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EFFECTS OF SOME SYNERGISTIC
AND ANTAGONISTIC AGENTS
ON HDEHP EXTRACTION OF STRONTIUM

Wallace W. Schulz

July 1968

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By

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ABSTRACT

HDEHP, diluted with TBP and kerosene, is used as the extractant in the Hanford B-plant to extract ^{90}Sr from various radioactive waste solutions. Process chemistry oriented studies were performed to determine the effects of various known and possible extractant components on extraction of strontium by the B-plant solvent. Small concentrations of TBP and of the more powerful synergist DBBP (dibutylbutyl phosphonate) enhance extraction of strontium (synergistic effect). Conversely, small concentrations of either H_2MEHP [mono(2-ethylhexyl) phosphoric acid] or 2-ethylhexanol depress strontium distribution coefficients (antagonistic effect). Consequences of these observations to plant operation are discussed.

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EFFECTS OF SOME SYNERGISTIC AND ANTAGONISTIC AGENTS
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INTRODUCTION

Solvent extraction removal of ^{90}Sr and fission product rare earths from various radioactive waste solutions is an important part of the Hanford Waste Management Program.^(1,2,3) These operations will be performed in the newly activated Hanford B-plant using as the extractant HDEHP [di(2-ethylhexyl)phosphoric acid] diluted with a hydrocarbon diluent and TBP (tributyl phosphate).

A comprehensive study of the effects of radiation on selected properties of the B-plant extractant is currently in progress.⁽⁴⁾ In conjunction with the radiolytic studies, the effects of some selected organic reagents on extraction of strontium from typical B-plant feed stock by HDEHP solvents were surveyed. The organic additives examined were chosen as being either known or likely components of typical B-plant solvent. The results of these studies and their consequences to plant operation are discussed in this report. An attempt is made also to relate these results to similar, but more fundamental, studies of synergistic and antagonistic effects on solvent extraction systems.

SUMMARY AND CONCLUSIONS

Extraction of strontium by a HDEHP-kerosene solvent is significantly altered when certain other organic reagents are present in the extractant. Small concentrations of some compounds, for example, neutral organophosphorous reagents such as TBP and DBBP, enhance extraction of strontium. Conversely, small amounts of other compounds such as H_2MEHP , 2-ethylhexanol, and 2-ethylhexanoic acid have an immediate, strong depressant effect.

Strontium distribution ratios under typical B-plant extraction column feedpoint conditions are increased 1.4 to 1.7-fold when the HDEHP (0.3M) extractant also contains 0.1 to 0.2M TBP or DBBP. The maximum synergistic effect for both additives occurs at about 0.1 to 0.15M neutral organophosphate. Over the concentration range 0.05 to 0.5M, DBBP has a stronger synergistic effect than TBP on strontium extraction. In particular, the strontium distribution ratio for a 0.3M HDEHP-0.2M DBBP solvent is about 25% greater than that for a 0.3M HDEHP-0.2M TBP solvent. Desirably, also, the more powerful synergistic effect of DBBP over TBP persists even upon irradiation of HDEHP extractants to exposures as high as 10^8 rads. Distribution ratio data for extraction and stripping of cerium (III) and (IV), as well as for those of strontium, demonstrate the substitution of 0.2M DBBP for the 0.2M TBP in the present plant solvent to be technically feasible.

The deleterious effects of small concentrations of H_2 MEHP on HDEHP strontium extraction contrast sharply with the beneficial effects of TBP and DBBP. Thus, as little as 0.05M H_2 MEHP in a 0.3M HDEHP extractant (with or without 0.2M TBP present) reduces the strontium distribution ratio by about a factor of two. This antagonistic effect is ascribed to strong intermolecular hydrogen bonding between H_2 MEHP and HDEHP. The antagonistic effect of H_2 MEHP is particularly important to B-plant operation because H_2 MEHP is a primary radiolysis product of HDEHP and, unless periodically removed, can reach a concentration as high as 0.05M upon even modest (10^8 rad) solvent exposure. These results underscore the importance of the dilute NaOH wash step incorporated in present B-plant flowsheets for removal of radiolytically-generated H_2 MEHP.

Because of hydrogen bonding effects also, 2-ethylhexanol and 2-ethylhexanoic acid have antagonistic effects on HDEHP extraction of strontium. However, much higher (~ 10 times)

concentrations of these materials are required to produce the same depressant effect as H_2MEHP . Furthermore, neither the alcohol nor 2-ethylhexanoic acid have been identified as radiolysis products. Thus, the antagonistic effects of the alcohol and acid are not considered of importance to B-plant operation.

EXPERIMENTAL PROCEDURES

MATERIALS

Extractant Components

As-purchased (Union Carbide Co.) HDEHP was shown, by titrimetric analysis⁽⁵⁾ to contain 94.9 wt% (2.84M) HDEHP, 1.9 wt% ($\sim 0.06M$) H_2MEHP , and 3.2 wt% inerts (presumably 2-ethylhexanol, pyroesters, and others). Traces of iron were also present. In connection with the inerts content, Campbell reports⁽⁶⁾ that at least some batches of HDEHP used at Hanford contain up to 1 vol% 2-ethylhexanol.

Two different procedures were used to prepare highly purified HDEHP from the as-purchased material. The more highly purified material (3.10M HDEHP, no detectable H_2MEHP) was prepared by a procedure developed by Partridge.⁽⁷⁾ This purification scheme involves conversion of HDEHP to its copper salt by treatment with an alkaline slurry of CuO and subsequent extraction of the copper salt into diethyl ether. Recrystallization of the copper salt several times from an ether solution, followed by treatment with an aqueous mineral acid, yields pure HDEHP.

Less pure (98.9 wt%) HDEHP was prepared by the purification procedure of Schmitt and Blake.⁽⁵⁾ Essential steps in this procedure include acid hydrolysis, conversion to the sodium salt, extraction of the neutral impurities with petroleum ether, reversion to the acid form, and extraction of H_2MEHP with ethylene glycol.

Synergistic and antagonistic reagents tested included H_2 MEHP, TBP, (Commercial Solvents Corp.), trioctylphosphine oxide (TOPO), di-sec butylphenylphosphonate (DSBPP), dibutyl butylphosphonate (DBBP), 2-ethylhexanol, 2-ethylhexanoic acid, and 2-ethylhexanal. The latter three compounds (Eastman practical grade) and TOPO (Eastman grade) were obtained from Eastman Kodak Co. The DSBPP was obtained from the Stauffer Chemical Co. The DBBP (Virginia Carolina Co.) contained⁽⁸⁾ 82 to 83 vol% DBBP, about 15% dibutylmethyl phosphonate, and about 2 to 3% low boiling fractions. The source and purification of H_2 MEHP are discussed later. TBP was used both as-purchased and after purification (vacuum distillation). All other reagents listed were used in the as-purchased condition. Except for H_2 MEHP, concentrations of synergistic and antagonistic agents were calculated on the basis of measured densities and an assumed 100% purity for each such reagent.

The H_2 MEHP used in this study was supplied by J. Partridge of this laboratory who isolated and purified it from irradiated ($\sim 10^8$ rads), as-purchased HDEHP according to the following procedure.⁽⁷⁾ H_2 MEHP was extracted from the irradiated HDEHP into ethyl ether and then removed from the ether phase by washing with Na_2CO_3 solution. After washing with several portions of ether to remove any 2-ethylhexanol as well as tri (2-ethylhexyl)-phosphoric acid and NaDEHP the aqueous phase was acidified with HCl to convert the sodium salt of H_2 MEHP to the acid form. The H_2 MEHP was extracted into ether, the ether phase was washed with water and, finally, the ether and dissolved water were evaporated using a rotating evaporator operating at 50 °C and 15 mm Hg pressure.

The density of the H_2 MEHP prepared by the above procedure was 1.082 g/ml at 25 °C. Peppard has reported⁽⁹⁾ the density at 20 °C to be 1.096 g/ml. Acid-base titrations showed the material obtained by Partridge to be 5.04M H_2 MEHP. Based on Peppard's density value, pure material should titrate 5.21M H_2 MEHP.

Extractants used in this study were prepared by diluting the appropriate HDEHP and synergistic (or antagonistic) reagent with NPH. NPH is the Hanford designation for a commercially available mixture of normal paraffin hydrocarbons, principally C_{10} through C_{14} . The NPH manufactured by the South Hampton Co., Houston, Texas was used throughout this work.

Synthetic Extraction Column Feedstocks

In the Hanford Waste Management program, one of the primary source materials from which ^{90}Sr and fission product rare earths will be removed by HDEHP extraction is Purex Acid Waste (PAW) solution. Typical PAW composition has been reported earlier.⁽¹⁰⁾ Extraction column feed solutions are prepared from the PAW by addition of a buffering agent (e.g. hydroxyacetic acid), a complexing agent [e.g. trisodium N-hydroxyethylethylenediamineacetate (Na_3HEDTA)], and NaOH to adjust to the desired pH. The compositions of the two synthetic extraction column feed stocks (1AF solutions) used in the studies reported here are listed in Table I.

TABLE I. *Composition of Synthetic Extraction Column Feed Solutions*

Component	Concentration, M	
	1AF-2	1AF-3
Na	1.51	1.3
Fe	0.072	0.15
Al	0.036	0.039
Cr	0.014	0.015
Ni	0.0072	0.0074
La	0.0024	0.0018
Ce	0.0012	0.0018
Sr	0.0009	0.0006
Ca	0.0006	0.0006
Hydroxyacetate	0.20	0.20
HEDTA	0.18	0.25
Tartrate	0.014	0.025
NO_3^-	1.14	1.3
$\text{SO}_4^{=}$	0.079	0.11
pH	3.5	4.0

Other Chemicals

The radioisotopes ^{85}Sr , $^{144}\text{CePr}$, ^{22}Na , $^{106}\text{RuRh}$, $^{152-154}\text{Eu}$, and ^{88}Y were used in this study. The chemical forms and sources of these isotopes are listed elsewhere. (11,12)

Stock solutions of 1.57M Na_3HEDTA and 11.5M hydroxyacetic acid were obtained from the Dow Chemical Co. and the duPont Co., respectively. All other chemicals used were of reagent grade quality.

DISTRIBUTION RATIO MEASUREMENTS

The distribution ratio (E_a^0) is defined as the ratio of the concentration of the element of interest in the less dense organic phase to the concentration of the element in the more dense aqueous phase after equilibration of the two essentially immiscible liquids.

Unless otherwise indicated, equal volumes of aqueous and organic phases were contacted (mechanical stirring) 10 min at 25 °C. Phases were separated by centrifugation.

Extraction column distribution ratios for strontium and cerium(III) were measured by contacting the various HDEHP extractants with 1AF solution containing either ^{85}Sr or $^{144}\text{CePr}$. In some cases, the organic phase containing ^{85}Sr was contacted twice at 40 °C with one-fifth volume portions of a scrub solution of the composition 0.6M hydroxyacetate-0.005M HEDTA-0.23M Na-pH 2.4. The scrubbed organic phase was then contacted with one-fifth volume of 0.028M HNO_3 to determine behavior of strontium under partition column conditions. In some cases also, the organic phase containing $^{144}\text{CePr}$ was contacted with 2M HNO_3 to determine the stripability of cerium(III) from the HDEHP extractant.

The cerium(IV) extraction capacity of various HDEHP extractants was determined by 60-min contact with an aqueous

solution initially of the composition 1.96M HNO_3 - $0.0143\text{M La(NO}_3)_3$ - $0.00712\text{M Ce(NO}_3)_3$ - $0.20\text{M (NH}_4)_2\text{S}_2\text{O}_8$ - 0.02M AgNO_3 and traced with $^{144}\text{Ce(III)}$.

ANALYSES

Gamma energy pulse height analyses were used to determine the concentrations of various radioisotopes in aqueous and organic phases.

The concentrations of both HDEHP and H_2MEHP in irradiated and unirradiated solvents was determined by electrotitrimetry using the derivative mode of a Sargent Model D Automatic Titrator.

RESULTS AND DISCUSSION

SYNERGISTIC EFFECTS ON STRONTIUM EXTRACTION

Schmitt⁽¹³⁾ at the Oak Ridge National Laboratory (ORNL) was the first to observe that certain combinations of dialkylphosphoric acids and neutral organophosphorous compounds produce distribution ratios for UO_2^{2+} much greater than would be predicted from the behavior of the separate reagents. Detailed investigations were made later by various ORNL workers,⁽¹⁴⁻¹⁷⁾ and the term synergistic extraction was applied to the effect by Coleman.

Following the early ORNL work, investigators in many countries have performed intensive studies of synergistic extraction in organophosphate as well as in other [eg. thenoyltrifluoroacetone (TTA) and 4-sec-butyl-2-(α -methylbenzyl) phenol] systems.⁽¹⁸⁻²³⁾ These studies have shown that synergistic extraction is not limited to uranyl ion but is a general phenomenon and can occur in extraction of cesium, alkaline earths, and trivalent lanthanides and actinides. The experimental evidence available to date indicates that an addition product rather than a substitution product is responsible for the synergistic effect in acidic-neutral organophosphate systems.* A substitution mechanism also appears to be operative in TTA synergistic systems.

* An exception, apparently, is the synergistic effect of TBP on HDEHP extraction of strontium discussed later herein.

These and other facets of synergistic extraction systems are discussed more fully in the recent reviews of Baes⁽²⁴⁾ and Healy.⁽²⁵⁾

A small (factor of about two) synergistic effect of TBP on HDEHP extraction of strontium was first noted by Schulz in 1962.⁽¹⁰⁾ McDowell and coworkers at ORNL subsequently confirmed the existence of this synergism when an aliphatic hydrocarbon (such as n-octane, decane, or dodecane) was used as the carrier solvent for the TBP and HDEHP.^(26,27) However, synergism did not appear when the carrier solvent was benzene. Also in these ORNL studies, the magnitude of the synergistic effect was observed to vary with aqueous phase pH but, in all cases, was a maximum at about 0.1 to 0.2M TBP.

McDowell has recently published⁽²⁸⁾ the results of a more detailed study of synergistic and other solvent effects on the extraction of strontium by HDEHP solutions. He reports two distinct effects. One, related to changes in the apparent acid strength of HDEHP and attributable to the Lewis acidity or basicity of the carrier solvent, involves a shift of the $\text{Sr } E_a^\circ$ versus pH curve along the pH axis. The other involves more direct molecular interaction of the carrier solvent or additive with extracted strontium (synergistic effect), or with HDEHP molecules (see Antagonistic Effects on Strontium Extraction in this report). Utilizing among other techniques the method of continuous variations as developed by Gal and Nikolic,⁽²⁹⁾ McDowell also established that the synergistic effect of TBP on strontium extraction was due to the substitution of TBP for HR (HR = HDEHP) in the compound $\text{SrR}_2 \cdot 4\text{HR}$. A range of substituted compounds from $\text{SrR}_2 \cdot 3\text{HR} \cdot \text{TBP}$ to $\text{SrR}_2 \cdot 4\text{TBP}$ was noted with maximum synergism occurring when 60% of the total phosphate was TBP and 30% of the HDEHP was as NaD2EHP.

Survey of Organophosphorous Compounds

Observation of the effect of TBP in enhancing HDEHP extraction of strontium prompted a brief survey of other types of organophosphorous compounds for evidence of similar synergistic effects. This search (Table II) was successful. Both phosphonate compounds tested, DSBPP and DBBP, exhibited a synergistic effect on HDEHP extraction of strontium. The effect for DBBP was greater than that for either DSBPP or TBP.

TABLE II. Synergistic Effects of Organophosphorous Compounds on HDEHP Extraction of Strontium

Organophosphorous Compound ^(a)		Strontium Extraction E_a°	
Name	Conc., M	pH 3.25 ^(b)	pH 3.4 ^(c)
None		2.33	2.9
TBP	0.01	-	3.48
	0.05	-	3.90
	0.1	3.38	3.99
	0.2	2.97	3.91
	0.3	2.91	3.42
	0.6	1.68	2.16
DBBP	0.01	-	3.43
	0.05	-	4.79
	0.1	4.65	4.82
	0.2	4.08	4.95
	0.3	3.23	4.01
	0.6	-	1.83
DSBPP	0.2	3.03	-
TOPO	0.2	2.06	-

(a) All extractants were also 0.3M HDEHP in NPH prepared from as-received reagents.

(b) Determined with 1AF-2 (Table I).

(c) Determined with 1AF-2 adjusted to slightly higher pH than shown in Table I.

The synergistic effects of TBP and DBBP on HDEHP extraction of strontium at pH 3.4 are further compared in Figure 1. Maximum synergism in both cases occurred at about 0.1M neutral

FIGURE 1. Synergistic Effects of TBP and DBBP on Strontium Extraction

organophosphate; occurrence of a maximum effect at this concentration is in agreement with McDowell's results.*⁽²⁸⁾ The gradual decrease in strontium extraction at TBP and DBBP concentrations greater than 0.1M is ascribable to increased interaction between HDEHP and TBP or DBBP. This interaction is so strong at sufficiently high (>0.45M) concentrations of TBP and DBBP that the strontium distribution ratio is less than it is for the HDEHP extractant alone. Such antagonistic effects, of which the case just cited is a typical example, are considered further in a later section.

In HDEHP extractions of UO_2^{2+} , TOPO is a more powerful synergist than either TBP or DBBP.⁽¹⁶⁾ However, under the conditions used in this study (Table II), 0.2M TOPO not only lacked a synergistic effect upon strontium extraction but actually displayed a slight antagonistic effect. The antagonistic effects of TOPO on extraction of strontium at pH's in the range 1 to 3 have also been observed by Horner at ORNL.⁽³⁰⁾ At higher pH's (ca. 5), however, TOPO does show the expected synergistic effect upon HDEHP extraction of strontium. At pH 5, according to McDowell's results,⁽²⁸⁾ TOPO is a more powerful synergist than TBP, just as is the case in extraction of uranium.

The few results reported here, and those of McDowell and Horner referred to earlier, appear to represent all that is known about the occurrence and mechanism of synergism in HDEHP- Sr^{2+} extraction systems. A more exhaustive survey of the effects of various types of neutral organophosphate and other compounds in this system might prove fruitful. Studies of the HDEHP-DBBP- Sr^{+2} system similar to those of McDowell for the HDEHP-TBP- Sr^{+2} system also appear warranted.

* McDowell's results would also predict, however, that at higher pH's, the maximum strontium distribution ratio would occur at concentrations of TBP and DBBP greater than 0.1M.

Further Studies of HDEHP-DBBP Extractant

The results noted for HDEHP-DBBP extractants in the initial survey encouraged further and more detailed studies of these extractants. These latter studies demonstrated convincingly that, for Hanford B-Plant processes, the properties of a HDEHP-DBBP extractant are comparable to and, in one important respect (strontium distribution ratio), are superior to those of the HDEHP-TBP solvent presently specified. Substitution of 0.2M DBBP for the 0.2M TBP in the B-plant extractant has been proposed formally. (31)

The HDEHP extractant is expected to receive radiation at the rate of about 10 to 20 watt-hr/liter per solvent extraction cycle when the B-plant is processing feeds prepared from PAW solution. The principal effect of solvent radiolysis, as far as B-plant operation is concerned, is a decrease in the strontium extraction capacity of the solvent. Results in Table III show, for example, that the strontium distribution ratio obtained with a HDEHP-TBP extractant falls by about a factor of two when the extractant is irradiated to about 10^8 rad. Antagonistic effects of radiolytically-generated H_2MEHP (see Subsection "Effect of H_2MEHP ") are accountable, at least partly, for decreased extraction of strontium by irradiated HDEHP solvents.

Substitution of DBBP for TBP in a HDEHP extractant does not prevent the radiolytic decrease in strontium distribution ratio. Significantly, however, the greater synergistic effect of DBBP over TBP on strontium extraction persists even after prolonged irradiation. Consequently, as the results in Table III show, the strontium distribution ratio for a HDEHP-0.2M DBBP extractant, even after irradiation to about 10^8 rads, is only slightly (~18%) lower than that obtained with an unirradiated HDEHP-0.2M TBP extractant. The strontium distribution ratio is limiting to B-plant extraction column operation. It is highly desirable, therefore, to maintain it as high as possible.

TABLE III. *Effects of Irradiation on HDEHP-TBP and HDEHP-DBBP Extractants*

Solvent Property	TBP Solvent ^(a)		DBBP Solvent ^(b)	
	Unirradiated	Irradiated	Unirradiated	Irradiated
HDEHP, <u>M</u>	0.303	0.290	0.309	0.296
<u>Sr E_a^o:</u>				
Extraction				
1AF-2:	2.97	1.45	4.08	2.44
1AF-3:	8.89	5.32	11.1	7.29
Partition:	0.0174	0.0116	0.0179	0.0138
<u>Ce(III) E_a^o:</u>				
Extraction:	259.	230.	386.	282.
Strip:	0.0133	0.0124	0.0708	0.0703
<u>Ce(IV) E_a^o:</u>				
	1000.	289.	370.	164.

(a) A 0.303M HDEHP-0.2M TBP-NPH extractant, prepared from as-purchased reagents, was irradiated 59 hr at 25 °C at 1.77 megarad/hr.

(b) A 0.309M HDEHP-0.2M DBBP-NPH extractant, prepared from as-purchased reagents, was irradiated 70 hr at 25 °C at 1.66 megarad/hr.

HDEHP-DBBP extractants, both unirradiated and irradiated, extract cerium(III) as well as or better than HDEHP-TBP solvents. During HNO₃ stripping, the former solvents retain cerium(III) a little more tenaciously than those containing TBP but not enough so to prohibit satisfactory B-plant "C" column operation. Dilute HNO₃ solutions remove strontium from both types of extractants without any difficulty. Other data in Table III show HDEHP-DBBP extractants to be inferior to their TBP counterparts in extracting cerium(IV). The capacity of HEDHP-DBBP extractants, however, is still more than adequate for oxidative separation of cerium from other fission product rare earths. This latter separation is not currently scheduled to be performed routinely in B-plant operations.

Strontium and fission product rare earths in B-plant 1AF solutions are associated with various inert and radioactive contaminants. The small sampling summarized in Table IV indicates that HDEHP-DBBP and HDEHP-TBP solvents both extract these elements to about the same extent.

TABLE IV. *Extraction of Various Elements by HDEHP-TBP and HDEHP-DBBP Extractants*

Conditions: 1AF-3 solution containing indicated radio-isotopes contacted with indicated HDEHP extractant.

Radioisotope	E _a	
	TBP Extractant (a)	DBBP Extractant (b)
⁸⁸ Y	660.	1040.
¹⁵²⁻¹⁵⁴ Eu	190.	100.
²² Na	0.0204	0.0193
⁹⁵ Zr	0.00043	0.00069
¹⁰⁶ RuRh	0.000072	0.00122

(a) *0.3M HDEHP-0.2M TBP-NPH prepared from as-purchased reagents.*

(b) *0.3M HDEHP-0.2M DBBP-NPH prepared from as-purchased reagents.*

Current B-plant flowsheets specify routine washing of HDEHP with NaOH solutions to remove various contaminants. Such washing converts HDEHP to its sodium salt, NaDEHP, a form much less soluble in kerosene. Addition of a diluent modifier such as TBP is necessary, therefore, to increase the solubility of NaDEHP and to prevent formation of a second organic phase in the washing step. Preliminary results indicate 0.2M DBBP to be at least as effective as the same concentration of TBP in preventing formation of a third phase in the solvent wash contact.

ANTAGONISTIC EFFECTS ON STRONTIUM EXTRACTION

The widespread occurrence of synergism in solvent extraction systems has been emphasized in the preceding discussion. The

inverse effect,* where the resulting extraction in a reaction between extractants is less than that due to either extractant alone, occurs with equal frequency. Thus, in all synergistic systems examined to date, an excess of the synergistic reagent produces an antagonistic effect. Such antagonistic effects were noted in the present work, as already mentioned, in the extraction of strontium by HDEHP-TBP and HDEHP-DBBP solutions. Similar antagonistic effects in HDEHP-neutral organophosphorous systems have been noted for extraction of uranyl ion^(15,16,20) trivalent lanthanides and actinides,⁽²¹⁾ and also calcium and barium ions.⁽²¹⁾ Healy, in his extensive studies of synergism in TTA systems,⁽³²⁾ also reported that antagonistic effects were produced when an excess of the various synergistic agents were present.

In certain extraction systems, combinations of extractants or other organic phase components produces an immediate antagonistic effect without any intervening synergistic action. Examples include the depressing effects of TBP on extraction of Np(IV) and Th(IV) by H₂MEHP-toluene solutions,⁽³³⁾ and of 2-ethylhexanol on extraction of uranium⁽¹⁶⁾ and strontium⁽³⁴⁾ by HDEHP solutions. Also included in this category are the antagonistic effects produced by certain so called inert diluents such as those of benzene in HDEHP extraction of strontium⁽²⁷⁾ and uranium,⁽²⁰⁾ and in TTA extraction systems.⁽³²⁾

Many workers have ascribed antagonistic effects to the formation, through hydrogen bonding, of association products from various components of the organic extractant. Infrared and other data supporting this contention have been obtained in several systems.^(35,36) In TTA extraction systems, on the other hand, Healy and coworkers believe antagonistic effects are connected with the water content of the organic phase and the destruction of anhydrous synergic species.⁽³²⁾

* *The inverse effect is referred to as an antagonistic effect in this paper although other workers have used the terms "negative synergism" and "antisnergism."*

Several instances of antagonistic effects in HDEHP extraction of strontium have been noted both in our work and by ORNL investigators. These effects, their magnitudes, and probable causes are discussed in the portions of this report immediately following. Such antagonistic effects and methods for their control or elimination are highly important to troublefree operation of the Hanford B-plant solvent extraction system. In this latter connection, it is again noted that strontium distribution ratios, being lower than those of the trivalent rare earths, limit extraction column phase volume ratios and capacities.

Effect of H_2MEHP

Commercially available HDEHP contains small amounts of H_2MEHP . H_2MEHP is also a primary product of the radiolysis of HDEHP.⁽³⁷⁾ Small concentrations of the diacid have a definite antagonistic effect on extraction of strontium by HDEHP solutions. The antagonistic effect occurs in the presence of TBP (Table V) as well as in its absence (Table VI). In both cases, strontium distribution ratios are decreased 50% by the presence of as little as 0.04 to 0.06M H_2MEHP . Also in both cases, addition of even small amounts of H_2MEHP produces an immediate antagonistic effect on strontium extraction (Figure 2) without evidencing any initial synergistic action at low H_2MEHP concentration.

The depressant effects of H_2MEHP on strontium extraction arise presumably because of the formation of hydrogen bonded H_2MEHP -HDEHP species. The net result of such interaction is to reduce the amount of HDEHP available to extract strontium. That HDEHP exists as a dimeric species in kerosene diluent is well substantiated. H_2MEHP in kerosene solvents has even greater propensity for self association through hydrogen bonding. For example, Ferraro and Peppard report⁽³⁸⁾ that the polymeric H_2MEHP species in hexane involves association of as many as 14 H_2MEHP molecules. Thus, formation of hydrogen bonded species containing

mixed H_2MEHP and HDEHP ligands would be expected from known chemistry and would surely account for the antagonistic effects of H_2MEHP on extraction of strontium by HDEHP.

TABLE V. *Effects of H_2MEHP on Extraction of Strontium and Cerium(III) by HDEHP-TBP-NPH Solvent*

Conditions: 0.29M HDEHP^(a)-0.2M TBP^(b)-NPH solutions containing indicated amounts of H_2MEHP were contacted with 1AF solutions.

H_2MEHP M	Strontium Extraction ^(c)		Cerium(III) Extraction ^(d)	
	E_a°	pH	E_a°	pH
0.0	9.74	3.75	265	3.4
0.0071	9.43	3.7	255	3.4
0.0216	8.04	3.7	266	3.3
0.0426	5.95	3.7	162	3.25
0.087	3.39	3.6	190	3.1
0.25	-	-	687	3.0

(a) Purified by Partridge procedure

(b) Vacuum Distilled.

(c) Determined with 1AF-3 solution.

(d) Determined with 1AF-2 solution.

TABLE VI. *Antagonistic Effects of H_2MEHP on HDEHP Extraction of Strontium*

Conditions: 0.295M HDEHP^(a)-NPH solutions containing indicated amounts of H_2MEHP were contacted with 1AF-3 solution.

H_2MEHP M	Strontium Extraction	
	E_a°	pH
0.00	6.28	3.70
0.0087	5.70	3.68
0.0239	4.75	3.68
0.0459	3.70	3.60
0.0919	1.58	3.60

(a) Purified by Partridge procedure.

FIGURE 2. Antagonistic Effects of H₂MEPH on Strontium Extraction

The antagonistic effects of H_2MEHP on strontium extraction are, of course, detrimental to B-plant ^{90}Sr removal operations. Fortunately, the disodium salt of H_2MEHP is considerably more soluble in dilute aqueous $NaOH$ and Na_2CO_3 solutions than is the sodium salt of HDEHP. Such aqueous solutions can be (and are) used in B-plant operations to remove any H_2MEHP which might be present in the virgin extractant or which might be produced subsequently by radiolysis.

The discussion of the effects of H_2MEHP is essentially complete save to comment on extraction of cerium(III) by mixed HDEHP- H_2MEHP solvents (Table V). At a fixed HDEHP molarity, small concentrations (0.007 to 0.04M) of H_2MEHP depress cerium(III) extraction probably for the same reason they reduce extraction of strontium. The depressing effect is reversed at higher ($\sim 0.25M$) H_2MEHP concentrations and cerium extracts better into the mixed HDEHP- H_2MEHP solvent than into HDEHP by itself. The strong affinity of H_2MEHP for trivalent lanthanides has been noted by Peppard and coworkers.⁽³⁹⁾

Other Antagonistic Agents

The antagonistic effects of 2-ethylhexanol on HDEHP extraction of uranium were noted in early ORNL studies.⁽¹⁷⁾ Later, McHenry and Posey, also at ORNL, observed similar antagonistic effects of the alcohol on HDEHP extraction of strontium and made use of the effect to devise a procedure for separating ^{90}Sr from inert calcium.⁽³⁴⁾ Our results (Table VII) substantiate the antagonistic effect on strontium extraction. Addition of 2-ethylhexanol to HDEHP solvents also affects adversely the extraction of both cerium(III) and cerium(IV).

In accordance with the suggestion of McHenry and Posey, the antagonistic effects of 2-ethylhexanol on strontium extraction (and, also on cerium(III) extraction) are believed to arise from the formation of an association compound between the alcohol

and HDEHP. Formation of such an association compound occurs, presumably, as the result of hydrogen bonding between alcohol and HDEHP molecules. The extent of this hydrogen bonding is considerably less, however, than that between H_2MEHP and HDEHP molecules. Thus, diminution of the strontium distribution ratio by a factor of two requires a concentration of about $0.5M$ 2-ethylhexanol, but only about $0.05M$ H_2MEHP .

TABLE VII. Effects of 2-Ethylhexanol on HDEHP Extraction of Strontium and Cerium(III) and (IV)

Conditions: $0.30M$ HDEHP^(a) - $0.2M$ TBP^(b) NPH solutions containing indicated amounts of 2-ethylhexanol were used to determine listed distribution ratios.

2-ethylhexanol		Ext'n ^(c,d)	Partition	Ext'n	Strip	Cerium(IV) Ext'n
vol%	M	E _a ^o	E _a ^o	E _a ^o	E _a ^o	E _a ^o
0	0.0	4.82	0.0174	418	0.0133	2100
1	0.212	3.82	0.0120	303	0.0100	148
3	0.633	2.09	0.0054	214	0.0059	51.5
5	1.06	1.33	0.0031	141	0.0047	31.0
10	2.18	0.594	0.0011	48.8	0.0027	16.7

(a) HDEHP purified by ORNL procedure.

(b) Vacuum distilled

(c) Determined with 1AF-2.

(d) pH of aqueous 1AF after contact was 3.25 to 3.35 in all cases.

The adverse effect of 2-ethylhexanol on cerium(IV) extraction arises probably as the result of a redox reaction between the alcohol and the powerful oxidant, cerium(IV). Reduction of cerium(IV) by alcohol in the organic phase competes with its oxidation by persulfate in the aqueous phase. The reduction reaction competes more strongly as the alcohol concentration increases and less cerium(IV) is extracted.

The antagonistic effects of 2-ethylhexanol are judged to be considerably less important to B-plant operations than are those

of H_2MEHP . Thus, as just observed, to produce a twofold reduction in strontium E_a° requires about 10 times as much alcohol as H_2MEHP . Commercially available HDEHP apparently contains only small amounts (~ 1 vol% or less) of 2-ethylhexanol.⁽⁶⁾ Further, whereas H_2MEHP is a primary radiolysis product, 2-ethylhexanol is produced only in negligible amounts, if at all, during radiolysis of the B-plant solvent.⁽⁴⁰⁾ There appears to be little possibility, therefore, of ever generating concentrations of 2-ethylhexanol deleterious to B-plant operations.

Both 2-ethylhexanol and 2-ethylhexanoic acid also have antagonistic effects on extraction of strontium by HDEHP-TBP solvents (Table VIII). As before, the antagonistic action in both cases results presumably from hydrogen bonding between HDEHP and the aldehyde or acid. The antagonistic effect for 2-ethylhexanoic acid is greater than that for either the aldehyde or, for that matter, 2-ethylhexanol (Figure 3). The ordinate in Figure 3 is calculated as $E/E_A = \frac{Sr E_a^\circ \text{ without additive}}{Sr E_a^\circ \text{ with antagonistic agent}}$.

TABLE VIII. Effects of Some Other Antagonistic Agents on Strontium Extraction

Conditions: 0.30M HDEHP^(a)-0.2M TBP^(b)-NPH solutions containing indicated amounts of 2-ethylhexanol and 2-ethylhexanoic acid were contacted with 1AF-3.

2-ethylhexanol			2-ethylhexanoic acid		
vol%	M	Sr E_a°	vol%	M	Sr E_a°
0	0.00	8.89	0	0.00	8.89
1	0.0631	9.30	1	0.0625	8.14
3	0.189	8.33	3	0.188	2.92
5	0.316	7.20	5	0.313	2.16
10	0.631	5.87	10	0.625	1.10

(a) HDEHP purified by Partridge procedure.

(b) As-received TBP.

FIGURE 3. Comparison of Effects of Some Antagonistic Agents on HDEHP Extraction of Strontium

Neither the aldehyde nor 2-ethylhexanoic acid have been detected in batches of HDEHP used at Hanford. These compounds might be produced by oxidation of 2-ethylhexanol but, as mentioned earlier, little, if any, of the parent alcohol is anticipated in B-plant solvent. Hence, although interesting, the antagonistic effects described in this section are deemed of no consequence to B-plant operations.

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