CHARACTERIZATION OF SURFACTANTS
IN ALUMINUM-URANIUM FUEL REPROCESSING SOLUTIONS

by

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A B S T R A C T

Surface active materials in aluminum nitrate-nitric acid fuel reprocessing solutions were characterized. Polymerized silica, zirconium-modified silica and soluble dibutyl phosphate species were found to contribute to stable emulsion formation. These surfactants were reduced in effectiveness by added acid.

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I. SUMMARY

Chemical reprocessing of silicon-containing aluminum-uranium reactor fuels may be complicated by the formation of stable emulsions in the pulsed extraction columns. A series of pilot plant experiments was run with synthetic solutions to investigate the effects of AlSi, zirconium, dibutyl phosphate and acid concentration on column operations. Extraction column interface samples from these experiments were examined to identify and characterize the surfactants present.

The coalescence time as determined in the single stage pulsed contactor was used as a measure of the surfactant concentrations. The effects of the suspected surfactants in 1.5M and 0M nitric acid streams were observed. Acid titration and centrifugation were used to characterize the surfactants.

Soluble silica which is not surface active is present in acid controlled concentrations and is slowly converted to a surfactant species in the 1.5M acid process solution. This polymerized silica species in the presence of zirconium shows surfactant properties in acid-free systems.

Dibutyl phosphate-containing solutions produce a soluble surfactant in the presence of zirconium.

All surfactant materials examined were reduced in effectiveness by the addition of 1M acid except the zirconium-dibutyl phosphate which required 3M added acid.

Feed clarification plus acid adjustment thus show promise as solutions to this type of emulsion problem.

II. INTRODUCTION

The chemical processing of spent reactor fuels containing high concentrations of silicon, either as an impurity in the aluminum cladding or as AlSi bonding material, leads to the formation of surface active materials in plant streams. These surfactants lead to the accumulation of bulky interfaces in pulsed extraction columns that cause flooding and reduce the efficiency of uranium transfer. This surfactant behavior has been associated in general with the soluble or colloidal silica derived from the fuel. Recent studies have indicated that other substances present in the process solutions, zirconyl dibutyl phosphate, for example,

could be surfactants. The zirconium present in these solutions is entirely fission product zirconium produced in macro quantities by high uranium burn-up in the fuel. The dibutyl phosphate present is a degradation product of the tributyl phosphate used as the uranium extraction agent and exists in an equilibrium concentration in the system, probably near 10^{-3} molar.

An extensive pilot plant experiment was designed to evaluate the effect of the solution composition variables of feed acidity and dibutyl phosphate, and the silicon and zirconium content of the fuel, on extraction column behavior. Plans were made to sample the column contents at the interface and study the surfactant properties of these solutions. It was anticipated that measurements and analyses made on these samples would produce some correlation between surfactant species, macro composition variations and column behavior.

III. PILOT PLANT EXPERIMENT

The Chemical Engineering Development Section ran a statistically-designed experiment to investigate the effects of acid, dibutyl phosphate, zirconium, AlSi, and aluminum scrub concentrations on column operations. The design concentrations for this experiment are given in Table 1. After the first 12 experiments were run, it was felt that the experimental series had defined a new set of optimized levels for further study and the initial series was discontinued. Analyses of the solutions of interest in this study are given in Appendix 1.

The zirconium concentration in Experiment 7 was low with respect to the design level and to the concentration reached in the other high zirconium experiments. Samples from Experiment 7 gave anomalous, nonreproducible results for the tests run. The irregular behavior of this sample obscures the character of zirconium-containing solutions in the absence of AlSi.

Aqueous feed solutions for this experiment were prepared by dissolving 2S aluminum in nitric acid catalyzed with about 0.01M mercuric nitrate in a continuous dissolver. For the high AlSi runs, AlSi * was dissolved with the aluminum charge. The dissolver was operated to produce a 1.6M aluminum

* The 0.3% silicon from the AlSi added brought the total silicon concentration to 0.4 to 0.5% with respect to the aluminum.

TABLE 1
DESIGN OF THE PILOT PLANT EXPERIMENT

Set. No.	Exp. No.	DBP <u>M</u>	Acidity	Zr Conc. <u>M</u>	Added Si From AlSi* %
1	1	none added	0	1.32×10^{-3}	.3
	2	1×10^{-3}	0	1.32×10^{-3}	.3
	3	none added	1.5	1.32×10^{-3}	.3
	4	1×10^{-3}	1.5	1.32×10^{-3}	.3
2	5	none added	1.5	1.32×10^{-3}	0
	6	1×10^{-3}	1.5	1.32×10^{-3}	0
	7	none added	0	1.32×10^{-3}	0
	8	1×10^{-3}	0	1.32×10^{-3}	0
3	9	1×10^{-3}	0	0	.3
	10	none added	0	0	.3
	11	1×10^{-3}	1.5	0	.3
	12	none added	1.5	0	.3
4	13	1×10^{-3}	1.5	0	0
	14	none added	1.5	0	0
	15	1×10^{-3}	0	0	0
	16	none added	0	0	0

* Si above that present in 2S Al.

nitrate solution in either 0 or 1.5M hydrogen ion depending on acid design level. The dissolver solution was collected in a feed adjustment tank and analyzed for aluminum and acid and secondary dissolutions were run when necessary to correct feed concentrations. Uranium as uranyl nitrate was added to give 2 to 5 grams of uranium per liter. For the high zirconium runs, zirconyl nitrate was added to this feed to make it 1.3×10^{-3} M. Dibutyl phosphate (obtained from Victor Chemical Company and determined to be 96.8 ± 0.3 percent dibutyl phosphate by titration) was added to this aqueous feed to make it 1×10^{-3} M. The change in aluminum

scrub concentration from 0.75 to 1.5M was assumed to have a negligible effect on the extraction column surfactants and was not considered here.

Interface solutions were removed from the extraction column after each 20-hour run for examination in this surfactant study.

IV. EXPERIMENTAL TECHNIQUES

The detection and identification of surfactants is complicated by the fact that trace amounts of these materials can lead to the undesirable effects noted in column operations. In the absence of a direct method for determination of surface active material, the coalescence time of a freshly prepared 3.25 percent solution of tributyl phosphate in Amsco, dispersed in the aqueous interface sample solution was used to detect any surfactant present. The surfactant composition was deduced from the solution composition in which it was found.

A. Sampling

When the interface solutions were removed from the columns, a one to three liter sample of both phases was taken for examination. The bottoms of these bottles were soon covered with a rather dense, dark solid which settled out of solution. A magnetic stirring bar was placed in each bottle and the solution was stirred to resuspend these solids and assure homogeneity of the sample. One hundred milliliters of aqueous phase was pipetted from just below the interface and transferred to a secondary container. Samples for testing were subsequently withdrawn from these small bottles after vigorous shaking.

B. Centrifugation

Suspended solids were separated from the solutions by centrifugation. Surface activity associated with these solids was determined by resuspending them in one-half volume of fresh aluminum nitrate-nitric acid solution similar to the original sample and measuring the coalescence time of the resulting suspension.

C. Acid Addition

The effect of acid on these solutions was determined by adding concentrated nitric acid in one-half milliliter increments to a twelve milliliter sample and measuring the coalescence time after each addition.

D. Dilution

Selected samples were diluted with aluminum nitrate-nitric acid solutions which approximated the aluminum and acid concentrations of the sample solutions and the coalescence times measured.

E. Analytical Techniques

Solids separated from the interface materials by centrifugation were analyzed by emission spectroscopy.

Soluble silica was determined colorimetrically by the molybdate method. This method does not measure elemental silicon or colloidal or polymerized silica and therefore represents only a small amount of the silicic material which could be contributing to the surface activity in the system.

The coalescence time measurement which was used as a measure of the tendency of a solution to form a stable emulsion was made in the single stage pulsed contactor as described in the literature⁽¹⁾.

V. OBSERVATIONS AND DISCUSSIONS

A. Soluble Silica-Acid Dependency

The soluble silica concentration as determined by the molybdate colorimetric method is a function of the acid concentration of the solution as shown in Figure 1. Soluble silica concentration in parts per million is plotted against hydrogen ion concentration.

Silicon is a common impurity in 2S aluminum and may exist there either as elemental silicon or as silica. The AlSi contains large amounts of elemental silicon and possibly some silica. Another possible source of silica in the system is a slow dissolution of the finely divided elemental silicon by the nitric acid present.

Hydrated soluble silica is not the surfactant causing the emulsion problems but the soluble silica polymerizes in acid solution to form one or more surfactant species. D. W. Rhodes⁽²⁾ and E. M. Whitener⁽²⁾ have observed the delayed appearance of surface activity in acid solutions to which soluble silica had been added.

-
- (1) Hill, O. F., Classified Report HW-26104 (1952).
Hill, O. F., Classified Report HW-26937 (1953).
Brite, D. W., Rev., The Determination of Dibutylphosphate, HW-30643
October 15, 1954.
- (2) Rhodes, D. W., This laboratory, Private Communication.
Whitener, E. M., This laboratory, Private Communication.

FIGURE I
SILICA SOLUBILITY IN NITRIC ACID

CPP-S-1160

B. Acid Dependency of Surface Active Materials

A plot of coalescence time of fresh organic dispersed in the interface samples versus hydrogen ion concentration (Figure 2) indicates two types of surface active materials. The first group which contains surfactants produced in zirconium-containing solutions shows a loss of activity with increasing hydrogen ion concentration. The surfactants in this group may include zirconyl dibutyl phosphate, colloidal hydrated zirconia or a mixed polymer of the latter with silica. Zirconium is well known for its tendency to form polymers in low acid systems. This leads to consideration of one or more polymeric zirconium surfactants whose formation is inhibited by high acid concentrations. The second group, derived from zirconium-free high AlSi feed materials, shows an increase in surface activity with increasing hydrogen ion concentration. This could be attributed to dehydration of soluble silica with the formation of a polymeric or colloidal silica which is surface active.

The effect of higher hydrogen ion concentrations on these surface active materials was determined by the incremental addition of concentrated nitric acid. The coalescence time was determined after each acid addition. Solutions having short initial coalescence times were unchanged by these acid additions. Solutions with long initial coalescence times showed a sharp decrease in coalescence time when a critical hydrogen ion concentration was reached. Table 2 gives the acid concentrations and coalescence times of these solutions before and after acid additions and the assumed surfactant components present in the system. The solutions containing zirconium and dibutyl phosphate did not improve until 3M acid had been added. This improvement could be either due to a gross change in environment which does not destroy the molecule involved but only its association with the organic phase or a reaction which slowly degrades the molecule to one or more innocuous species.

C. Surfactant State

Selected samples were centrifuged and also allowed to settle for at least two weeks and coalescence times associated with the supernatant liquids were measured. The solids were resuspended in aluminum nitrate-nitric acid solutions similar to the originals and tested for surface activity. Table 3 shows the compositions and coalescence times for these solutions. A zirconium-modified silicic surfactant which is removed from the solution on settling or centrifuging appears to be present in Sample 1. A comparison of Samples 1 and 10 reveals a zirconium dependency on the formation of the silicic surfactant in a low acid dissolver solution.

Dibutyl phosphate produces a soluble surfactant in the presence of either the silicic or zirconium compounds produced in these solutions. The surface activity associated with these substances is shown in the results of the tests on the supernates from Samples 8 and 9. The separated solids show no surface activity when resuspended in fresh solutions.

Samples containing aluminum dibutyl phosphate alone were not available for testing for surface activity.

FIGURE 2
 SURFACTANTS IN ACID SOLUTIONS

TABLE 2

SURFACTANT SENSITIVITY TO ADDED ACID

Aliquots of aqueous aluminum nitrate interface solution produced from systems having high levels of zirconium, AlSi, or dibutyl phosphate, as indicated, were titrated with acid and the coalescence times measured. The acidity associated with a marked reduction in surface activity is noted with an asterisk (*).

Sample No.	Constituents	Titration Data							
		H ⁺ (N)							
1	Zr, AlSi	Coalescence	0.30	.89	1.46*	2.42	3.26	4.03	4.70
		Time (sec)	600	600	145	112	109	101	98
11	DBP, AlSi	H ⁺ (N)	1.68	2.22*	2.72				
		Coalescence							
		Time (sec)	600	2.19	229				
12	AlSi	H ⁺ (N)	1.36	1.91*	2.42				
		Coalescence							
		Time (sec)	600	234	146				
2	Zr, DBP, AlSi	H ⁺ (N)	0.23	.83	1.38	2.36	3.22*	3.98	4.65
		Coalescence							
		Time (sec)	600	600	600	600	240	149	105
8	Zr, DBP	H ⁺ (N)	0.02	.58	1.14	2.15	3.02*	3.79	4.47
		Coalescence							
		Time (sec)	600	600	600	600	188	132	131

TABLE 3
CHARACTERIZATION OF INTERFACE SURFACTANTS

Original solutions were 1.5M aluminum nitrate and 0M nitric acid from dissolution of aluminum metal.
 Those marked (*) were 1.5M aluminum nitrate reagent in water.

Samples		Zr milligrams/liter	Added Silicon From AlSi w/o of Fuel	Dibutyl phosphate moles/liter	Coalescence Time seconds	Surfactants
1	Original feed	194	0.3	None added	600	Surface active solids
	Supernate from settling	194	0.3	None added	184	
	Supernate from centrifuging	194	0.3	None added	171	
	Resuspended centrifuged solids*				600	
8	Original feed	110	0	10^{-3}	600	Soluble surface active material
	Supernate from settling	110	0	10^{-3}	600	
	Supernate from centrifuging	110	0	10^{-3}	600	
	Resuspended centrifuged solids*				100	
9	Original feed	0	0.3	10^{-3}	360	Soluble surface active material
	Supernate from settling	0	0.3	10^{-3}	600	
	Supernate from centrifuging	0	0.3	10^{-3}	600	
	Resuspended centrifuged solids*				125	
10	Original feed	0	0.3	None added	285	No significant surface active material
	Supernate from settling	0	0.3	None added	215	
	Supernate from centrifuging	0	0.3	None added	290	
	Resuspended centrifuged solids*				151	

D. Bulk Components Near Interface

Analysis of the aqueous phase near the interface in several random samples showed no apparent difference in zirconium, aluminum, and acid concentrations between feed and interface solutions.

Spectrochemical analysis of solids removed from Sample 1 by centrifugation revealed major amounts of silicon and zirconium with minor amounts of corrosion products associated with the pilot plant system.

VI. CONCLUSIONS

Examination of these solutions has shown the presence of several surfactant species in the nitric acid-aluminum nitrate system.

Soluble silica which is not surface active is present in low concentrations but is slowly converted to a surfactant species in these solutions. This surfactant character is not apparent in an acid concentration of about 0M but does show up at 1.5M. With zirconium present in the solution, the character of the surfactant changes markedly, ranging from pronounced surface activity at the low acid level to no effect at the 1.5M acid level. This effect is due to a particulate material which readily settles or centrifuges out of the solution.

Dibutyl phosphate-containing solutions show the presence of a soluble surfactant which is not removed by centrifugation. The soluble zirconium-dibutyl phosphate surfactant is formed in the low acid solutions while the dibutyl phosphate with or without silicic material becomes a problem in the 1.5M acid system. All the surfactants observed in these solutions were destroyed or reduced in effectiveness by the addition of approximately 1.0M nitric acid except those found in solutions containing both zirconium and dibutyl phosphate. In the latter case, no improvement in surface activity was noted until 3M nitric acid had been added. It would appear possible to attenuate the effect of any surfactant combination by feed clarification combined with adjustment of the solution acidity. Where analysis of the process solutions or flowsheet estimates suggests the presence of a particular surfactant, specific measures may be taken for treatment.

The values in the fourth column
are intended to read; 1.32×10^{-3}
 1.97×10^{-3}
etc

VII. APPENDIX 1

ANALYSIS OF SOLUTIONS *

<u>Run No.</u>	<u>H⁺ N^A</u>	<u>Al³⁺ M</u>	<u>ZrMX10⁻³</u>	<u>SiO₂ ppm</u>
1				
Designed	0		1.32	
Measured	0.29	2.06	1.97	42.14
	0.30		2.28	
2				
Designed	0		1.32	
Measured	0.24	2.19	1.34	43.26
	0.22		2.00	
3				
Designed	1.5		1.32	
Measured	1.53	2.06	1.61	9.03
	1.48		1.55	
4				
Designed	1.5		1.32	
Measured	1.68	1.68	1.16	12.94
			1.41	
5				
Designed	1.5		1.32	
Measured	1.50	1.96	1.69	
6				
Designed	1.5		1.32	
Measured	1.66	1.72	1.26	
	1.53		1.19	
7				
Designed	0		1.32	
Measured	0.15	1.97	.91	
8				
Designed	0		1.32	
Measured	0.3N ^B	1.92	1.25	
	0.1		1.17	
9				
Designed	0			
Measured	0.11N ^B	2.20		103.32
	0.11N ^B			

VII. APPENDIX 1 (Cont.)

<u>Run No.</u>	<u>H⁺ N^A</u>	<u>Al⁺³ M</u>	<u>ZrMX10⁻³</u>	<u>SiO₂ ppm</u>
10				
Designed	0	2.33		130.49
Measured	0.08N ^B 0.08N ^B			
11				
Designed	1.5			
Measured	1.68	1.41		16.47
12				
Designed	1.5			
Measured	1.36 1.3	1.65		12.95

- *. A postoperational clean-up of the pilot plant equipment revealed a deposit of aluminum dibutyl phosphate in the feed adjustment tank. No analytical method for dibutyl phosphate was available, so it was impossible to know the dibutyl phosphate concentration in any given run. References to dibutyl phosphate concentrations are, therefore, not considered in the evaluation of the data except in cases where there is an obvious effect due to its presence.