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USE OF SURFACE ACTIVE AGENTS

TO PREVENT EMULSIONS IN SLUREX EXTRACTIONS

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TO PREVENT EMULSIONS IN
SLUREX EXTRACTIONS.

Author: R. Piper and A. E. Ruehle

ABSTRACT

Preliminary investigations indicate that several surface active agents are effective in preventing the formation of emulsions in the extraction of uranium from pitchblende slurry with TBP diluted with kerosene or with CCl_4 . About 50 surface active agents have been tested with both diluents in cylinder shakeouts and those found effective run in a Scheibel column. The use of surface active agents has given satisfactory operation in Scheibel column runs both with kerosene and with CCl_4 under conditions which would otherwise produce emulsions.

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INTRODUCTION

In the slurex process for extraction of uranium using TBP, the use of slurry feeds increases the difficulties with emulsion formation so that the physical operability of the extraction column is a major problem in the conventional operation using kerosene as a diluent, and even more of a problem when CCl_4 is substituted as a diluent to avoid flammability hazards. A possible means of attacking this problem was suggested by work done by Lewis, Klopper, and Ruehle⁽¹⁾ of this laboratory who found that certain surface active agents were very effective in preventing the formation of emulsions in the ether extraction of uranium from otherwise emulsifiable feeds.

In this study, slurex extractions using both kerosene and CCl_4 as diluents were investigated from the standpoint of physical operability and the effect of surface active agents. The work was of a preliminary nature and only a brief survey of some of the large variety of surface active agents available was made. Although more work would be required to establish the exact conditions needed and to determine the effect of the surface active agent on product purity, the results reported here indicate that several of the surface active agents tested can produce a considerable reduction in the amount of emulsification.

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EXPERIMENTAL

A. TBP-Kerosene System

With no surface active agent present, cylinder shakeouts of different concentrations of TBP in Shell Dispersol with current production lots of pitchblende slurry made 3N in HNO_3 gave in every case "fish egg" oil-in-water emulsions which broke rather slowly. The addition of a surface active agent generally either prevented these emulsions or formed a much worse emulsion. Frequently, a surface active agent would give excellent separation when first added to the slurry and shaken, but when shaken again several minutes later would give a very heavy emulsion. This is probably due to the decomposition of the surface active agent by the nitric acid.

In order to test the effectiveness of several surface active agents systematically, the following procedure was adopted: (1) The desired amount of surface active agent was measured into a 100 ml. shaking cylinder, (2) two ml. of water added to dissolve the surface active agent, (3) eighteen ml. of pitchblende digest slurry, containing 260 g/l uranium and 3N excess HNO_3 , added and shaken, (4) forty ml. of 30% TBP in Dispersol added and shaken for 10 seconds, (5) the volume of the aqueous phase, plus emulsion, read 2 minutes after shaking, (6) the shaking procedure repeated, on those that did not emulsify, every 5 minutes for at least 30 minutes.

The results of testing 48 surface active agents obtained as manufacturer's samples, according to this procedure are summarized in Table I. The numbers in the "vol. of aq. phase" column refer to the volume including emulsion so that 20 indicates complete separation and 60 indicates complete emulsification.

The six surface active agents found most effective and stable were further tested by a similar procedure except after each shaking the organic layer was removed and fresh organic added. Nytron, Hercules B-29, Nonis 218, Ethomeer P-20, and Triton X100 (all at the concentration of 1%) remained effective through 5 such shakeouts. The same 5 remained effective for at least 24 hours at room temperature in the 3N HNO_3 slurry, but when warmed only Nytron remained effective above 50° C.

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TABLE I

Effect of Surface Active Agents on Cylinder Shakeouts with Dispersol

Name	Manufacturer	Composition	Surface Active Agent 1% of Slurry Vol.		Surface Active Agent 0.2% of Slurry Vol.	
			Vol. of Aq. Phase (ml)	Time Effective (min.)	Vol. of Aq. Phase (ml)	Time Effective (min.)
(Blank with no surface active agent)			40			
Santomerse D	Monsanto	Alkyl Amyl Sulfonate	26	15	20	5
Nacconal NR	Nat. Analine	Alkyl Amyl Sulfonate	20	25	21	5
Antaron L-135	Antara Chem.	Alkyl Amide Sulfonate	20	30	20	5
Aerosol OT	Amer. Cyanamid	Dioctyl Na Sulfosuccinate	20	15	20	10
Aerosol MA	" "	Dihexyl Na Sulfosuccinate	60	0		
Aerosol AY	" "	Diamyl Na Sulfosuccinate	60	0	60	0
Aerosol TB	" "	Di-isobutyl Na Sulfosuccinate	60	0	60	0
Aerosol 18	" "	Octadecyl " "	20	15	20	10
Aerosol C-61	" "	(Cationic)	40	10	60	0
Wetsit Single	Jacques Wolf		20	20	60	0
Parnol J	" "	(Anionic)	20	10	23	5
Glucaterge 28	Com'l Solv.	(Non-ionic)	50	5	60	0
Synthetic B-79	Hercules	Phenol polyethylene glycol	20	>24 hrs.	21	10
Nytron	Solvay	Organic Na Sulfonate	21	>24 hrs.	22	15
Tergitol 7	Carbide & Carbon	Na Decyl Sulfonate	20	10	21	5
Tergitol 08	" "	Na Octyl "	60	0	60	0
Tergitol EH	" "	Na Ethyl Hexene Sulfonate	60	0	60	0
Tergitol NPX	" "	(Non-ionic)	20	>60	20	10
Tret-o-lite L16445	Tret-o-lite Co.		60	0	60	0
Myrj	Atlas Powder	Polyoxyethylene Stearate	60	0	60	0
Hypodyne 1	Ferro Chem. Co.	(Anionic)	60	0	60	0
Hypodyne 2	" "	" "	60	0	25	5
Hypodyne 3	" "	" "	60	0	60	0
Hypodyne 4	" "	" "	22	5	60	0
Hypodyne 5	" "	" "	60	0	60	0

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TABLE I (Cont'd.)

Name	Manufacturer	Composition	Surface Active Agent 1% of Slurry Vol.		Surface Active Agent 0.2% of Slurry Vol.	
			Vol. of Aq. Phase (ml)	Time Effective (min.)	Vol. of Aq. Phase (ml)	Time Effective (min.)
Triton NE	Rohm & Haas	Polyether Alcohol	24	5	20	5
Triton X100	" "	" "	22	15	60	0
Triton X200	" "	" Sulfonate	20	10	30	5
Nonic 218	Sharples	(Non-ionic)	22	>24 hrs.	20	>30
Petrowet R	duPont	(Anionic)	20	5	60	0
Monsanto AE-1	Monsanto		23	10	20	15
Ethomeen 18/60	Armour	Polyoxyethylene Amine	60	0	25	5
Ethomeen T/20	"	" "	22	>24 hrs.	60	0
Ethomeen 18/20	"	" "	22	10	60	0
Ethomeen T/60	"	" "	22	5	60	0
Ethomeen C/20	"	" "	23	5	40	5
Ethomeen S/20	"	" "	22	10	60	0
Ethomeen S/60	"	" "	21	5	60	0
Ethomeen T/60	"	" "	23	5	60	0
Ethomid HT/60	"	" Amide	23	5	60	0
Ethomid RO/15	"	" "	20	5	60	0
Ethofat 60/60	"	" Fatty Acid	22	5	60	0
Ethofat 242/60	"	" "	24	5	60	0
Ethofat 60/20	"	" "	25	10	40	5
Oronite D-60	Oronite Chem.	Organic Na Sulfonate	20	10		
Oronite D-40	" "	" "	20	5		
Oronite S	" "	" "	20	5		
Brig 35	Atlas Powder	(Non-ionic)	24	10	24	10

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An eleven mechanical stage Scheibel column was used to test the performance of the surface active agents in column operation. Although satisfactory operation was achieved using filtered pitchblende feed, attempts to use a slurry feed produced very heavy emulsions both with and without surface active agents. A major cause for this failure seemed to be the tendency for the slurry to build up on the packing sections until it could be whipped up by the stirrer just above it. Whenever this happened an emulsion formed which gradually built up until it filled the column. In order to avoid this the Scheibel packing was replaced by sections made from pieces of stainless steel screen about 3" x 6" folded into 5 or 6 accordin folds and bent around the shaft to fit into the column. This modification gave much more satisfactory operation with slurry feeds. With it a pitchblende slurry with no surface active agent was run at stirrer speeds up to 550 RPM, but the higher speeds needed for good extraction gave heavy emulsions.

Using the modified column the surface active agents that looked good in cylinder shakeouts were tested in column runs. Flow rates were 30 ml/min. for the slurry and 50-60 ml/min. for the organic. Triton X100, Ethomeen T/20, and Hercules B-29 gave considerable emulsification even at stirrer speeds below 600 RPM. Nytron prevented emulsification at speeds up to 900 RPM, but at speeds above 600 RPM the organic was very cloudy and carried over a considerable amount of solids. Nonic 218 gave clean separation and fairly clear organic at stirrer speeds up to 700 RPM and in this respect looked the most promising of those tested.

The above runs were all made with the organic phase continuous. An attempt to run the column with the aqueous phase contin. as gave a very heavy emulsion even at very slow stirrer speeds.

B. TBP-CCl₄ System

Preliminary cylinder shakeouts using 15%, 30%, and 50% TBP in CCl₄ gave quite stable emulsions and very poor phase separation. Even when shaken very gently to avoid forming an emulsion, separation was achieved very slowly with part of the slurry settling to the bottom and part going to the top. An examination of density values, determined with a float hydrometer, listed in Table II show the cause for the poor separation.

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TABLE II
Densities in the TBP-CCl₄ System

<u>Material</u>	<u>Density</u>
Pitchblende Slurry (3N in HNO ₃)	1.65
15% TBP-CCl ₄	1.48
30% TBP-CCl ₄	1.40
50% TBP-CCl ₄	1.29
15% TBP-CCl ₄ saturated with U	1.55
Raffinate of pitchblende slurry	1.47

These values indicate that as the uranium passes from the aqueous to the organic, an inversion from aqueous phase heavy to organic phase heavy will occur. This would make a continuous extraction impossible.

One way to avoid this difficulty is to dilute the slurry until its density is less than that of the organic. A 50% dilution was found necessary to bring the density of a digest slurry containing 255 g/l uranium down to 1.47. This diluted slurry gave good phase separation with 15% TBP in CCl₄ and in all subsequent testing slurry diluted to a density of 1.47 and 15% TBP-CCl₄ was used.

A testing program of surface active agents similar to that used for the TBP-kerosene system using the diluted slurry (3N in HNO₃) and 15% TBP in CCl₄ was carried out and the results are listed in Table III.

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TABLE III

Cylinder Shakeouts with CCl₄ Solvent and Surface Active Agent 1% of Slurry Volume

Name	Manufacturer	Composition	Vol. of Phase (ml)	Time Effective (min.)
(Blank with no wetting agent)			60	
Myrj	Atlas Powder	Polyoxyethylene Stearate	60	0
Hypodyne 1	Feno Chem.	(Anionic)	21	15
Hypodyne 2	" "	"	18	15
Hypodyne 3	" "	"	21	10
Hypodyne 4	" "	"	24	10
Hypodyne 5	" "	"	22	10
Triton NE	Rohm & Haas	Polyether Alcohol	19	15
Triton X100	" "	" "	27	10
Triton X200	" "	" Sulfonate	21	10
Nonic 218	Sharples Chem		60	0
Petrowet R	duPont	Na Alkyl Sulfonate	20	10
Monsanto AE-1	Monsanto		20	15
Brij 35	Atlas Powder		60	0
Oronite D-40	Oronite Chem.	Na Sulfonate	20	>30
Oronite D-60	Oronite Chem.	" "	20	>30
Oronite S	Oronite Chem.	" "	20	5
Santomerse D	Monsanto	Alkyl Amyl Sulfonate	21	5
Nacconol NR	Nat. Analine	" " "	22	10
Antaron L-135	Antara Chem.	Alkyl Amide Sulfonate	22	5
Aerosol OT	American Cyanamid	Dioctyl Na Sulfosuccinate	20	10
Aerosol MA	" "	Dihexyl Na Sulfosuccinate	20	30
Aerosol AY	" "	Diamyl Na Sulfosuccinate	20	5
Aerosol IB	" "	Di-isobutyl Na Sulfosuccinate	60	0
Aerosol 18	" "	Octodecyl Na Sulfosuccinate	30	10
Aerosol C-61	" "	(Cationic)	60	0
Wetsit Single	Jacques Wolf		23	5
Parnol 5	Jacques Wolf	Dodecyl Benzene Na Sulfonate	20	5
Glucaterge 28	Com'l Solv.	(Non-ionic)	60	0
Synthetic B-29	Hercules	Phenol Polyethylene Glycol	60	0
Nytron	Solvay	Organic Na Sulfonate	22	>1 hr.

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TABLE III (Cont'd)

Name	Manufacturer	Composition	Vol. of Phase (ml)	Time Effective (min.)
Tergitol 7	Carbide & Carbon	Na Decyl Sulfonate	20	10
Tergitol 08	" "	Na Octyl Sulfonate	60	0
Tergitol EH	" "	Na Ethylhex Sulfonate	60	0
Tergitol NPX	" "	Polyglycol ethers	21	5
Tergitol P-28	" "	Na Dioctyl Phosphate	20	10
Tret-o-lite L16445	Tret-o-lite Co.		20	10
Ethomeen T/20	Armour	Polyoxyethylene Amine	25	>30
Ethomeen 18/60	" "	" "	60	0
Ethomeen C/20	" "	" "	60	0
Ethomeen 18/20	" "	" "	30	>30
Ethomeen S/60	" "	" "	60	0
Ethomeen S/20	" "	" "	30	10
Ethomeen T/60	" "	" "	60	0
Ethofat 242/60	" "	" Fatty Acid	20	15
Ethofat 60/60	" "	" "	25	>60
Ethofat 142/25	" "	" "	38	5
Ethofat C/20	" "	" "	20	>30
Ethofat 60/20	" "	" "	21	>30
Ethofat 242/20	" "	" "	25	5
Ethomid HT/60	" "	Polyethoxy Amide	60	0
Ethomid C/20	" "	" "	45	30
Ethomid RO/15	" "	" "	30	15
Ancowet N	Arnold-Hoffman		20	>60
Ancowet RS	" "		20	>60
Ancowet LR	" "		20	>60
Antaron R-158	Antara Chem.		20	>45
Antaron S-370	" "	Sulfated Fatty Amides	20	>45
Antarsene U-490	" "	Alkyl Carboxylate	25	5
Antaron A-402	" "	Polyoxy Ether Glycol	25	10

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TABLE III (Cont'd)

<u>Name</u>	<u>Manufacturer</u>	<u>Composition</u>	<u>Vol. of Phase (ml)</u>	<u>Time Effective (min.)</u>
Antaron L-121	Antara Chem.	Alkyl Amide Sulfonate	20	10
Antaron K-430	" "	Polyethoxy Sulfonate	22	5
Antarox A-400	" "	Polyoxyethylene Glycol	38	5
Antarox A-403	" "	" "	20	5
Antarox A-200	" "	Alkyl Phenoxy Polyethoxy Ethanol	30	5
Antarox A-404	" "	Polyoxyethylene Glycol	60	0
Antarox A-401	" "	" "	20	5
Nullapon BFC	" "	" "	20	10
Nullafoam S	" "	" "	20	5
Glyceryl Riccinolate	Kessler Chem.	" "	24	5
Loamar PW	Jacques Wolf Co.	" "	60	0

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The Scheibel column, modified as described above for use with slurries, was used to test the more promising appearing surface active agents. Diluted pitchblende slurry and 15% TBP in CCl_4 were used and the column was operated with the organic phase continuous, but "upside down" - with the slurry going in the bottom and the raffinate out the top. Flow rates were, unless otherwise noted, 20 ml/min. for the slurry and 50 ml/min. for the organic.

It was found virtually impossible to operate the column with no wetting agent present since stirrer speeds sufficient to keep the slurry from just running along the wall of the column produced very thick emulsion. With effective surface active agents present, it was found necessary to introduce the slurry above the bottom stirrer to prevent some of the heavier solids from settling to the bottom, but when this was done no difficulty was experienced with heavy solids going down with the organic.

With 1% Nytron satisfactory operation was achieved at a stirrer speed of 500 RPM, but the organic was somewhat cloudy and there was a little entrainment of organic in the raffinate. At 700 RPM the column filled with emulsion. In order to remove the cloudiness from the organic, a column was arranged so that the bottom three stages could be used for a scrub. Undiluted slurry was used and the necessary dilution was made up with scrub water, which was made 3N in HNO_3 , and contained 1% Nytron. The scrub did not help much in clarifying the organic and there was some emulsification at the top scrub stage.

A similar scrub arrangement was used with 1% Ethomeen T/20, but at a stirrer speed of 500 RPM. Considerable emulsion was carried over with the organic in the form of flocculent clumps. A run with Ethomid 60/60 gave similar results except that in addition considerable organic was entrained in the raffinate.

Oronite D-60, Antaron S-370, and Ahcowet LR all gave good results in column runs. Stirrer speeds of 600-700 RPM were used with no emulsification. However, in every case the organic was slightly cloudy. Full column scrubs at organic 50 ml/min. to water 5 ml/min. somewhat reduced the cloudiness, but did not completely remove it. The cloudiness remained in the organic even after stripping and did not seem to increase on recycling the cloudy organic so it might not be harmful.

A sample of the raffinate from the run with Ahcowet LR was analyzed giving 0.06 g/l soluble and 0.02 g/l insoluble uranium indicating that satisfactory extraction was obtained under the conditions used.

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DISCUSSION

The data shown in Tables I and III showed no apparent correlation between composition of surface active agent and effectiveness. The actual effectiveness of the surface active agent is, in this system, overshadowed by the importance of its stability to nitric acid as indicated by the large number that were effective at the start but which failed on standing. This, together with the lack of information on the composition and properties of many of the surface active agents makes any theoretical interpretation very difficult.

It seems likely that the 1% concentration of surface active agent used in this preliminary work could be considerably reduced by proper control of conditions and selection of surface active agent. Use of a lower nitric acid concentration probably would permit a considerable reduction in necessary concentration.

Very little difference in effectiveness of the surface active agents for different lots of current production pitchblende slurry was noticed, indicating that minor changes in feed would not be an important factor. More work along this line is needed to establish the conditions under which a given surface active agent would be of optimum effectiveness.

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REFERENCES

- (1) Lewis, G. W., Jr., Kloepper, H. C., and Ruehle, A. E. - Unpublished Data.

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