THE DETERMINATION OF EXCESSIVE EMULSIFICATION
BY COALESCENCE BEHAVIOR MEASUREMENTS

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Contract AT(10-1)-205

IDAHO OPERATIONS OFFICE
U. S. Atomic Energy Commission

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A B S T R A C T

The development of a remotely operated device for determining the coalescence times of plant process streams suspected of containing surfactants such as silicic compounds and fission product zirconium compounds is described.

A general correlation between the coalescence times of pilot plant extraction column aluminum nitrate feeds and 3.25 percent tributyl phosphate extractant streams and the observations of column behavior of these streams is demonstrated.

The application of the coalescence test to plant streams is given.

Work done under Contract AT(10-1)-205 to the U.S. Atomic Energy Commission.

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I. SUMMARY

As an aid to the successful processing of aluminum-uranium reactor fuels containing surfactant-producing materials, it has been desirable to determine the emulsifying trends of the feed streams prior to their entry into the extraction cycle with a laboratory measurement of their coalescence behavior. The coalescence behavior of these streams was determined by measuring their coalescing time and observing the appearance of the emulsions formed by the surfactant-containing feeds and solvents. For this purpose a remotely operated emulsion stability indicator was installed in the plant analytical facilities.

A correlation was developed between extraction column operability in the presence of surfactants and the coalescence behavior by the comparison of observations of the degree of emulsification experienced in 97 pilot plant solvent extraction experiments with a variety of feed compositions and the corresponding laboratory coalescence behavior of the end streams. In these cold tests, it was shown that extraction systems with equilibrium coalescence times of greater than 600 seconds were inoperable at volume velocities of 500 gal/hr ft², that systems with coalescence times between 100 and 300 seconds were operable and systems with coalescence times in the interval of 300 to 600 seconds were infrequently observed and thus not readily correlatable.

Although determinations on plant samples were frequently confused by the appearance of a residual stable film (termed "spider web") after true coalescence, general trends of extraction column operability were observed with the measurements. It was concluded that these coalescence time measurements of plant streams could be a valuable aid in predicting plant extraction column behavior with surfactant-containing feeds.

II. INTRODUCTION

The highly surface-active feeds that are produced in the chemical reprocessing of silicon-containing aluminum-uranium fuels have led to extraction column operating problems.

Plant column end stream analysis and column control instrumentation records have indicated varying degrees of flooding culminating in forced processing rate reduction below extraction column volume velocities of 300 gal/hr ft² to regain column stability. The accumulation of excessive interfacial crud was inferred but could not be observed.

These erratic operations have indicated the presence of surface-active materials in the plant streams, such as silicic compounds or fission product zirconium compounds⁽¹⁾. However, the inability to isolate and analyze the responsible surfactant has necessitated the development of an analytical tool by which a quantitative measurement of the excessive emulsive tendencies of the plant streams could be determined.

It was found that by correlating the laboratory determined coalescence behavior of pilot plant streams with their actual column performance, the emulsifying trends of these streams could be determined prior to their entry into the extraction cycle. The coalescence behaviors of these pilot plant streams were determined by a laboratory test that was originally developed at Hanford⁽²⁾. These coalescence behavior determinations consisted of, (1) the coalescence time, or the time required for a liquid-liquid system, that has been dispersed for a given length of time, to disengage; (2) the observations that were made concerning the physical characteristics of the emulsion and, (3) the properties of any residual formation.

Utilizing the relationship between laboratory determined coalescence behavior and extraction column behavior, a study was made to establish the emulsifying trends of plant extraction column feeds to evaluate preventative measures, such as gelatin treatment⁽³⁾ or acid addition⁽¹⁾.

III. EQUIPMENT DESCRIPTION

A. Laboratory Emulsification Test

The coalescence behavior of the process streams was observed by a standard test with an emulsion stability indicator. This instrument was adapted from the laboratory single-stage pulsed contactor developed at Hanford⁽²⁾ which utilized the vibrational disengaging test to measure dispersion and coalescence times of a liquid-liquid system. This test was originally made with an instrument consisting of a wire screen which, when moved in rapid oscillation across the liquid-liquid interface, produced a dispersion which is aqueous continuous if the screen were preferentially aqueous-wetted or organic continuous if the screen were preferentially organic-wetted. A miniature pulse column is created by replacing the screen with four small perforated plates, having holes 0.47 inches in diameter and attached concentrically to a 0.0625 inch stainless steel rod, spaced 0.25 inches apart. A 25 milliliter graduated cylinder is used as the mixing vessel. With this apparatus, (See Figure 1) it is possible to measure with a 5 percent reproducibility the time required for a complete dispersion, the coalescence time, and to determine the effect of aging, temperature, and impurities on these quantities.

The dispersion time is defined as the time required for a dispersion to form from the interface to the dispersion level, the 23 milliliter mark on the graduated cylinder. The characteristics of the normal dispersion are shown in Figure 2. The coalescence time is defined as the time required for

NRTS 59-4046

FIGURE 1 - EMULSION STABILITY INDICATOR This instrument was adapted from the laboratory single stage pulsed contactor.

Dispersion level
23 ml

Coalescence level
15 ml

FIGURE 2 - NORMAL DISPERSION This sample was dispersed in 20 seconds. Dispersion time is time required to form an emulsion from the interface to the dispersion level. (NRTS 59-4142)

a dispersion that has been formed by mixing for 30 seconds, to disengage from the top of the liquid, 25 milliliter mark, to the disengaging level, the 15 milliliter mark. The characteristics of the normal coalescence are shown in Figure 3.

B. Remote Apparatus for Plant Feed Testing

A remote emulsion stability indicator was developed to measure the dispersion times and coalescence times of highly radioactive streams prior to their entry into the columns in order to predict the tendencies of these plant streams to form stable emulsions in time to take preventative measures necessary to insure the proper operation of the column.

The remote apparatus is shown in Figure 4. Basically the remote instrument is the same as the laboratory model with the following exceptions: In order to handle the conical shaped sample bottles used in plant sampling, an adaptation was needed to transfer the feeds and extractants from the sample bottles to the mixing vessel. A standard needle system was employed with one line running to the graduated mixing vessel and another line going to the externally operated syringe via a trap. The air pressure provided by the syringe was used to push the liquid to the mixing vessel. A platform was supplied to raise and lower the sample bottles onto the needles. This platform system is operated by a double action pneumatic cylinder. Less than one milliliter is left in the sample bottles. In order to keep the necessary manipulation to a minimum, a wash system was utilized consisting of nitric acid, water, and acetone, in that order. In this way only one graduated cylinder is used and this is equipped with a drainage outlet that is valved by means of a pneumatically-operated pinchclasp. Separate syringes used for the aqueous feed and for the extraction to prevent cross contamination. The oscillation is provided in the same manner as the laboratory equipment except the stop positioning is obtained by an air operated cylinder.

IV. RESULTS

A. Correlation of Coalescence Behavior to Pilot Plant Column Observations

In order to determine the effect of existing surfactants upon the extraction process, it was necessary to observe the columns during operation. Therefore, a series of experiments was designed to simulate plant conditions. These pilot plant experiments⁽⁴⁾ utilized the continuous dissolution of natural uranium fuels to provide plant-like process streams. A head-end evaporation step was included in order to simulate full-scale blending of scrub effluent and dissolver effluent. Three glass columns, two inches in diameter, made up the extraction cycle which consisted of extraction, scrub, and strip columns. Two mixer-settlers were provided for extraction solvent clean up.

Top of liquid
25 ml

Organic phase

Interface

Aqueous phase
11 ml

Dispersion level
23 ml

Coalescence level
15 ml

NRTS 59-4045

FIGURE 3 - NORMAL COALESCENCE This sample was dispersed for 30 seconds. The coalescence time was 100 seconds. This is the time required for the emulsion to disengage from the top of the liquid to the coalescence level, 15 milliliter mark.

NRTS 59-3998

FIGURE 4 - THE REMOTE EMULSION STABILITY INDICATOR

The dispersion and coalescence times of samples of the feeds and extractants were measured periodically with the emulsion stability indicator (See Figure 1) and the corresponding behavior of the system was observed in the pilot plant glass columns. The dispersion times appeared to be insensitive to the observed emulsifying trends of the column and were ignored; however, a definite relationship was experienced using the coalescence times. Only the extraction column exhibited problems associated with excessive emulsification. The other two columns were normal except when disturbed as a result of the malfunction of the extraction column.

In Table 1, the pilot plant column observations were correlated with the coalescence times of eight consecutive samples. For the purpose of interpretation, the pilot plant extraction column operation was considered bad if the column flooded at a volume velocity of 500 gal/hr ft²; if there were greater than six inches of stable, heavy emulsion gathered at the interface; and also if there were little or no organic coalescing in the column. The coalescence times were considered bad if they were greater than 600 seconds.

TABLE 1
THE CORRELATION OF DISPERSION-COALESCENCE MEASUREMENTS
TO PILOT PLANT COLUMN OBSERVATIONS **

This list consists of the first 8 of 97 determinations

<u>Sample Number</u>	<u>Equilibrium Coalescence</u>	<u>Pilot Plant Column Observations</u>
	<u>Times (Seconds)</u>	
Standard	100	
1	160	Column Good
2	166	Column Good
3	>600	Very Little Organic Coalescing
4	>600	Emulsion Building Up
5	>600	Column Flooded
6	>600-200*	Large Amounts of Heavy Emulsion
7	300-175*	Heavy Emulsion
8	130	Column Good

* This is the spider-web effect as detected by the laboratory test. The main body of the emulsion disengaged in around 200 seconds. However, a spider-web-type film was left behind and remained stable for greater than 600 seconds. (See Figure 5)

** The complete table appears in Appendix 1.

FIGURE 5 - SPIDER-WEB EFFECT This sample was dispersed for 30 seconds and then allowed to coalesce. The main body of the dispersion disengaged in 200 seconds leaving a stable spider-web type film.

The samples of the feeds and extractants that were taken during the normal operation of the pilot plant columns (Samples 1, 2, and 8) gave coalescence times of about 150 seconds. A coalescence time of about 150 seconds was considered normal when compared to the 100-second coalescence time experienced with a standard feed which contained no surface active materials. The appearance of a test solution during normal coalescence can be seen in Figure 3.

With samples 3, 4, and 5, the column was observed to have very little organic coalescing and as a result, emulsion began to build up causing the column to flood. The coalescence times of samples taken during this column observation were greater than 600 seconds. With sample number 6, large amounts of heavy emulsion appeared at the interface. The laboratory test concurred with these observed characteristics in that the main body of the dispersion disengaged in around 200 seconds; however, a film was left behind and remained stable for greater than 600 seconds. This film can best be described as being similar to a spider web in appearance. The spider web forms as the dispersed phases begin to separate by the breaking of small bubbles (See Figure 2) forming stable larger ones which often continue to grow in this manner until they have attained the diameter of the cylinder. In contrast, normal coalescence is characterized by the clean separation of the two phases (See Figure 3). These films of linked large bubbles attach themselves tenaciously to the opposite walls of the mixing cylinder, sometimes making horizontal films. In this manner they appear to filter or adsorb the particulate solids from the falling aqueous phase. In Figure 5, this formation can be followed and the individual stages noted. At the upper levels of the organic phase, around the 23 milliliter mark, the effect appears as a single film stretching horizontally from the cylinder walls. At the lower ends of the organic phase, around the 15 milliliter mark, the effect is still in the smaller bubble stage. The spider web is easily broken with any physical contact, such as the addition of aqueous solution or manipulation of the mixing plunger. The actual identification of this laboratory observed characteristic with the presence of heavy emulsion in the column was not conclusive since heavy emulsion aggregation also produced samples having extremely long coalescence times, greater than 600 seconds. Other samples indicated that this spider web effect might be characteristic of borderline cases and the interpretation as to good or bad column operation was difficult and not conclusive.

The coalescence behavior and the observed emulsifying trends were compared in 97 samples of pilot plant column feeds and extractants and these comparisons are tabulated in Appendix 1. The test concurred with the pilot plant column observations in all but nine of the 97 trials. In all but one of the nine disagreements the test predicted excessive emulsification behavior while the column operation was observed to be good.

These data showed that the measurement of coalescence time of column end streams can be utilized to predict major changes in emulsification. However, the sensitivity of the test is such that the interpretation and evaluation of borderline cases, such as those possessing spider web effects, would be difficult and subject to error.

B. Coalescence Measurements of Plant Streams

The remote emulsion indicator was employed to measure the coalescence times of plant process streams to determine the emulsifying tendencies of these feeds prior to their entry into the extraction process. In order to obtain a standard, measurements were made with samples taken during the normal operation of the plant which produced feeds from the continuous dissolution of entire fuel elements. These feeds contained silicon equivalent to about 0.4 percent by weight of the dissolved aluminum and 0.001M zirconium. Coalescence measurements were also made on feeds of this composition which had been gelatin treated. In order to isolate the responsible surfactant and further evaluate gelatin treatment a special plant experiment was designed which utilized feeds containing silicon equivalent to 3.0 percent by weight of the dissolved aluminum and 0.0001M zirconium.

1. Coalescence Behavior of Untreated Plant Streams

The coalescence measurements of samples taken during normal operation of the plant gave the spider web effect. These samples are described in Table 2, samples numbered 1, 2, and 3. These plant streams contained silicon equivalent to about 0.4 percent by weight of the dissolved aluminum and 0.001M zirconium. In the coalescence measurement the main body disengaged in about 90 seconds but the spider web type film remained stable for greater than 600 seconds. The plant extraction column was determined by instrumentation to be operating properly at a moderate volume velocity.

TABLE 2

COALESCENCE MEASUREMENT OF PLANT STREAMS

Sample Number	Feed Description Silicon Weight %	Zirconium M	Acidity M	Specific Gravity g/cc	TBP %	Gelatin Dosage PPM	Coal. Time Sec.	Remarks
COALESCENCE BEHAVIOR OF UNTREATED PLANT STREAMS								
1	0.4	0.001	0.6	1.27	3.3	none	>600-90	Spider Web
2	0.4	0.001	0.9	1.28	3.3	none	>600-90	Spider Web
3	0.4	0.001	0.8	1.27	3.5	none	>600-90	Spider Web
COALESCENCE BEHAVIOR OF GELATIN-TREATED PLANT STREAMS								
4	0.4	0.001	0.98	1.29	3.0	100	>600-31	Spider Web
5	0.4	0.001	0.49	1.28	3.3	100	>600-35	Spider Web
COALESCENCE BEHAVIOR OF HIGH SILICON LOW ZIRCONIUM FEEDS								
6	3.0	0.0001	1.46	1.27	3.3	none	>600	Stable Emulsion
7	3.0	0.0001	----	----	3.3	100	90	Some Inter-Facial Crud
8	3.0	0.0001	0.20	1.29	3.3	none	>600	Stable Emulsion
9	3.0	0.0001	----	----	3.3	100	50	Clean

2. Coalescence Behavior of Gelatin-Treated Plant Streams

These normal feeds were also treated with gelatin to a level of 100 parts per million of feed. These samples are described in Table 2, samples numbered 4 and 5. Since samples of the gelatin treated feeds are unobtainable prior to their entry into the extraction column, the raffinates corresponding to these feeds were used in the coalescence measurements. However, the coalescence times of plant feeds and that of the corresponding plant raffinates compared sufficiently to determine major changes in emulsification. (See Appendix 2). The coalescence measurement of these gelatin-treated streams showed that the time required for the main body of the emulsion to disengage was reduced greatly; however, the spider web effect persisted.

3. Coalescence Behavior with High Silicon-Low Zirconium Plant Streams

In a special plant experiment feeds were produced containing silicon equivalent to about 3.0 percent by weight of the dissolved aluminum and 0.0001M zirconium. Two samples of untreated feeds are described in Table 2, numbered 6 and 8. A very stable emulsion resulted in the coalescence measurement of these untreated feeds giving coalescence times of greater than 600 seconds. However, the corresponding gelatin-treated raffinates, samples numbered 7 and 9, produced clean separations in 50 to 90 seconds. There was small amounts of interfacial crud present at the interface of one sample but no spider web effect was experienced. Plant operation was not attempted with the untreated feed but was successful with the gelatin treated material.

V. CONCLUSIONS

From these data it was concluded that the measurement of coalescence times on plant column process streams can be utilized to predict major changes in emulsification such as were experienced in the evaluation of the gelatin treatment. However, the sensitivity of the test is such that the interpretation and evaluation of borderline cases, such as those tests possessing spider web effects would be difficult and subject to error.

ACKNOWLEDGEMENT

The mechanical design and construction of the remote testing device was done by R. D. Fletcher of the Hot Laboratory Equipment Development Group of CPP Technical and George Davis of the CPP Maintenance Group.

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VII. APPENDIX 1

CORRELATION OF PILOT PLANT AND COALESCENCE TEST DATA

Pilot Plant Run A

<u>Sample Number</u>	<u>Coalescence Times (sec)</u>	<u>Column Observation</u>	<u>Sample Number</u>	<u>Coalescence Times (sec)</u>	<u>Column Observation</u>
1	200	Good	46	173	Good
2	166	Good	47	182	Good
3	>600	Bad(2)(1)	48	179	Good
4	>600	Bad(1)	49	>600-160*	Bad(1)
5	>600	Bad(1)	50	>600-170*	Bad(1)
6	>600	Bad(3)	51	>600-180*	Bad(1)
7	>600	Bad(3)(1)	52	>600	Bad(2)(3)
8	130	Good	53	>600	Bad(2)
9	130	Good	54	116	Good
10	180	Good	55	130	Good
11	190	Good	56	126	Good
12	85	Good	57	125	Good
13	81	Good	58	125	Good
14	>600-142*	Bad(1)	59	122	Good
15	>600-142*	Bad(1)	60	125	Good
16	>600-150*	Bad(1)	61	125	Good
17	>600-165*	Bad(2)			
18	238	Good			
19	129	Good			
20	129	Good			
21	142	Good			
22	141	Good			
23	115	Good			
24	111	Good			
25	120	Good			
26	123	Good			
27	112	Good			
28	112	Good			
29	113	Good			
30	205	Good			
31	121	Good			
32	121	Good			
33	120	Good			
34	157	Good			
35	177	Good			
36	>600	Good ✓			
37	---	----			
38	>600	Good ✓			
39	>600-171*	Good ✓			
40	>600-167*	Good ✓			
41	>600	Bad(1)			
42	>600	Bad(1)			
43	>600-170*	Good ✓			
44	>600-170*	Good ✓			
45	>600-150*	Good ✓			

Column Operation Classification - Bad

- (1) >6 inches of interfacial "crud"
- (2) Column flooded
- (3) Little or no organic coalescing
- (✓) Dissagreement between test and observed column observation
- (*) Spider web effect. Main body coalescence time.

(Continued)

CORRELATION OF PILOT PLANT AND COALESCENCE TEST DATA (cont.)

Pilot Plant Run B

Pilot Plant Run C

<u>Sample Number</u>	<u>Coalescence Times (sec)</u>	<u>Column Observation</u>	<u>Sample Number</u>	<u>Coalescence Times (sec)</u>	<u>Column Observation</u>
1	156	Good	1	>600-113*	Bad (1)
2	---	---	2	135	Bad (1) ✓
3	174	Good	3	>600	Bad (3)
4	151	Good	4	>600	Bad (1)
5	155	Good	5	127	Good
6	155	Good	6	144	Good
7	146	Good	7	>600	Bad (1)
8	218	Good	8	>600-230*	Good ✓
9	>600-215*	Bad (2)	9	301	Good
10	>600-210*	Bad (2)	10	283	Good
11	>600-241*	Bad (2) (3)	11	288	Good
12	>600-221*	Bad (2) (3)	12	>600	Bad (1)
13	248	Good			
14	297	Good			
15	267	Good			
16	272	Good			
17	266	Good			
18	280	Good			
19	267	Good			
20	300	Good			
21	240	Good			
22	243	Good			
23	252	Good			
24	246	Good			
25	265	Good			

Column Operation Classification - Bad

- (1) >6 inches of interfacial "crud"
- (2) Column flooded
- (3) Little or no organic coalescing
- (*) Spider-web effect. Main body coalescence time.
- (✓) Dissagreement between test and observed column operation

APPENDIX 2

THE COMPARISON OF THE COALESCENCE BEHAVIOR OF FEEDS AND RAFFINATES

<u>Sample Number</u>	<u>Feed Coalescence Times (sec)</u>	<u>Raffinate Coalescence Times (sec)</u>
3	>600	>600
4	>600	>600
5	>600	>600
6	>600	>600
7	>600	>600
8	300	130
9	255	130
10	300	180
11	165	190
12	160	85
13	156	81
14	>600-150*	>600-142*
15	>600-146*	>600-142*
16	>600-137*	>600-150*
17	>600-141*	>600-165*
18	280	238
19	144	129
20	149	129
21	142	142
22	158	141

PLANT STREAMS

9	>600-88*	>600-73*
10	>600	>600
11	>600	>600

(*) Spider web effect. Main body coalescence time.