRTC indicated K_ds of ≥1 x 10^3 for plutonium upon contact of between 0.2 and 0.4 g/L MST and concentrated alkaline salt solutions ranging from 3 x 10^{-8} to 8 x 10^{-7} molar in plutonium. The MST also removed uranium and neptunium. However, the measured K_ds for these actinides generally proved much lower than that of

plutonium. Uranium and neptunium exhibit much higher solubilities than plutonium under alkaline conditions. Consequently, testing at SRTC featured higher initial concentrations of these two actinides (~ 2 x 10^{-6} molar for neptunium and ~4 x 10^{-5} molar for uranium).

Actinide removal data for the alternate sorbents proves much more limited than that for strontium. The reported K_d for plutonium using SrTreat appear similar to that for MST given the lower ionic strength and solution volume to sorbent quantity used in the testing with the SrTreat. One would expect similar performance since the SrTreat is also a sodium titanate material. Marsh and coworkers reported K_ds for americium (1.2 x 10^{-7} molar) of a number of sorbents. Materials exhibiting high distribution constants (>400) included bone char (calcium phosphate), hydrous titanium oxide, experimental porous resins containing titanium oxides (LANL-TIP, TiO-PAN), nickel ferrocyanide (NiFC-PAN) and manganese oxide (MnO-PAN). Production of the experimental resins distributed the sorbent onto a solid phase for improved packed-bed operation. Based on these results, good sorbents for actinides include titanium oxides, manganese oxides, calcium phosphate and nickel ferrocyanide. We do not recommend testing any of the experimental resins because of the high organic content of the polymer (divinylbenzene/styrene copolymer for the LANL-TIP and polyacrylonitrile for the TiO-PAN, NiFC-PAN and MnO-PAN materials). One could envision developing processes to decompose the resin and reduce the organic content in the melter feed as previously done for the tetraphenylborate precipitate. However, this would involve a significant research effort.

Bostick and coworkers examined the sorption properties of calcium phosphate in the form of bone char, the mineral apatite and substituted apatites for radionuclides including actinides in groundwaters. Researchers attribute radionuclide removal and stabilization at the solid surface to the precipitation of phosphate phases. Use of this sorbent for treating highly alkaline wastes would send increased quantities of calcium and phosphate to the DWPF. For example, if used at the same concentration as currently proposed for MST (0.4 g/L), we estimate that the equivalent metal oxides in the melter to be 1.9 lb/h CaO and 2.6 lb/h P_2O_5. These quantities greatly exceed present projected values. Impact of higher calcium and phosphorus levels in the melter would require testing for glass durability and other important processing characteristics.

We do not recommend the use of nickel ferrocyanide because of its instability in strongly alkaline solutions and the potential for release of hydrogen cyanide and ammonia in the DWPF. Ferrocyanides reportedly liberate hydrogen cyanide upon addition of acids and hydrolyze under elevated acidic conditions producing iron oxides, ammonia and formate. The potential for large releases of hydrogen cyanide within the DWPF represents a new chemical hazard for this facility. Ammonia releases occur within the DWPF under existing conditions. Depending on the amount of ferrocyanide used, significantly increases in ammonia production could occur within the DWPF.

McCabe and Walker investigated the use of sodium nonatitanate (ST) as an alternate material to MST in the In-Tank Precipitation process. Their findings concluded that compared to MST, the ST exhibited a higher strontium decontamination factor, exhibited a similar loading of plutonium and uranium, produced a 35% decrease in filter flux relative to MST and had no negative influence on chemical cleaning of the Mott filters. The authors attributed the poor filtration characteristics of the ST to the smaller particle size of the ST (average particle size of 3.1 m m compared to that of the MST sample, 17.2 m m). S. Yates of Honeywell informed the author that the vendor can increase the average particle size and control the size distribution to customer specifications. Thus, we recommend sodium nonatitanate for testing as an alternate to MST provided materials of larger particle size can be procured.

The SrTreat is a modified titanium oxide that exhibits batch distribution constants for strontium and plutonium comparable to other sodium titanates. The vendor does not report removal rates. The reported K_ds follow contacting an alkaline waste solution for 72 hours with an engineered form of the material developed for column use. The engineered form reportedly contains no binders. P. Augustyn of Graver Technologies indicates a powdered form is available, but it contains binders.

Industrial applications of SrTreat include treatment of relatively dilute waste effluents from refueling nuclear-powered ships in Murmansk, Russia and a reprocessing effluent from the Japanese Atomic Energy Research Institute in Japan. Column testing with two simulated Hanford waste solutions, designated DSSF and NCAW, indicated breakthrough

bed volumes in excess of 400 for strontium. The high K_ds for strontium and plutonium, availability in both engineered and powdered forms, and successful laboratory and industrial applications make SrTreat an attractive alternate to MST. Thus, we recommend testing SrTreat for strontium and actinide removal from SRS high level waste salt solutions.

CST (IONSIVÒ IE-910) exhibits a high affinity for cesium in the presence of high concentrations of sodium and potassium. Previously, McCabe investigated this powdered material as an alternate to the tetraphenylborate precipitation process. He reported removal of strontium, plutonium, uranium and neptunium removal in addition to cesium from Tank 43H waste supernate. He did not extensively investigate capacity and removal rates to determine if they are sufficient to meet the Z-Area limits for ^{90}Sr, total alpha and ^{237}Np concentrations. However, if the CST removes these radionuclides in addition to ^{134,137}Cs, significant savings would result in the N-IX flowsheet. We recommend testing of CST as an alternate to MST because of the demonstrated ability to remove strontium and actinides and possible benefits presented below.

Combining strontium and actinide removal with cesium removal eliminates the equipment and time associated with strontium and actinide removal at the front end of the treatment facility. The process will still require filtration of sludge; however, development of a flocculent system to increase filter performance may prove easier to accomplish based singly on sludge chemistry and not a combined sludge and sodium titanate chemistry. Reduced titanium content in the HLW glass may result by eliminating the use of the MST and if strontium and actinide removal does not reduce significantly the cesium capacity of the CST. Such an implementation does require, however, that the relative kinetic performance for the various radionuclides approximate the relative concentrations and removal requirements, which provides a challenging goal.

The use of CST as a batch sorbent may also prove valuable. Use of CST as the sorbent in the Alpha Removal Tank, would also result in removal of a portion of the ^{134,137}Cs at this stage. This could serve to decrease the size of the ion exchange columns or extend the operating period of the currently specified columns.

Precipitation and Coprecipitation

In general, precipitation processes proceed rapidly due to the large driving force (high supersaturation) to reduce the liquid phase concentration of the newly formed chemical species. In addition to nucleation, ripening of the precipitated solids must occur to produce a solid easily separated from the solution by a suitable technique. A number of factors affect the ripening process including temperature, composition of the liquid phase and solute solubility. The ripening process involves both removing waters of hydration and increasing the crystallite particle size. Generally the time required for ripening the precipitate solids to an appropriate size for filtration or other solid/liquid separation process becomes the rate-controlling step in this process technology.

Strontium will precipitate from alkaline solutions upon the addition of non-radioactive strontium or other alkaline earth ions (e.g., calcium and barium). The addition of non-radioactive strontium exceeds the solubility of strontium in the system resulting in precipitation of both radioactive and non-radioactive strontium. Thus, the concentration of radioactive strontium in solution becomes diluted by the addition of non-radioactive strontium. With the addition of other alkaline earth ions, strontium removal occurs as a result of precipitation (i.e., due to decreased solubility due to presence of other alkaline earths) as well as by sorption, inclusion and occlusion of strontium in the precipitated alkaline earth phase.

Removal of actinides occurs upon the precipitation of hydrated metal oxide phases (e.g., ferric oxide, manganese oxide, uranium oxide) upon the addition of a metal nitrate solution to the highly alkaline waste solutions. The likely mechanism for actinide removal involves adsorption, inclusion and occlusion in the precipitated hydrous metal oxide matrix.

Researchers demonstrated strontium and actinide removal by this combined precipitation/sorption method with Hanford wastes and simulants using non-radioactive strontium and ferric nitrate.' Testing indicated very poor filtration characteristics of the strontium/ferric hydrous iron oxide precipitates produced in the presence of organic complexants.

Modification of the process using a strike with metal ions and chemical oxidant resulted in adequate strontium and actinide removal and a solid phase that exhibited good filtration characteristics.'

Based on recent testing at SRTC, the recommended precipitating reagent for the Hanford application consists of a mixture of strontium nitrate, calcium nitrate and sodium permanganate.[38] The results indicate excellent decontamination factors for strontium, plutonium and americium (see Table II) and excellent filtration characteristics for the resulting mixture. The addition of calcium benefited both strontium and actinide removal when added prior to the sodium permanganate. Calcium forms strong complexes with ethylenediaminetetraacetic acid (EDTA), a component of the Hanford complexant wastes. Upon addition of calcium, strontium and actinide ions complexed with EDTA release into solution as the calcium ions complex with the EDTA. Permanganate reduces upon addition of the waste solution resulting in the formation of freshly precipitated hydrous manganese oxide.

Reaction kinetics indicate an initial rapid decrease in radionuclide concentrations in the first 30 minutes followed by a slower steady decrease. An additional order of magnitude increase in the decontamination factor occurred every hour until completion of the test after four hours.

Table II. Strontium, Plutonium and Americium Decontamination Factors by Precipitation

	Decontamination Factors		
Precitating Agents[a]	**Sr**	**Pu**	**Am**
0.075M Sr^{2+}/0.075M $NaMnO_4$	63	150	140
0.075M Sr^{2+}/0.2M Ca^{2+}	170	2.7	3.8
0.075M Sr^{2+}/0.0375M Ca^{2+}/0.075M $NaMnO_4$	477	691	558
0.075M Sr^{2+}/0.004M Ca^{2+}/0.01M $NaMnO_4$	36	1.6	2.1

[a] concentrations are final in-tank concentration

In 1998, the Institute of Physical Chemistry (IPC) of the Russian Academy of Sciences completed a study of the coprecipitation of technetium and actinides from alkaline solutions. Carriers for the actinides included $UO_2 \cdot nH_2O$, $U_3O_8 \cdot nH_2O$, sodium uranate, tetraalkylammonium salts, and transition metal hydroxides. Testing investigated two methods of introducing the carrier; (1) direct strike and (2) method of appearing reagent (MAR).

In the direct strike approach one adds the carrier as a water-soluble salt that immediately hydrolyzes and precipitates upon contact with the alkaline waste solution. In the MAR one adds a chemical reagent to the waste solution containing the carrier in a soluble form. The reagent reacts with the soluble carrier to form an insoluble form of the carrier. Results indicated higher decontamination factors and lower carrier requirements for the MAR compared to the direct strike method. The authors attributed these improvements to the homogeneous distribution of the carrier when precipitation occurs.

The authors report decontamination factors (DF: i.e., the ratio of the final to initial soluble concentration of the sorbate removed) of 100 for plutonium by the direct strike method using either Fe^{2+}/Fe^{3+} and UO_2^{2+} carriers. Using the MAR and the same carriers, decontamination factors increased to between 150 and 2000. Carrier concentrations ranged from 0.075 and 0.2 molar in the direct strike method and 0.01 to 0.015 molar in the MAR tests.

Improved plutonium removal by direct strike occurred using U^{4+} instead of UO_2^{2+}. Plutonium DF values ranged from 95 to 1130 depending on the carrier concentration (0.001 – 0.05 molar) and sodium hydroxide concentration (0.5 – 4.0 molar). This carrier also removed neptunium and americium. Neptunium and americium DF values ranged from 24 to 153 and 110 to 430, respectively. Decontamination factors increased with increasing carrier concentrations and decreasing sodium hydroxide concentration. Neptunium DF values decreased to <100 in the presence of air. Plutonium

and americium DF values did not change whether the tests occurred under an air or argon atmosphere.

Removal of the actinides by the coprecipitation technique occurs rapidly. The DF values reported above for the direct strike method and MAR occurred within 1-2 hours upon contact. Researchers separated the solids by filtration through a filter containing a 0.45-m m pore size membrane. The authors did not report filtration characteristics.

Testing also investigated the effectiveness of adding hydrazine (N_2H_4), a reductant, in addition to sodium uranate as the carrier. The purpose of adding the hydrazine is to reduce a portion of the UO_2^{2+} to U^{4+}. Having both U(IV) and U(VI) present to precipitate as hydrous oxides may prove more effective in coprecipitating actinides in any oxidation state. Results indicated high actinide removal not only due to the mixed valence-state uranium carrier, but also due to the reduction of higher oxidation actinide species to a less-soluble lower oxidation species. The presence of pertechnetate (TcO_4^-) and chromate (CrO_4^{2-}) impact the actinide reduction by hydrazine as both of these species reduce more readily.

Carriers investigated for the MAR included hydroxides of Fe(III), Mn(II), Co(II,III) and Cr(III), manganese(IV) oxide (MnO_2) and sodium uranates. The iron, manganese and chromium carriers formed by the reduction of the appropriate high oxidation oxide anion, MO_4^{n-} (where M = Fe, Mn, Cr and n = 1 or 2). The cobalt carrier formed by the hydrolysis of cobalt amine complexes (e.g., $[Co(NH_3)_6]^{3+}$). Catalytic decomposition of uranyl peroxo complexes produced the sodium uranate carrier.

All of the carriers except MnO_2 exhibited good plutonium removal. The results indicated that the oxidation state of the plutonium showed little influence on efficiency of removal. In contrast to plutonium, neptunium removal proved poor with all of the carriers except the sodium uranates.

Based on the results from SRTC and IPC, precipitation/coprecipitation of strontium and actinides appears a promising alternative to the use of MST. Based on quantities used in the testing, we estimated the quantity of reagents required and the resulting metal oxide products sent to the DWPF using three different treatment process consisting of (1) $Sr^{2+}/Ca^{2+}/MnO_4^-$,

(2) $Sr^{2+}/Ca^{2+}/Fe^{2+}\cdot 2Fe^{3+}$ and (3) $Sr^{2+}/Ca^{2+}/UO_2^{2+}$. We decreased the reagent quantities required for use since SRS waste does not contain the level of organic complexants present in the Hanford Complexant Concentrate waste. Table III presents the calculated quantities of reagents and products.

The use of these reagents does not add any new element into the HLW and DWPF operations. However, the use of these reagents at the concentrations specified increases the waste solids transferred to the DWPF. The much higher atomic weight of uranium compared to manganese and iron makes the use of sodium uranates less attractive unless the uranates prove much more effective than the manganese and iron oxides in removing the actinides. Precedent exists for improved sorption of neptunium by precipitated uranium oxides (see ref. 39).

At the recommended MST usage, 4.2 lb/h of MST solids transfer forward for vitrification in the DWPF.[15] The use of any of the three reagent combinations produces a total of 18 – 40 lb/h of solids or 14 – 36 lb/h more solids than that produced with MST in the reference process. These quantities of solids are significant and would result in an increased number of HLW glass canisters. Comparable solids production would be possible if the reagent concentrations decreased by about a factor of between 4 and 5. In view of the rapid reaction kinetics for precipitation, we recommend that this removal method be tested at reagent concentrations that do not significantly increase quantity of waste sent to the DWPF.

Table III. Calculated Solids Production Rates for Precipitating/Sorption Agents Used to Remove Strontium and Actinides

Reagent	Concentration (M)	Product	DWPF Rate[a] (lb/h)
$Sr(NO_3)_2$	0.01	SrO	9.1
$Ca(NO_3)_2$	0.005	CaO	2.5
$NaMnO_4$	0.01	MnO_2	7.6
$FeSO_4 + Fe(NO_3)_3$	0.0033/0.0067[b]	Fe_3O_4	6.8
$UO_2(NO_3)_2$	0.01	$Na_2U_2O_7$	28

[a] rate sent to the DWPF based on supernate processing rate of 17.5 gpm as reported in Table 3.2-16 of reference 15.
[b] total Fe concentration equal 0.01M.

Liquid/Liquid Extraction (Solvent Extraction)

A few reports of strontium and alpha separation from alkaline salt solutions by solvent extraction exist in which the extracting phase features an organic diluent and organophillic complexants. McDowell and coworkers reported the extraction of strontium from alkaline nitrate solutions using neocarboxylic acid and crown ethers and related macrocycles dissolved in toluene. The crown ether, di-t-butylcyclohexano-18-crown-6 (DC18C6) proved the best synergistic agent for strontium extraction.

Lumetta and coworkers investigated this extractant system with simple alkaline salt solutions and a simulated Hanford Complexant Concentrate waste solution. The distribution coefficient for strontium in a 0.5M sodium carbonate and 0.5M sodium hydroxide solution measured 131. However, the results indicated that organic complexants (e.g., ethylenediaminetetraacetic acid and citric acid) adversely impact strontium extraction as evidenced by distribution coefficients well below 1.0 when either of these complexants are present in the alkaline salt solutions.

More recently, Miller and coworkers reported the extraction of strontium from alkaline salt solutions using tetra-C-alkyl derivatives of cobalt dicarbollide dissolved in nitrobenzene, mesitylene and diethylbenzene. The hexyl derivative of cobalt dicarbollide in diethylbenzene proved the best system for strontium extraction over a sodium hydroxide concentration range of 0.01 to 1.0 molar.

Myasodedov and coworkers reported the extraction of actinides and lanthanides from alkaline solutions using a variety of extractants including quarternary salts, primary amines, alkylpyrocatechols and b -diketones. These studies generally tested only Am(III) as the actinide and Eu(III) as the lanthanide. Testing indicated increasing hydroxide concentration decreased the distribution coefficients for the actinides. No testing occurred at sodium hydroxide concentrations above 1.0 molar.

Lumetta and coworkers investigated the use of catechol derivatives with simple alkaline salt solutions and a simulated Hanford Complexant Concentrate waste solution for americium separation.[24] Catechol derivatives tested included (1) 4-t-butylcatechol, (2) 3,5-di-t-butylcatechol and (3) 4-(1-methyl-1-octylnonyl)catechol. Diluents tested included 1-octonol and n-paraffin. Testing results indicated a similar behavior for americium in this solvent system as observed for strontium with the neocarboxylic and crown ether system from alkaline solutions. In the absence of organic complexants, americium extraction proved good. In the presence of organic complexants, americium extraction became very poor.

A solvent extraction method for strontium and actinide removal becomes is particularly attractive if combined with the cesium extraction process in the CSSE flowsheet. Based on the literature results reported above, precedent suggests the feasibility of developing a caustic side extraction process for strontium and the actinides. However, the extraction systems tested to date for strontium and the actinides differ from that demonstrated for cesium. In principle one could modify the cesium extractant to operate effectively with the different ionic radii and charges of strontium and the actinides. However, this would require a considerable research effort. Because of the scope of effort required, we do not recommend testing of a solvent extraction system at SRTC for strontium and actinide removal at this time.

Polymer Separation

This separation technique involves a variation of liquid/liquid extraction that uses two immiscible aqueous phases. This separation method adds a water-soluble polymer (e.g., polyethylene glycol (PEG) or polypropylene glycol (PPG)) to the aqueous salt solution containing the component for separation. Two aqueous phases result, a salt-rich phase and a polymer-rich phase. The component of interest extracts into the polymer-rich phase. One can extract the separated component from the polymer-rich phase into a small volume for further processing. A variation of this technique uses immobilized PEGs, which limits polymer extraction into the salt-rich phase.

Testing indicated successful extraction of ^{99}Tc and ^{129}I from simulated Hanford tank wastes using PEG, immobilized PEG and PPG. Irradiation of the polymers did not affect partition coefficients. Temperature, ionic strength and presence of colloids can have significant impact on the radionuclide partition coefficients. Back extraction of the radionuclides proved difficult with a PEG-based system. The immobilized-PEG and PPG-based systems exhibited improved back extraction characteristics.

Removal of strontium and actinides using this technique lacks extensive study. The ANL studies tested the influence of uranyl ion on the extraction of pertechnetate since uranyl pertechnetate complexes exist. Results indicate that the presence of uranyl ion did not significantly affect the ^{99}Tc partition coefficients.[23] Due to the lack of data regarding the strontium and actinide separation using this extraction method, we do not recommend testing of this method for the separation of strontium and actinides from SRS waste solutions at this time.

Polymer Filtration

This technology utilizes water-soluble chelating polymers that selectively bind with metal ions (e.g., actinides) in solution. The polymers have sufficient molecular weight to allow separation and concentration using ultrafiltration (UF). Water and other uncomplexed species pass freely through the UF membrane. The process can recover polymers by changing the solution conditions, which releases the metal ions into a concentrated solution. A second UF operation separates the uncomplexed polymer and the concentrated metal ion solution.

Testing at Los Alamos National Laboratory (LANL) demonstrated plutonium and americium separations in the presence of other metal ions such as Fe(II), Cu(II), Ca(II), Mg(II), Zn(II) and Ni(II) in dilute and concentrated brine solutions (ionic strengths 0.1 to 4.0). Chelating groups investigated included phosphonic acid, acylpyrazolone and hydroxamic acid. Solutions tested ranged in pH from 1 to 6.

Jarvinen reported actinide separations at slightly alkaline conditions. Strontium removal testing does not exist. Jarvinen informed the author that, under highly alkaline conditions (pH $\geq$ 10), the polymers tested to date would experience separation due to surface charge resulting in poor filtration performance. Due to the lack of testing for strontium and actinide removal under the highly alkaline conditions, we do not recommend testing of this method for the SRS application at this time.

4.0 Conclusions

A literature survey indicated a number of alternate materials and methods for the removal of strontium and alpha-emitting radionuclides (actinides). We evaluated the use of these alternate materials versus proposed flowsheets for salt processing at the Savannah River Site. From this evaluation we recommend the following materials for further testing to determine the rate and extent of removal:; (1) sodium nonatitanate, (2) SrTreat, (3) crystalline silicotitanate, (4) pharmacosiderites and (5) coprecipitation with $Sr^{2+}/Ca^{2+}/NaMnO_4$. We do not recommend testing of liquid/liquid extraction and polymer filtration methods at this time.

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