APPLICATION OF INORGANIC SORBENT
IN ACTINIDE SEPARATION PROCESSES

J. Koenst -- - Mound
W. Schulz -- Hanford
D. R. Tallant - Sandia

The attached manuscript forms about 1/3 of the coauthored paper submitted for approval. The other authors are preparing their inputs separately. The inputs will be combined and edited by W. Schulz (Hanford) who will add introductory remarks for each section. The total length of the paper is limited to 14 pages (double-spaced) plus figures and tables.

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For several reasons - poor hydraulic behavior, unsatisfactory sorption kinetics, unavailability, in some cases of commercial quantities, etc. - inorganic sorbents have not heretofore been used extensively in the backend of the nuclear fuel cycle. A potential breakthrough in plant scale application of such sorbents in nuclear liquid waste treatment may ensue from research currently underway at several U.S. Department of Energy sites. At Mound Laboratories, calcium hydroxyapatite \([\text{Ca}_{10}\text{(PO}_4)_6\text{(OH)}_2]\), obtained from the Kerr-McGee Co., has been shown in both batch and column tests to effectively remove \(^{238}\text{Pu}\) from certain aqueous wastes generated there: costs and benefits of incorporation of one or more beds of \(\text{Ca}_{10}\text{(PO}_4)_6\text{(OH)}_2\) in the Mound Laboratory waste treatment circuit are being evaluated. An ion exchange process which takes advantage of the great affinity and capacity of sodium titanate \([\text{Na(Ti}_2\text{O}_5\text{H})]\) for \(>^{+2}\) ions from high alkaline salt solutions has been successfully developed and demonstrated for reduction of plutonium and \(^{241}\text{Am}\) concentrations of Hanford Plutonium Reclamation Facility salt waste to drinking water levels. Batch distribution data obtained at Sandia Laboratories indicates \(\text{Na(Ti}_2\text{O}_5\text{H})\) may also be useful in chromatographic separation of \(\text{Am}^{3+}\) and \(\text{Cm}^{3+}\). Pertinent properties of these inorganic sorbents as well as separation process flowsheets and data are reviewed in this paper.
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The feasibility of partitioning high level liquid nuclear waste resulting from Purex reprocessing into long-lived and short-lived radionuclide fractions is being assessed in a joint study by Department of Energy laboratories that is coordinated by Oak Ridge National Laboratory. Two areas of study in which improvements in partitioning technology are being actively sought are (a) the separation of heavier actinides (mainly americium and curium) from the chemically similar lanthanides, and (b) the decontamination of the relatively large volumes of low-level waste that would be produced in a full scale nuclear waste treatment plant incorporating an actinide partitioning process. Sandia Laboratories, with support from Oak Ridge National Laboratory and Rockwell Hanford Operations, undertook to determine the feasibility of using inorganic ion exchange materials, investigated during the development of the Sandia Solidification Process, to perform the lanthanide/actinide separation and to decontaminate low-level waste streams.

The ion exchange materials investigated are hydrous oxides of niobium, zirconium, and titanium synthesized via the hydrolysis of the metal alkoxide, $\text{Nb}(\text{OC}_2\text{H}_5)_5$, $\text{Zr}(\text{OC}_2\text{H}_5)_4$, or $\text{Ti}(\text{OC}_2\text{H}_5)_4$. The syntheses are analogous to that of sodium titanate ($\text{Na}[\text{Ti}_2\text{O}_5\text{H}]$) described earlier in this paper. The ion exchange materials were converted to their hydrogen form by acid equilibration, dried at room temperature under vacuum, and sieved between 40 and 140 standard mesh sieves prior to use. The materials in their hydrogen form are believed to be aggregates of the empirical chemical formulae: $\text{H}[\text{Nb}_2\text{O}_6\text{H}]$, $\text{H}[\text{Zr}_2\text{O}_5\text{H}]$, or $\text{H}[\text{Ti}_2\text{O}_5\text{H}]$. All three materials may contact solutions of moderate acidity (dilute nitric acid) for a period of a week or more without significant dissolution. The titanate is the least stable, but it shows no evidence of dissolution in solutions of 0.01M or less acidity. Contact with 0.1M acid in the presence of vigorous shaking for a week produces
"fines" and probably some dissolution of hydrogen titanate. The zirconate appears to be indefinitely stable in solutions up to 0.5M nitric acid, at which point a few percent dissolution is observed over a period of two days. The niobate appears to be indefinitely stable in 0.5M nitric acid and dissolves only very slowly, if at all, in 2.5M nitric acid. Other physical and chemical properties of these materials have been described elsewhere.\(^3\)

A series of batch equilibrations was carried out to determine the relative affinities of selected lanthanides and actinides for niobate, zirconate, and titanate ion exchange materials as a function of pH. These affinities are here expressed as distribution coefficients, \(K_d\), where

\[K_d = \frac{\text{(Fraction of Tracer on Ion Exchanger)}}{\text{(Fraction of Tracer in Solution)}} \times \frac{\text{(Milliliters of solution)}}{\text{(grams of Ion Exchanger)}}\]

A \(K_d\) ratio of 1.2 or greater is considered sufficient for the separation of two nuclides by column elution chromatography.\(^4\) Adjustment of pH was accomplished by the addition of dilute sodium hydroxide or nitric acid. Typically, one milliequivalent of ion exchanger (\(0.35\) gram of niobate, \(0.37\) gram of zirconate, \(0.25\) gram of titanate) contacted about 15 milliliters of solution. Maximum loading was less than 1\% of the ion exchanger capacity. After the equilibration the solutions were filtered and gamma, beta, or alpha-scintillation counted to determine the fraction of tracer remaining in solution. For those equilibrations in which most of the tracer was removed from solution, desorption of nuclides from the ion exchange material was investigated by adding to the solids 15 milliliters of 0.1M nitric acid (zirconate and titanate) or 0.5M nitric acid (niobate), equilibrating the mixture, filtering and counting the solution. Both sorption and desorption experiments were allowed to equilibrate for five days with moderate
shaking at 20-28°C (ambient temperature). The equilibration time reflected personal convenience and is believed to be much longer than that required to reach equilibrium.

The results of batch equilibrations for three actinides and four lanthanides are presented in Figures 1 through 3, utilizing, respectively, niobate, zirconate, and titanate ion exchange materials. To improve clarity, the actinide data points have been connected by solid lines. The accuracy of the distribution coefficients is estimated to be within ±10% for 5 ml/g < K_d < 10^5 ml/g but degrades rapidly outside these limits. Two aspects of distribution coefficient versus pH behavior as shown in the figures are particularly significant. First, the rapid increase in distribution coefficients with pH implies that, with the possible exception of neptunium, the tested nuclides can be quantitatively sorbed and then eluted from these inorganic ion exchange materials by pH adjustment. The nuclide desorption experiments tend to confirm this implication. Second, the actinides exhibit significantly different behavior from the lanthanides. Neptunium retains a relatively large distribution coefficient down to low pH, while the distribution coefficients of americium and curium are generally larger than those of the lanthanides across the acid range of pH. Curium exhibits larger distribution coefficients than americium, but the discrimination between americium and the lanthanides appears sufficient to effect a separation by column elution chromatography.

The results of the nuclide desorption experiments (Table I) are presented as the percentage of activity recovered from an ion exchange material as compared to that removed from solution during the initial equilibration. The recoveries listed are the averages of two, three, or four desorption experiments. Except for fortuitous circumstances, the maximum recovery expected was about 90%. The recovery was limited by:
1) Loss of ion exchange material containing nuclide activity during filtering; and 2) the inability to completely filter off all the equilibration solution from the ion exchange material prior to backfilling for desorption, resulting in an unknown dilution factor for the desorbed activity.

In addition the nuclides present in lowest concentration appear to have suffered significant loss of tracer due to absorption on the walls of containers. This could be accounted for in the calculation of distribution coefficients but not in the calculation of desorption recoveries. This is probably the cause of the (apparently) lower recoveries listed for promethium and curium, which were present at only the part-per-billion level. Given these experimental considerations, the recoveries listed in Table I are believed to represent complete or nearly complete removal of sorbed nuclides from the ion exchange materials.

If a distribution coefficient ratio of 1.2 is sufficient for separation of nuclides by column elution chromatography, then (from Figures 1 through 3) there is a range of pH values for each ion exchange material in which the partitioning of tested actinides from tested lanthanides appears feasible. Further, it appears that these ion exchangers could be used to concentrate nuclides in secondary waste processing streams by sorption at pH 4-5 and then elution into a smaller volume at pH 1-2.

Due to the limited scope of this project, the questions of whether the distribution coefficient ratio will remain favorable for actinide partitioning as the nuclide concentrations are scaled up and whether the kinetics of sorption and desorption will limit the efficiency of the separations have not been addressed. These studies and column elution experiments to perform the predicted
actinide/lanthanide separation are the next logical steps in evaluating the feasibility of partitioning nuclear waste with niobate, zirconate, and titanate ion exchange materials.
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3) "Sandia Solidification Process - Cumulative Report,"
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Figure 1. Distribution coefficients (\(K_d\)) of certain lanthanides and actinides on niobate ion exchange material. Actinide data points connected by solid lines.
Figure 2. Distribution coefficients \(K_d\) of certain lanthanides and actinides on zirconate ion exchange material.
Figure 3. Distribution coefficients ($K_d$) of certain lanthanides and actinides on titanate ion-exchange material.
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