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SUBJECT: STATUS OF SUBCONTRACT WORK ON EFFECTS OF RADIATION ON
SOLVENT EXTRACTION PROCESSES

TO: F. L. Culler

FROM: W. Davis, Jr.

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ABSTRACT

The results of the Stanford Research Institute studies of the effects of radiation on solvent extraction processes are summarized and a desirable direction for future work is indicated. Studies performed to date have shown that: 1) nearly all of the irradiation-induced increase in time required for TBP-Amsco-aqueous phase separation is due to formation of a polymer, of unknown chemical structure; 2) uranium retention by the TBP-Amsco phase during stripping operations is due approximately 65% to dibutyl phosphate and 20% to the polymer; 3) each 100 ev of energy absorbed forms about 0.5 hydrocarbon double bonds, with which fission product iodine could readily react; 4) dibutyl phenylphosphonate is about six times as resistant, and dibutyl butylphosphonate is twice as resistant, to radiation damage as is tributyl phosphate.

Future work under this subcontract should emphasize the following four items: 1) determination of radiolysis products and effects of radiation on phase separation and uranium retention properties of new solvents such as phosphine oxides, amines, and phosphonates; 2) further testing of solvents, such as dibutyl phenylphosphonate and dibutyl butylphosphonate, that are appreciably more resistant to radiation damage than is TBP-with respect to phase separation and uranium retention during stripping operations; 3) determination of the origin of emulsion and complex forming agents in the radiolysis of TBP-Amsco solutions; 4) identification of polymeric radiolysis products. The latter item should be studied in collaboration with Dr. W. H. Baldwin of the ORNL Chemistry Division.

NOTES

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INTRODUCTION

In any solvent extraction process for separating fissionable materials from fission products, radiolytic decomposition of the extractant and diluent will occur. The extent of this decomposition will be nearly linearly dependent on the radiation energy density. Since this energy density is very low in existing extraction plants, the amount of decomposition, and the monetary values of extractant and diluent that are decomposed, is trivial. However, the effects of radiolytic decomposition of extractant and diluent are far from trivial in present Thorex process operations or in contemplated power reactor fuel reprocessing operations.

As summarized by Bruce (1), "Tributyl phosphate degradation produces di- and mono-butyl phosphates, which form insoluble compounds with thorium, and solvent-soluble complexes with zirconium, niobium, uranium, and plutonium. Diluent degradation produces unsaturated compounds which may be emulsion formers, and enhance iodine extractability".

Processing of short-cooled heterogeneous reactor fuels will involve solvent exposures of 2-3 β watt-hr/liter of solvent per cycle, a level 100-fold in excess of present Hanford experience. Processing of 5-day-cooled homogeneous reactor fuel would involve 4.5 watt-hr/liter per cycle. In the Thorex Pilot Plant a solvent exposure of 0.05 β watt-hr/liter per cycle was experienced with feed cooled for one year. Solvent dosage was increased to 1-2 β watt-hr/liter per cycle when 30-day-cooled material was processed. Ruthenium decontamination dropped 300-fold in a single solvent extraction cycle.

On the basis of these known, deleterious effects of radiation on solvent extraction processes, and of other considerations, a subcontract was established with the Stanford Research Institute, whose studies were to include: 1) identification of decomposition products; 2) investigation of copolymer formation by tributyl phosphate and diluent degradation products; 3) studying the effects of these products on the extraction process; 4) performing scouting investigations of other solvents that may be resistant to radiation decomposition and capable of yielding moderate separation of uranium from fission products.

The purpose of this memo is to summarize the most pertinent results of the Stanford Research Institute studies and to indicate a desirable direction for future work. The latter aspect has been very much clarified as a result of conversations of the author with E. M. Kinderman of SRI and with C. F. Coleman and C. R. Blake, Jr., of this Division.

SUMMARY OF STANFORD RESEARCH INSTITUTE STUDIES

The Stanford Research Institute has published details of studies of products formed during the radiation decomposition of several extractants and diluents and of the effects of these products on extraction, stripping, and emulsification tendencies in monthly and semiannual reports (2). These

studies involved the use of nominal 1-Mev electrons. Radiation densities ranged from ca. 100 to 2000 watt-hr/liter. Products of radiolysis that were identified included hydrocarbons, saturated and unsaturated, ranging from methane to octenes and octanes, monobasic acids, dibasic acids, tri-basic acids, alcohols, and other compounds. Yields of those compounds most likely to affect solvent extraction processes in an adverse manner are summarized in Table I. The individual components should be examined on the basis of the following criteria:

- 1) The yield of extractant decomposition is a measure of the basic instability of the extractant. It is apparent that dibutyl phenylphosphonate is about six times as resistant and dibutyl butylphosphonate about twice as resistant to radiation damage as is tributyl phosphate. Other compounds studied have nearly the same resistance to radiation damage as does TBP.
- 2) The yields of mono-, di-, and tri-basic acids give a measure of the extent to which insoluble compounds of thorium and solvent-soluble complexes of zirconium, niobium, uranium, and plutonium can be formed. Yields of these acids during the radiolysis of dibutyl phenylphosphonate is only 1/3 to 1/4 as great as those obtained during the radiolysis of dibutyl butylphosphonate and only 1/3 to 1/6 as great as those obtained during the radiolysis of TBP.
- 3) Emulsification studies have shown a polymer, whose composition has not yet been determined, to be the principal cause for the increase in time required for separation of TBP-Amsco solutions from a 2 M HNO_3 - 0.2 M UNH aqueous phase. Yields of the polymer have been determined in only a few cases, and it is apparent in each that this component is of major importance.
- 4) The yields of unsaturated components are measures of the degree to which iodine can become chemically combined with the organic extraction system. Numbers listed in Table I were obtained by adding the yields of the various unsaturated hydrocarbons with less than nine carbon atoms per molecule. Unsaturated components with more than eight carbon atoms were not determined. Hence, the table values are lower limits. They do, however, indicate the formation of significant unsaturation whereby iodine could be chemically combined.
- 5) Alcohol yields have been listed, but there is no criterion on which to base a statement of its effects. In studies of many compounds as potential extractants for uranium from ore leach liquors, members of K. B. Brown's section have found that alcohols can be detrimental or beneficial to the extraction process. Thus, effects of alcohol must be stated after defining the nature of the extraction or stripping system.

Several other compounds, including tri-isooctyl amine, tri-n-octyl phosphine oxide, and diethyl carbonate have been irradiated at SRI. Products from the first two have not been analyzed completely at the present time. Diethyl carbonate is being studied more extensively since, although it has a

moderately high decomposition yield, equal to or greater than 3.5 molecules per 100 ev of energy absorbed, the products have not yet been shown to be very deleterious in a solvent extraction system.

It should be noted that the dose densities used in the SRI experiments are, in most cases, 100-200 times higher than those employed in the recent, high level, Thorex Pilot Plant operations with 3000 g/t material cooled only 30 days. By use of these high levels, adequate quantities of products were obtained for good analysis.

FUTURE WORK

As might be expected, studies performed at the Stanford Research Institute have provided important answers to several questions and, in turn, raised other questions concerning the effects of radiation on solvent extraction processes.

Maximum energy densities now anticipated in solvent extraction processes are in the range 5-15 watt-hr/liter per solvent cycle; the corresponding power densities in the high level Thorex Pilot Plant runs were in the range 2.5 to 5 watt/liter. In contrast with these values, SRI experiments have been performed in many cases at average energy densities in excess of 1000 watt-hr/liter and power densities of 1000 watt/liter. Point power densities in the SRI work are considerably higher. The experimental set-up involves mixing, with a magnetic stirrer, a liquid sample of about 10 mm depth wherein all the incident radiation is absorbed in the top 2 mm of depth. This corresponds to the top 2 mm of liquid receiving 5 times the average energy listed in Table I, or to point power densities as high as 10,000 watt/liter. When it is recognized that an average power density of 1000 watt/liter of tributyl phosphate would produce about 30% decomposition in one hour, it is likely that this and higher doses are producing considerable secondary reactions that would not be encountered in any solvent extraction process. Although it is desirable to study the deleterious effects of radiation on extractants and diluents under accelerated conditions, the extent of decomposition should be maintained below 10 to 15% of the reactant to avoid the secondary reactions. Thus, dose densities should not exceed 500 watt-hr/liter. It would also be preferable to maintain point densities below this value and to maintain point power input densities at or below 500 watts/liter.

Future work should emphasize the following items:

1. Exploratory tests of the effects of radiation on new solvents, such as amines, phosphine oxides, and phosphonates. Quantitative identification of several of the radiation decomposition products is useful since some of their effects on the solvent extraction processes are known. This applies to the acidic components, polymer, and unsaturated hydrocarbons. However, the effects on extraction of other components, which may or may not have been isolated, are unknown. Therefore simple measurements of extraction or stripping coefficients and of emulsification tendencies should be performed with any new solvent that

is irradiated and the results of such tests compared with those obtained with unirradiated samples.

2. Further study of those extractants that show appreciably greater resistance to radiation damage than does TBP. Dibutyl phenylphosphonate and dibutyl butylphosphonate fall in this category. Effects of radiation on the stripping and emulsion forming tendencies of these two materials should be determined. It might be desirable to include a tracer quantity of a radioactive element, such as zirconium, that could form the basis of a solvent quality control test (3).
3. Tributyl phosphate can be hydrolyzed thermally when heated to 60 to 100°C while in contact with an acid aqueous solution. This degradation is in addition to radiolytic decomposition. The relative effects of radiation on stripping and emulsification properties of TBP-Amsco solutions should be separated from effects produced by hydrolysis of TBP in contact with both high acid Purex solutions and acid deficient Thorex solutions.
4. Polymeric materials are produced during the radiation decomposition of 2,2,4,6,6 pentamethyl heptane and TBP (4). Since the former compound is probably typical of the components of Amsco, it is apparent that either two polymers and/or copolymers can be formed in the TBP-Amsco systems. One polymer will contain phosphorous, the other will not. It is probable that polymer produced during the irradiation of TBP is not identical with that produced during the irradiation of TBP-Amsco solutions or of other extractants in Amsco. Although full characterization of these polymers may not be necessary to understand, and possibly minimize, their effects on solvent extraction processes, it would be desirable to determine molecular weight, phosphorus content, and acidity. In addition, W. H. Baldwin has indicated he will perform other studies of polymers that are made by or sent to him.

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3. Garrett, T. P., et al, A Test for Solvent Quality, E. I. du Pont de Nemours Chemical Company, Savannah River Operation, August, 1957 (DP-237).
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TABLE I Summary of Yields of Potentially Deleterious Products

Yields, G, Molecules/100 ev of Energy Absorbed*											
Extractant Type	Diluent	R ₁	R ₂	Reactant Decomp.	Monobasic Acid Formed	Dibasic Acid Formed	Tribasic Acid Formed (H ₃ PO ₄)	Polymer ⁺	Unsat. H-C Formed**	Alcohol Formed	Average Dose Density, watt-hr per liter
$\begin{array}{l} R_1O \\ \diagdown \\ R_1O-P \rightarrow O \\ \diagup \\ R_2O \end{array}$	(a) None	n-Butyl	H	3.9-5.4	---	2.81	0.42	1.42	0.24	<0.01	1277
	(b) None	n-Butyl	n-Butyl	≥ 2.9	2.1-2.5	0.3-0.4	0.01-0.07	(0.9)	0.1-0.4	0.14-0.21	520-1420
	(b) Amsco	n-Butyl	n-Butyl	≥ 0.9	(0.6)	0.12	(0.01)	N.D.	0.46-0.93	0.11-0.14	822-1550
	(b) Benzene	n-Butyl	n-Butyl	≥ 1.97	1.54	0.41	N.D.	N.D.	0.3	0.1	1455
	(b) Toluene	n-Butyl	n-Butyl	≥ 2.2	1.97	0.19	N.D.	N.D.	0.2	0.15	1455
	(b) {Dissolved HNO ₃	n-Butyl	n-Butyl	N.D.	N.D.	2.1		N.D.	N.D.	N.D.	80
	(b) {2 M HNO ₃ 2nd Phase	n-Butyl	n-Butyl	N.D.	N.D.	1.8		N.D.	N.D.	N.D.	252
	(b) {Amsco + Aq. HNO ₃ 2nd Phase	n-Butyl	n-Butyl	N.D.	N.D.	0.3-0.6		N.D.	N.D.	N.D.	221-479
	(c) None	2-Ethylhexyl	H	4.7-5.7	---	1.2	2.5	(0.6)	N.D.	N.D.	1493
$\begin{array}{l} R_1O \\ \diagdown \\ R_1O-P \rightarrow O \\ \diagup \\ R_2 \end{array}$	(d) None	n-Butyl	n-Butyl	≥ 1.49	1.4	N.D.	N.D.	N.D.	0.07	0.27	1230
	(d) Amsco	n-Butyl	n-Butyl	≥ 0.84	0.8	N.D.	N.D.	N.D.	0.16	N.D.	1325
	(e) None	n-Butyl	Phenyl	≥ 0.39	0.36	N.D.	N.D.	N.D.	0.01	(0.08)	1507
	(e) Amsco	n-Butyl	Phenyl	≥ 0.26	0.24	N.D.	N.D.	N.D.	0.16	(0.06)	1455
	(e) Toluene	n-Butyl	Phenyl	≥ 0.32	0.30	N.D.	N.D.	N.D.	0.04	(0.07)	1455
	(f) None	n-Amyl	n-Amyl	≥ 1.97	1.9	N.D.	N.D.	N.D.	0.03-0.04	0.22	1220
	(f) Amsco	n-Amyl	n-Amyl	≥ 1.0	1.0	1.17		N.D.	0.06	N.D.	1325
	(g) None	n-Decyl	n-Decyl	N.D.			N.D.	N.D.	N.D.	N.D.	1210

N.D. indicates component not determined

a. Dibutyl Phosphate

b. Tributyl Phosphate

c. Di-(2-Ethylhexyl) phosphate

d. Dibutyl butylphosphonate

e. Dibutyl phenylphosphonate

f. Diamyl amylphosphonate

g. Didecyl decylphosphonate

* All yields are based on the total energy absorbed by the liquid, not, in the case of solutions, by the extractant only.

** This is the summation of yields of all hydrocarbons containing double or triple bonds with less than 9 carbon atoms per molecule. A triple bond was counted as two double bonds.

+ Numerical values in this column correspond to molecules of reactant that were converted to polymer per 100 ev of energy absorbed, not to molecules of polymer formed.

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