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SEPARATION OF TRIVALENT LANTHANIDES AND ACTINIDES BY SOLVENT EXTRACTION WITHOUT AQUEOUS COMPLEXING AGENTS[*]

by

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ABSTRACT

A method of separating the trivalent actinides, mainly Am and Cm, from trivalent lanthanides is presented. This method embodies the sequential use of two different solvent extractants; the first extractant would remove the heavy lanthanides from the lighter lanthanides and Am-Cm, while the second would extract Am-Cm in preference to the lighter lanthanides. In this scheme, no additional complexing agents are required. Thus, waste disposal and corrosion problems are minimized. Overall separation factors for Am-Cm from lanthanide fission products in reactor wastes may be as high as several thousand.

INTRODUCTION

The projected use of fission nuclear reactors to meet the power needs of the United States in the next several decades poses the serious problem of disposal of the highly radioactive waste products from fission and neutron capture in the reactors. One of the most critical aspects of this problem is long-term storage of the waste, necessitated by the need to protect the environment from the long-lived transplutonium elements generated as neutron-capture products of the nuclear fuel. Although the fission products from freshly-processed spent fuel elements present a more immediate radiation hazard, this danger decreases at a considerably faster rate than that for the α-emitting actinides. Thus, while there is a need to store the fission products safely for about a thousand years, the presence of the long-lived actinide elements in the nuclear waste doubles or triples the required storage period.

Several solutions to this problem have been suggested; among them is to separate the α-emitting species from the fission products, storing them separately or returning them to the reactors to be consumed by the (n, fission) reaction. This reaction has a considerable cross-section for the actinide elements, and would thus

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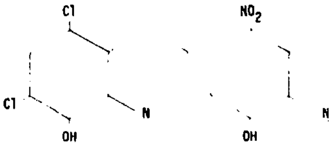
transform the long-lived α-emitting nuclides into less dangerous fission products.

The chemical separation of transplutonium elements from fission products generally fails to eliminate the lanthanide fission products (primarily La to Eu) because of similarities in ionic radii and electronic structures between these two *families of elements. Thus, the separation of the* transplutonium actinides from the lanthanide elements is crucial to partitioning the short-lived from the long-lived waste products.

Current laboratory separation schemes rely *upon the slightly larger complexation strengths of* the actinides over the lanthanides, followed by partitioning of the lanthanides into an organic solution by ion-exchange or solvent extraction.[1-3] The most effective complexants for this separation *are Cl^-, SCN^-, and certain aminocarboxylic acids* such as EDTA. However, each has drawbacks when applied to large-scale systems. High concentrations of Cl^- must be used, producing very corrosive solutions and adding significantly to the bulk of the wastes.[4] Thiocyanate shows a tendency to polymerize in acid solutions, especially in the presence of α-radiation.[5,6] The separation processes employing aminocarboxylic acids (i.e., TALSPEAK and related processes)[2,3] leave large quantities of these compounds in their various waste streams, and also require a low-acidity feed solution in which hydrolysis or precipitation of some of the fission products and actinides becomes a problem.[1]

We are investigating a solvent-extraction process for the separation of Am(III) and Cm(III) from the trivalent lanthanides in which no aqueous complexants are used. Instead, two successive extractions are performed. For the first, an extractant in which Am and Cm behave like the early lanthanides is used, and for the second, a different extractant in which Am and Cm behave like middle or heavy lanthanides is used.

Numerous studies have shown that Am and Cm behave like Pr or Nd in extractions with di-(2-ethylhexyl)orthophosphoric acid (HDEHP) from dilute mineral acids.[7,8,9] The heavier lanthanides are progressively more extractable, with an average separation factor $SF_{Z/Z-1}$ of 2.4,[10] where the separation factor is defined as the ratio of the distribution coefficients for each species between an organic and an aqueous phase. Hence, Am and Cm can be separated from the heavier lanthanides by extraction with HDEHP.



5,7-dichloroxine (HDCO)

5-nitroxine

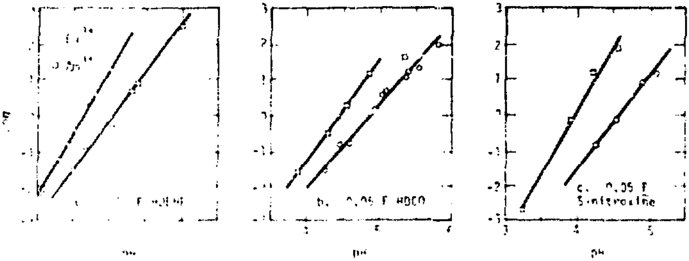
Fig. 1. Structural formulas of the extractants, HDCO and 5-nitroxine.

*To separate Am and Cm from the lighter lan*thanides, which contain the major lanthanide fission products, we are investigating several derivatives of 8-hydroxyquinoline (oxine) including 5,7-dichloroxine (HDCO) and 5-nitroxine (Fig. 1). Sekine and Dyrssen[11] have reported Am/Eu separation factors of 10 for extraction from dilute $HClO_4$ solutions with 0.05 F HDCO in chloroform. If the lanthanide extractabilities increase with Z as expected, Am would behave roughly like Tb, and a clean separation of Am and Cm from the lanthanide fission products should be feasible. The present work was concerned with testing the validity of the separation scheme and determining the optimum conditions for separations.

EXPERIMENTAL

The radioactive tracers used in this work for determining lanthanide-actinide distribution ratios were ^{241}Am and $^{152,154}Eu$. The Eu tracer was chosen because of its immediate availability and its identity as a medium-heavy lanthanide. The HDEHP and HDCO extractants were obtained commercially, and 5-nitroxine was graciously donated by Dr. H. Gershon, Boyce Thompson Institute for Plant Research, Yonkers, New York, who first synthesized this compound in 1972.

Stock solutions of the radioactive tracers were added to the extraction mixture immediately prior to extraction; the aqueous phases for the oxine-derivative extractions had previously been



[illegible] and Eu^{+3} from 0.1 [illegible] NaNO$_3$ [illegible]. Organic phases: [illegible] heptane; (b) 0.05 F HDCO in chloroform; [illegible] in chloroform.

[illegible] with a [illegible] extractions.

[illegible] the extraction mixtures was effected [illegible] either by vibration or, in the case of HDEHP extraction, by stirring motor and was [illegible] to the longer equilibration period required. The mixture was then centrifuged, and the separated phases were drawn off. [illegible] was counted in a NaI(Tl) well-counter to determine the distribution ratio. The pH of the aqueous phase was determined by material balance for [illegible], and by a pH meter otherwise.

RESULTS AND DISCUSSION

The extraction stoichiometry is assumed to be of the form

$$M^{+3}_{aq} + (n + 3) HA_{org} \rightleftharpoons MA_3(HA)_{n\,org} + 3H^{+}_{aq} , \qquad (1)$$

where M is the metal species to be extracted and HA is the extractant. This implies that the equilibrium position of this reaction is dependent upon the aqueous acid concentration to the third power; it can be shown that a plot of the logarithm of the distribution ratio (log D_M) versus the pH should be a straight line with a slope [illegible].

The results of our experiments are presented in Fig. 2 as plots of log D_M versus pH for [illegible] HDEHP in heptane, 0.05 F HDCO in chloroform, and 0.05 F 5-nitroxine in chloroform. The data are also summarized in Table I along with some corresponding literature values.[11-13] All six extraction curves show deviations from the third-power acid dependency. This may be because we used reagent concentrations rather than ionic activities in calculating the pH values, and also because of the rather high solubility of the quinoline-derivative extractants in aqueous solution. In each case, the more extractable element shows the higher acid dependency, so that the separation factor increases with pH.

The Am/Eu separation factors of 0.04 for HDEHP and 90 for 5-nitroxine imply an overall separation factor of 550 for one pass through each extractant, and a recovery of about 75 percent for the Am. This may be increased in actual experience, since Eu is not a major fission product, and since those lighter lanthanides that are, should be even less susceptible to extraction by the HDCO.

TABLE I

[illegible]

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