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Odorless Kerosene Degradation and the Formation of Interfacial Deposits During the Alkaline Solvent Wash in the PUREX Process

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ABSTRACT

In addition to the widely reported emulsions and interfacial deposits (cruds) encountered in the first extraction stage of the PUREX process, disturbances may also occur in the alkaline solvent wash. Experiments have shown that visually similar, nonradioactive deposits may be generated in vitro using either irradiated or chemically degraded solvents or diluents. Further experiments investigated the occurrence and composition of these deposits using a variety of techniques including physical measurements and spectroscopic methods, resulting in the identification of potential crud-forming species and proposals for mechanisms of crud formation

Key Words. Crud; Diluent degradation; Interfacial deposit; Odorless kerosene; PUREX; Solvent wash

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INTRODUCTION

A problem associated with the operation of many solvent extraction processes is the formation of a stable phase called "crud." This material often forms at liquid interfaces and may coat the containing vessels and moving parts. Ritcey (1) defined crud as "the material resulting from the agitation of an organic phase, an aqueous phase and fine solid particles that form a stable mixture." The occurrence of such deposits is undesirable since it may detrimentally affect the solvent extraction process in a number of ways including emulsion stabilization, hindered mass transfer, and process disturbances. There are many causes of crud formation, and each type of solvent extraction plant may have a crud problem particular to that plant. Ritcey identified factors such as feed type, solution composition, solvent composition, the presence of other organic constituents, and design and type of agitation as all possibly influencing the occurrence and nature of crud.

The occurrence of interfacial deposits in the first contactor stage of the PUREX process have been widely reported, and complexes of the extractant degradation product di-*n*-butylphosphate (DBP) with zirconium or fines from the dissolution process are usually proposed as a principal cause (2–6). During the operation of the Thermal Oxide Reprocessing Plant miniature active pilot plant (TMAPP) at Sellafield, UK, interfacial deposits were observed in the alkaline solvent wash, a stage introduced to recycle degraded solvent through the elimination of acidic degradation products such as DBP. Very little was known about the causes and composition of solvent wash cruds, although solvent degradation products were suspected of involvement. The work described here forms part of a larger project commissioned to examine the formation of interfacial deposits in the PUREX process (7). Preliminary experiments generated interfacial deposits visually similar to those observed in the pilot plant by contacting radiochemically degraded process solvent (30% TBP/OK; TBP = tri-*n*-butylphosphate, OK = odorless kerosene) with an equal volume of sodium carbonate solution (0.25 M). Mixing the two phases gave a cloudy yellow organic phase with a clear pale yellow aqueous phase and a stable interfacial emulsion; both emulsion and organic phase were cleared by centrifugation. Microscopic examination of samples from the initial emulsion and the interfacial region following centrifugation revealed the presence of crystalline fines. Attempts to record the Raman spectra of the fines using a MOLE, Raman microprobe (7, 8) were generally unsuccessful as the sample was found to be photosensitive and fluoresced. However, a weak broad band was observed in the 2900–3000 cm^{-1} region, characteristic of C–H vibrational modes, therefore supporting the idea that the interfacial deposits were organic in character.

Solvent degradation is primarily due to the intense radiation encountered in the first extraction stage where the solvent is contacted with a highly radioactive aqueous nitric acid solution of the spent fuel rods. Recent work (9, 10) has established the identity of many of the solvent degradation products formed through radiolytic and chemical reactions occurring during irradiation of process extraction systems. The principal diluent degradation products formed in the system 30% TBP/*n*-alkane–nitric acid are the same as those obtained from the radiolysis of the corresponding hydrocarbon; namely, alcohols, ketones, nitroalkanes, alkylnitrates, etc. Bifunctional phosphorus-containing compounds are much less abundant.

Historically, a distinction has been made between chemical and radiolytic degradation. However, since both proceed via free radical mechanisms, the degradation products formed by the two processes may be similar (11, 12). The mechanism of nitric-acid-induced diluent degradation is thought to involve monomeric radical like $.NO_2$ molecules generated from the nitric acid (13–17):

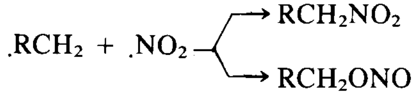
$$HNO_3 \rightarrow .OH + .NO_2 \tag{1}$$

$.NO_2$ molecules or $.OH$ radicals may react with alkanes to form nitrous acid or water and free hydrocarbon radicals:

$$RCH_3 \rightarrow .NO_2 \rightarrow .RCH_2 + HNO_2 \tag{2}$$

$$RCH_3 + .OH \rightarrow .RCH_2 + H_2O \tag{3}$$

The hydrocarbon radical may then react with further $.NO_2$ molecules to give nitro or nitrite compounds:



$$.RCH_2 + .NO_2 \rightarrow \begin{cases} RCH_2NO_2 & \text{(4a)} \\ RCH_2ONO & \text{(4b)} \end{cases}$$

The nitro compound may react with nitrous acid to form a nitroso compound:

$$RCH_2NO_2 + HNO_2 \rightarrow RCH(NO)NO_2 + H_2O \tag{5}$$

or may be hydrolyzed to form a carboxylic acid (18):

$$RCH_2NO_2 + H_2O \rightarrow RCO_2H + H_2NOH \tag{6}$$

Further side reactions may also occur to give a wide range of organic compounds, including alcohols and unsaturated compounds. For example, the nitrite formed in Reaction (4b) may be hydrolyzed to give an alcohol:

$$RCH_2ONO + H_2O \rightleftharpoons RCH_2OH + HNO_2 \qquad (7)$$

which may then be oxidized to form a carboxylic acid:

$$RCH_2OH + 2(O) \rightarrow RCO_2H + H_2O \qquad (8)$$

This mechanism is thought to apply to the PUREX process since it fits with many of the known facts concerning solvent degradation, including the identity of the degradation products formed (9, 10, 12, 19). Several authors (20–22) have reported the validity of using chemically degraded solvents to simulate radiolytically degraded solvents.

Odorless kerosene is a complex hydrocarbon mixture, with variable composition depending upon the source; however, a typical analysis might be *n*-alkanes (62%), cycloalkanes (26%), branched alkanes (7%), and aromatics (5%) (Goreley, unpublished). The order of stability of hydrocarbons to radiolytic degradation has been established as: *n*-alkanes > branched alkanes > cycloalkanes > alkenes; evidence on the behavior of aromatic hydrocarbons is conflicting (23). Thus, a diluent such as *n*-dodecane (nDD) is expected to be more stable than OK, and indeed this has been found to be the case (24). However, with this as with much of the published literature, the principal measure of diluent stability was the retention of fission products through the Z-test (25), No investigations of the diluent's interfacial-deposit-forming characteristics have been reported.

EXPERIMENTAL

This study consisted of a series of small-scale batch tests supplemented by physical and spectroscopic analytical methods. The tests were performed sequentially with the results of each test influencing the scope and design of the next.

Batch Tests

The basic method used for the batch tests was essentially constant throughout the work; an organic phase (2 mL) was agitated with an aqueous phase (2 mL) in all-glass sealed test-tubes (approximately 1.5 mL capacity) for 1 hour. The appearance of the two-phase system was recorded following agitation and then at regular intervals for a period of several months. Preliminary experiments (7) indicated that solid contaminants tended to become suspended at the liquid interface; to prevent this potential complication, the components of each phase were predissolved and the resulting solutions filtered (pore size = 50 μm) before the two liquids were contacted.

Chemical Degradation of Organic Liquids

Organic liquids (500 mL) were chemically degraded by stirred reflux with an equal volume of nitric acid (6 M) at 105 ± 2°C. Temperature regulation was achieved using an Electrothermal electronic temperature controller connected to an Electrothermal heating mantle. The conditions used to degrade the solvent were selected on the basis of the literature (20, 26) and preliminary experiments.

Chemicals and Spectroscopic Equipment Used

Odorless kerosene (Shell, HC 261 288), *n*-dodecane and tri-*n*-butyl phosphate, B.D.H. Analar reagents.

Infrared spectra were recorded using a Perkin-Elmer 1720-X Fourier Transform Infrared Spectrophotometer, with a 0.4 mW, 633 nm He/Ne laser and a liquid-nitrogen-cooled MCT detector, resolution = 0.5 cm^{-1}, scan speed = 1 cm^{-1}. The spectra presented are the accumulation of 10 scans. Liquid samples were recorded using either KRS-5 or NaCl windows. The spectra of crud II (Fig. 2c) was obtained using KRS-5 windows.

Ultraviolet/visible spectra were recorded using a Pye Unicam PU8800 spectrophotometer with the following scan conditions: λ range = 900–190 nm, bandwidth = 2 nm, scan speed = 5 $nm \cdot s^{-1}$, mode = absorption, λ scale = 20 nm, response = 2 s, step = 0.1 nm. Quartz cells with a path length of 1 cm were used, with fresh solvent in the reference cell providing the background.

Experiment A: Preliminary Screening Test

A series of screening tests to investigate the role of solvent degradation products in the formation of interfacial deposits was undertaken. Combinations of both fresh and chemically degraded organic phase constituents (TBP, OK, nDD) were shaken with sodium carbonate solution (0.25 M) to simulate the first alkaline solvent wash, see Table 1.

Experiment B: Odorless Kerosene Degradation

OK and nDD were separately chemically degraded using the method described above. Samples (25 mL) of both the aqueous and organic phase were collected at regular intervals throughout the reflux. The ultraviolet/visible and infrared spectra of the organic phase samples were recorded,

TABLE 1
Experiment A: Preliminary Screening Tests:
Summary of Batch Tests and Results[a]

Test	Organic phase	Result
1	TBP	No interfacial deposit
2	OK	No interfacial deposit
3	nDD	No interfacial deposit
4	TBP*	No interfacial deposit
5	OK*	Interfacial deposit
6	nDD*	Interfacial deposit
7	30% TBP/OK	No interfacial deposit
8	30% TBP/nDD	No interfacial deposit
9	30% TBP/OK*	Interfacial deposit
10	30% TBP/nDD*	No interfacial deposit
11	30% TBP*/OK*	Interfacial deposit
12	30% TBP*/nDD*	Interfacial deposit
13	30% TBP*/OK	No interfacial deposit
14	30% TBP*/OK	No interfacial deposit
15	(30% TBP/OK)*	No interfacial deposit
16	(30% TBP/nDD)*	No interfacial deposit

[a] The aqueous phase in all batch tests was sodium carbonate solution (0.25 M), phase ratio = 1:1. An asterisk denotes chemical degradation by a 5-hour reflux with an equal volume (100 mL) of nitric acid (6 M) at 105 ± 2°C.

and absorption bands characteristic of degradation products were assigned on the basis of the literature and by reference to known compounds (20, 26–28, 33–35).

Reaction profiles were prepared using the UV/Vis and IR spectra. IR reaction profiles were produced by determining the intensity of the infrared transmission peaks of degradation products relative to the 1380 cm^{-1} peak (C-H deformation mode) which remained effectively constant throughout the degradation and so may be adopted as an internal standard.

The interfacial tension of the system-degraded OK/HNO_3 (6 M) was determined using a du Nouy ring pull tensiometer, and a further portion (2 mL) of each sample (OK and nDD) was used for batch tests with sodium carbonate solution (0.25 M). The particle size of the fines formed in the system-degraded OK/sodium carbonate solution after contacting for 1 hour were determined using a Malvern Instruments Master Particle Sizer.

Experiment C: The Influence of Aqueous Phase Composition

A series of batch tests was carried out with chemically degraded (2 hour reflux with 6 M nitric acid) odorless kerosene contacted with a range of different aqueous phases at a phase ratio of 1:1. Tests are summarized in Table 3.

Experiment D: The Effect of Long-Chain Carboxylic Acids

A series of batch tests was carried out with both fresh and lightly degraded (45 minute reflux, noncrud forming), odorless kerosene doped with a range of both linear (C_8–C_{12}) and aromatic (C_7–C_{12}) carboxylic acids, representative of species found in degraded solvent contacted with sodium carbonate solution (0.25 M). Two supplementary tests were also carried out with 30% TBP/OK organic phase. Details of the batch tests performed are given in Table 4.

Experiment E: The Influence of Added Fines on Crud Formation

Two series of batch tests were carried out. In the first, chemically degraded OK (2 hours reflux with 6 M nitric acid) was contacted with a nonalkaline aqueous phase (distilled water or sodium chloride solution 0.25 M). In the second, lightly degraded OK (45 minutes reflux with 6 M nitric acid) was contacted with sodium carbonate solution (0.25 M). In both cases fines, silica (TLC silica gel, 60–210 μm diameter), carbon (activated charcoal, 80–150 μm diameter), and sodium laurate (B.D.H., Analar reagent ground in a pestle and mortar) were dispersed in the aqueous phase prior to contacting aqueous and organic phases. Batch tests are summarized in Table 5.

Experiment F: The Yield of Interfacial Deposit (Crud II) and Determination of the Extinction Coefficient of Type II Deposits

Odorless kerosene (500 mL) was chemically degraded by reflux with an equal volume of nitric acid (6 M) for a period of 5 hours, as described earlier, Samples (50 mL) were removed at 1-hour intervals. Aliquots of degraded diluent (30 mL) were contacted with an equal volume of sodium carbonate solution (0.25 M) in sealed brown bottles (100 mL capacity). The two-phase system was agitated for 2 hours and then left to stand for 4 weeks. After this time both phases were filtered using Buchner filtration equipment with Whatman number 1 filter paper. The quantity of insoluble material was determined by weighing the filter papers daily until a constant weight was obtained.

A calibration plot of the intensity of the characteristic ultraviolet/visible adsorption (λ_{max} = 240–260 nm) against the concentration of the deposit dissolved in the process solvent (30% TBP/OK) was prepared using the dry interfacial deposit collected.

RESULTS

Experiment A

Results of Experiment A are summarized in Table 1. No interfacial deposits were formed by contacting fresh organic phase, degraded extractant, or degraded solvent with sodium carbonate solution (batch tests 1–4, 7 and 8, 13–16). However, interfacial deposits visually similar to those observed in the alkaline solvent wash of TMAPP were generated with chemically degraded diluent (OK or nDD, tests 5, 6). Tests with degraded diluent and either fresh or degraded extractant (tests 9–12) generally produced cruds, although the test with 30% TBP/nDD* failed in this respect.

Experiment B

As the reflux proceeded, the diluents became yellow in color. The ultraviolet and infrared spectra obtained, Figs. 1–4, were consistent with those previously reported (20, 26, 28). Assignments of degradation product absorption bands are summarized in Table 2.

The ultraviolet/visible spectra of chemically degraded OK (Fig. 1) showed a principal absorption between 235 and 250 nm, with a shoulder at 280 nm and other weaker absorptions between 330 and 390 nm. Tentative assignments are given in Table 2. The UV/Vis reaction profile (Fig. 5) shows a rapid increase in the intensity of the 235–250 nm absorption over the first couple of hours of reflux, followed by a leveling out of the band intensity after approximately 5 hours reflux. The infrared reaction profile (Fig. 6) hows the appearance and rapid increase of a band at 1555 cm^{-1} (nitroalkane); this also stabilizes after a few hours reflux. The concentrations of other peaks, 1644 and 1720 cm^{-1}, assigned as alkyl nitrate or nitrite and carbonyl degradation products, increase steadily throughout the course of the degradation.

The UV/Vis and infrared spectra of chemically degraded nDD (Figs. 3 and 4) are analogous to those of chemically degraded OK, with IR peaks consistent with the presence of nitroalkane (1555 cm^{-1}), alkyl nitrate or nitrite (1644 cm^{-1}), and carbonyl (1715 and 1738 cm^{-1}) degradation products, and UV/Vis absorptions at λ_{max} = 220, 275, and 355 nm. The ex-

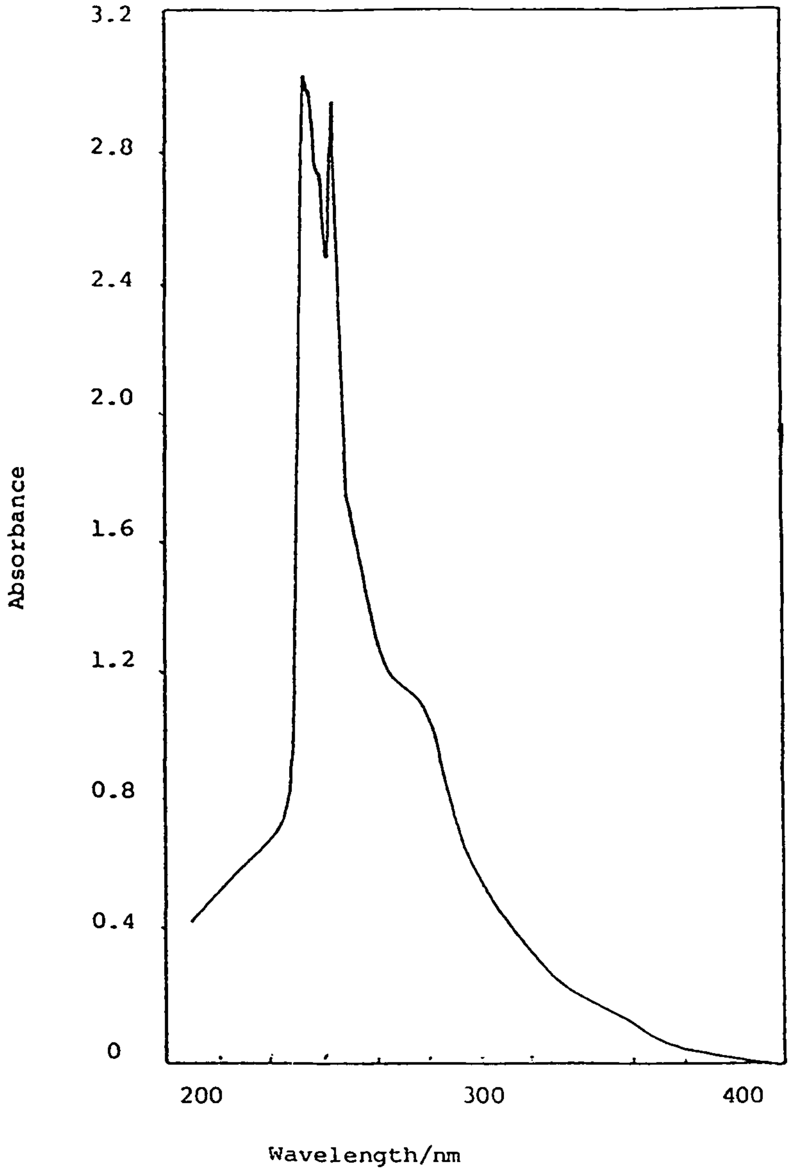


FIG. 1 Ultraviolet spectrum of chemically degraded odorless kerosene (6-hour reflux with 6 M nitric acid, pathlength = 1 cm, reference = OK).

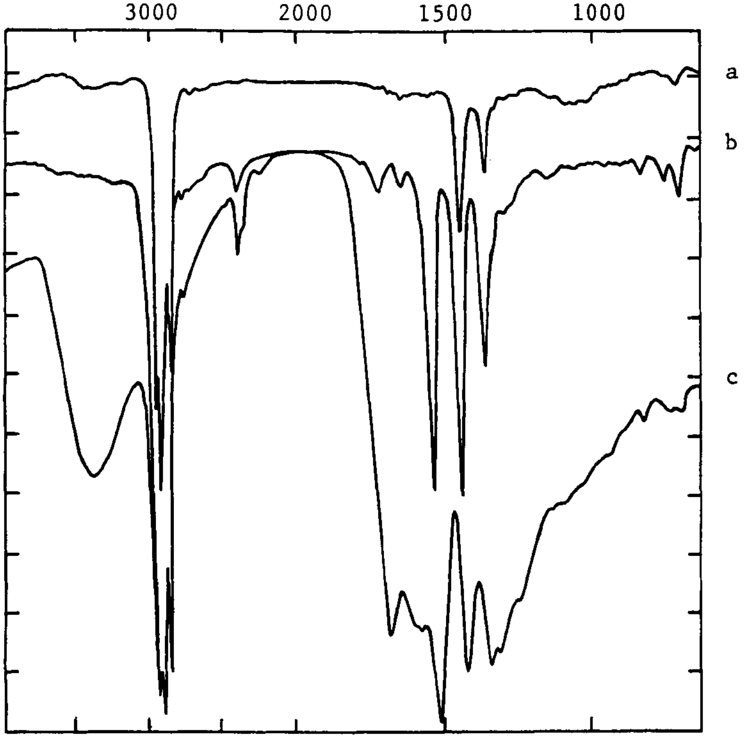


FIG. 2 Infrared spectra of odorless kerosene. (a) Fresh OK. (b) Chemically degraded OK (6-hour reflux with 6 M nitric acid). (c) Type II crud.

TABLE 2
Sectroscopic Characterization of Chemically Degraded Diluent

Spectroscopic technique	Absorption band	Assignment	General formula
UV/Vis[a]	235–250 nm and 280 nm shoulder	Nitroalkane	RNO_2
		Alkylnitrate	$RONO_2$
		Alkylnitrite	RONO
		Carbonyl	RCOR′
	330–390 nm	Aliphatic nitrite	RONO
IR[b]	1555 cm^{-1}	Nitroalkane	RNO_2
	1644 cm^{-1}	Alkylnitrate	$RONO_2$
		Alkylnitrite	RONO
	1715–1740 cm^{-1}	Carbonyl	RCO_2H

[a] UV/Vis assignments: Refs. 27, 33, 34.
[b] IR assignments: Refs. 20, 26, 28.

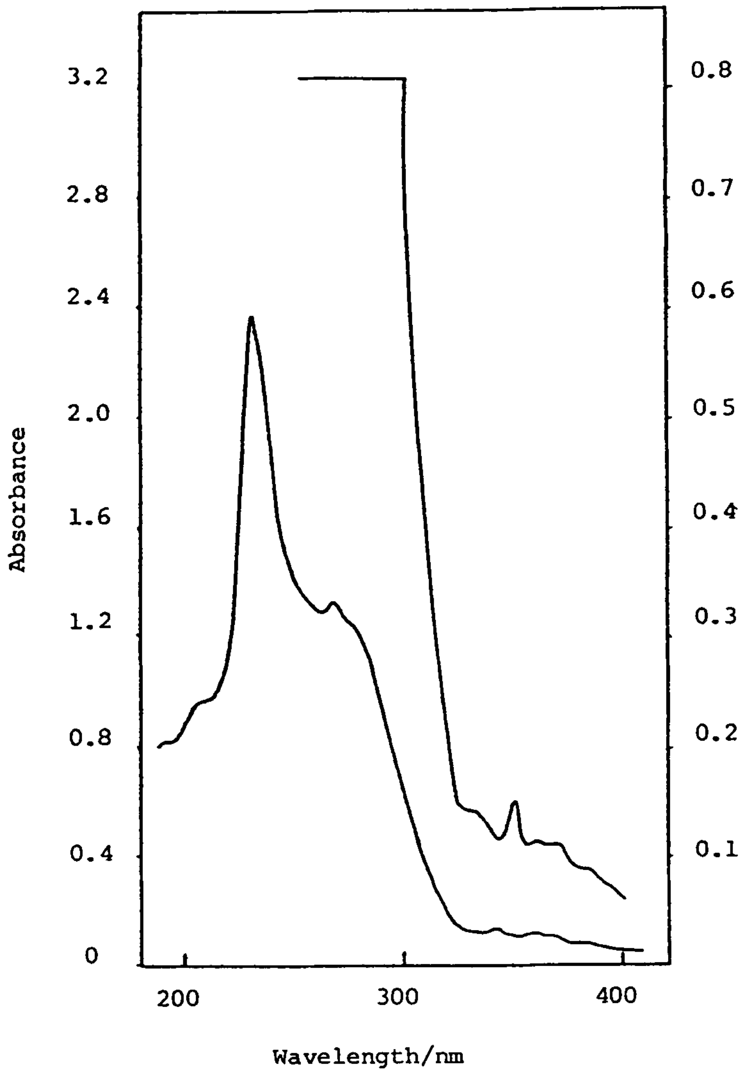


FIG. 3 Ultraviolet spectrum of chemically degraded *n*-dodecane (14-hour reflux with 6 M nitric acid, pathlength = 1 cm, reference = nDD).

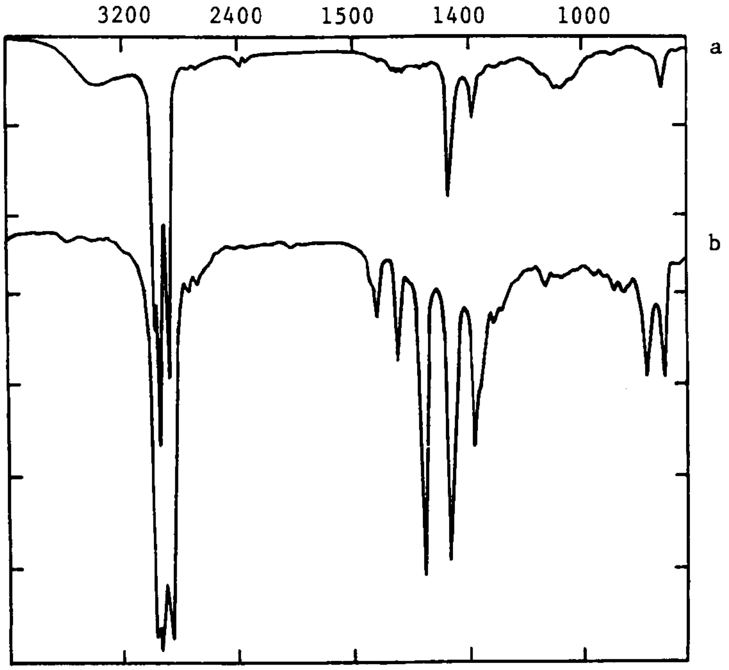


FIG. 4 Infrared spectra of chemically degraded *n*-dodecane. (a) Fresh nDD. (b) Chemically degraded nDD (13-hour reflux with 6 M nitric acid).

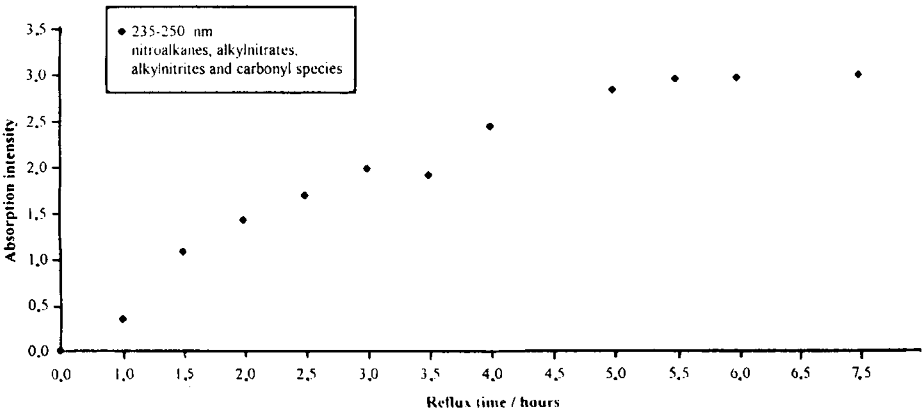


FIG. 5 Ultraviolet spectroscopic reaction profile for chemical degradation of odorless kerosene.

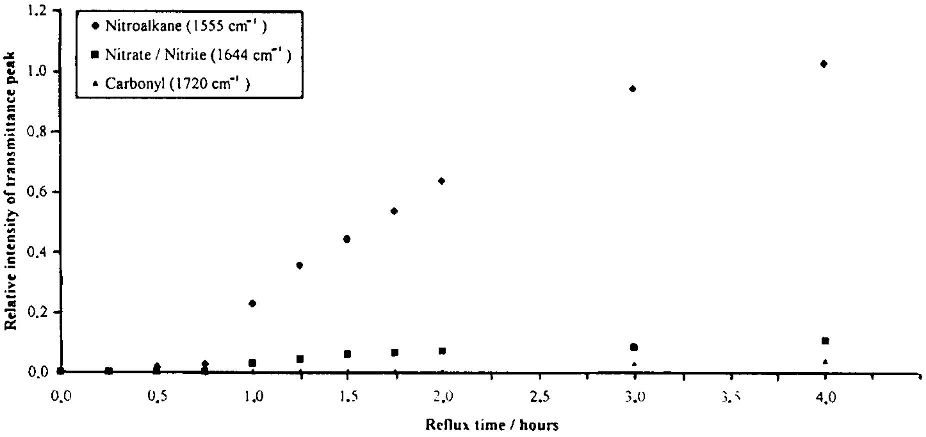


FIG. 6 Infrared spectroscopic reaction profile for chemical degradation of odorless kerosene.

pected increased resistance to chemical degradation is borne out by the comparison of reaction profiles of nDD (Figs. 7 and 8) with those of OK (Figs. 5 and 6).

The interfacial tension of the system OK/HNO_3 (6 M) was found to decrease with reflux time, from 37.0 mN·m^{-1} for fresh OK down to 21.4 mN·m^{-1} for chemically degraded OK after 5 hours reflux (Fig. 9).

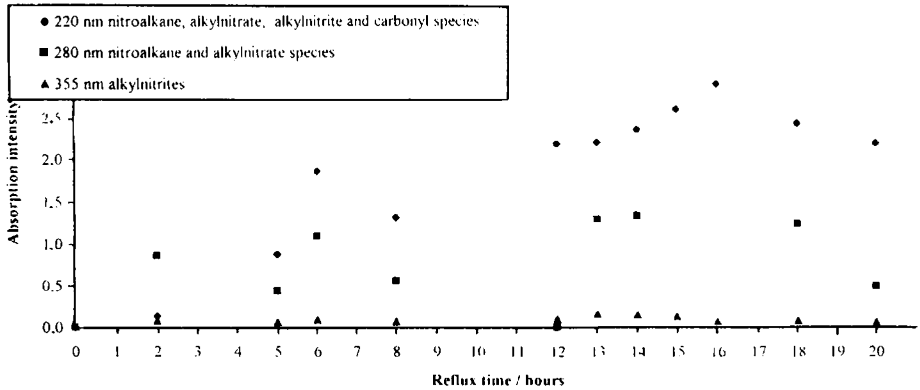


FIG. 7 Ultraviolet/visible spectroscopic reaction profile for chemical degradation of *n*-dodecane.

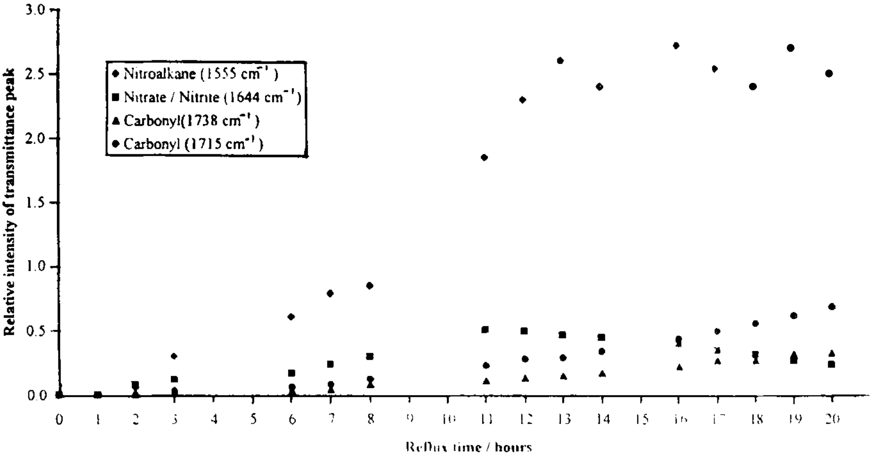


FIG. 8 Infrared spectroscopic reaction profile for chemical degradation of *n*-dodecane.

The behavior of degraded OK in the batch tests with sodium carbonate solution was found to be dependent upon the extent of chemical degradation. Very lightly degraded samples, refluxed for less than 1 hour, generally failed to produce interfacial deposits when contacted with sodium carbonate solution (0.25 M). However, the shape of the organic/aqueous

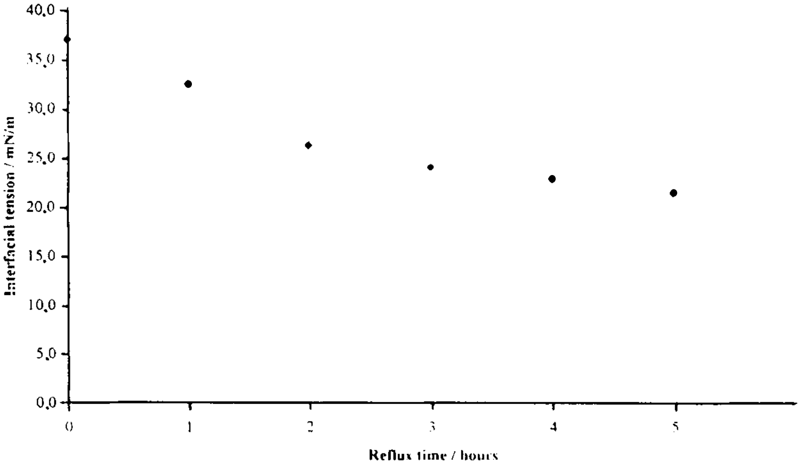


FIG. 9 Interfacial tension of the system odorless kerosene/nitric acid (6 M).

interface formed changed from the curved meniscus observed with fresh OK to a flat interface with a cloudy organic phase in batch tests with OK samples refluxed for 15 minutes or longer. Interfacial deposits were obtained in tests with more highly degraded diluent.

Detailed investigation of the interfacial tension of the system OK/$Na_2CO_{3(aq)}$ was prevented by the opaque nature of the organic phase. However, the interfacial tension was found to be less than 1.0 $mN \cdot m^{-1}$.

Because of the gradual change in the behavior of degraded OK with the sodium carbonate solution, it was impossible to give a precise reflux time/degree of chemical degradation required for the formation of interfacial deposits. However, samples refluxed for periods in excess of 1 hour generally produced cruds when washed with sodium carbonate solution. When OK degraded for 1 hour or longer was washed with sodium carbonate solution, it behaved as follows:

1. There was a darkening of the yellow color of the organic phase, accompanied by transfer of some color to the aqueous phase. UV spectra (not shown) indicated that the darkening in color of the organic phase was due to an increase in intensity of the 235–250 nm degradation product absorption rather than any new absorptions.
2. The organic phase became cloudy, spreading from the interface due to the formation of fines which settled out at the interface to give "Type I crud" after standing for several days. If test tubes were reshaken, emulsions formed with slow phase separation (>1 hour). The fines were found to have a diameter of approximately 100 μm. Further, while preparing the sample for the particle size measurements, it was observed that the particles were soluble in fresh OK. They were, however, insoluble in filtered degraded OK (7).
3. Agitation of the chemically degraded OK/sodium carbonate solution system for 1 hour, or alternatively standing for several days, produced a coarse dark brown/black oily viscous liquid/particulate deposit at the interface; "Type II crud." On standing for several days this deposit tended to adhere to the glass of the test tube at the liquid interface. Further aging resulted in a slow increase in the amount of deposit present and also the coalescence of the deposits. These cruds either remained at the interface or broke away to be precipitated in the aqueous phase. Infrared spectra of the deposits (Fig. 2c) showed increased intensity absorptions for all the bands previously assigned to degradation products.
4. In some tests, mixing the degraded OK with sodium carbonate solution resulted in the almost immediate formation of an interfacial film; "Type III crud." This type of interfacial deposit was less frequently

TABLE 3
Experiment C: The Effect of Aqueous Phase Composition, Summary of Batch Tests and Results[a]

Test	Aqueous phase	Result
1	<0.25 M Li_2CO_3	Interfacial deposit, I and II
2	0.25 M Na_2CO_3	Interfacial deposit, I and II
3	0.25 M K_2CO_3	Interfacial deposit, I and II
4	0.25 M $NaHCO_3$	Emulsion, interfacial deposit, I and II
5	0.1 M NaOH	Interfacial deposit, I and II
6	Deionized H_2O	No interfacial deposit
7	0.25 M NaCl	No interfacial deposit
8	0.1 M HNO_3	No interfacial deposit

[a] In all tests the organic phase consisted of odorless kerosene chemically degraded by reflux with nitric acid (6 M) for 2 hours.

TABLE 4
Experiment D: The Effect of Long-Chain Carboxylic Acids, Summary of Batch Tests and Results

Test	Organic phase[a]	Result
1	OK*	No interfacial deposit
2	OK + lauric acid	Stable emulsion
3	OK* + lauric acid	Stable emulsion
4	OK + undecanoic acid	Stable emulsion
5	OK* + undecanoic acid	Stable emulsion
6	OK + decanoic acid	No interfacial deposit
7	OK* + decanoic acid	Type I interfacial deposit
8	OK + octanoic acid	Precipitate formed on standing
9	OK* + octanoic acid	Type I interfacial deposit
10	OK + benzanoic acid	Precipitate formed on standing
11	OK* + benzanoic acid	Type I interfacial deposit
12	OK + naphthalic acid	No interfacial deposit
13	OK* + naphthalic acid	Type I interfacial deposit, cleared on standing
14	30% TBP/OK + lauric acid	Type I interfacial deposit, cleared on standing, third phase formation
15	30% TBP/OK* + lauric acid	Type I interfacial deposit, cleared on standing, third phase formation

[a] OK* degraded by reflux with 6 M nitric acid for 45 minutes. All carboxylic acids 0.05 M, except for naphthalic acid which was almost insoluble in OK, and for which a saturated solution was used $\leqslant$0.05 M.

observed than the other two types and had no discernible pattern to its occurrence.

n-Dodecane samples showed a similar decline in solvent wash performance, with a gradual increase in the time required for phase separation, followed by clouding of both phases (10+ hours reflux) and emulsions visually similar to Type I crud after 18–20 hours reflux.

Experiment C

Results of Experiment C are summarized in Table 3. The occurrence and nature of the interfacial deposits formed was dependent upon the

TABLE 5
Experiment E: The Influence of Fines on the Formation of Type II Crud. Summary of Batch Tests and Results

Test	Organic phase[a]	Aqueous phase[b]	Fines introduced	Result
1	OK**	Na_2CO_3	None	Type I crud followed by formation of Type II crud on standing
2	OK**	H_2O	None	Two clear phases, no crud, fully formed meniscus
3	OK**	NaCl	None	Two clear phases, no crud, fully formed meniscus
4	OK**	H_2O	Silica	Emulsion, followed by sedimentation of fines
5	OK**	NaCl	Silica	Emulsion, followed by sedimentation of fines
6	OK**	H_2O	Carbon	Fines suspended at the interface
7	OK**	NaCl	Carbon	Fines suspended at the interface
8	OK**	H_2O	Sodium laurate	Fines initially suspended at the interface, cleared on standing
9	OK**	NaCl	Sodium laurate	Fines initially suspended at the interface, followed by Type III crud
10	OK*	Na_2CO_3	None	Type I crud
11	OK*	Na_2CO_3	Silica	Type I crud, fines sedimented in aqueous phase
12	OK*	Na_2CO_3	Carbon	Type I crud, fines suspended at interface
13	OK*	Na_2CO_3	Sodium laurate	Type I crud

[a] OK* degraded by 45 minute reflux with 6 M HNO_3. OK** degraded by 2 hour reflux with 6 M HNO_3.

[b] Sodium carbonate and sodium chloride solutions 0.25 M.

composition of the aqueous phase. Interfacial deposits I and II were found to be pH dependent and formed in all tests with an alkaline aqueous phase. However, the identity of the base influenced the relative amounts of deposit formed; carbonate and bicarbonate solution favored the formation of deposit type II, whereas sodium hydroxide solution favored the formation of deposit type I. The metal cation made no observable difference to the type or quantity of deposit formed.

Experiment D

The results of Experiment D are summarized in Table 4. Tests using fresh OK and short chain carboxylic acids (C_6–C_8) did not form cruds, however, aqueous phase precipitates formed on standing (tests 6 and 8). Longer chain acids (C_{11}–C_{12}) produced stable emulsions (tests 2 and 4). Tests (7, 9, 11, and 13) with lightly degraded (noncrud forming) OK and C_6–C_{10} carboxylic acids produced interfacial deposits visually similar to Type I crud on contacting with the aqueous phase, whereas longer chain acids (C_{11}–C_{12} tests 3 and 5) produced stable emulsions. The additional tests (14 and 15) with process solvent doped with lauric acid (C_{12}) initially produced interfacial deposits similar to Type I crud. However, this cleared on standing.

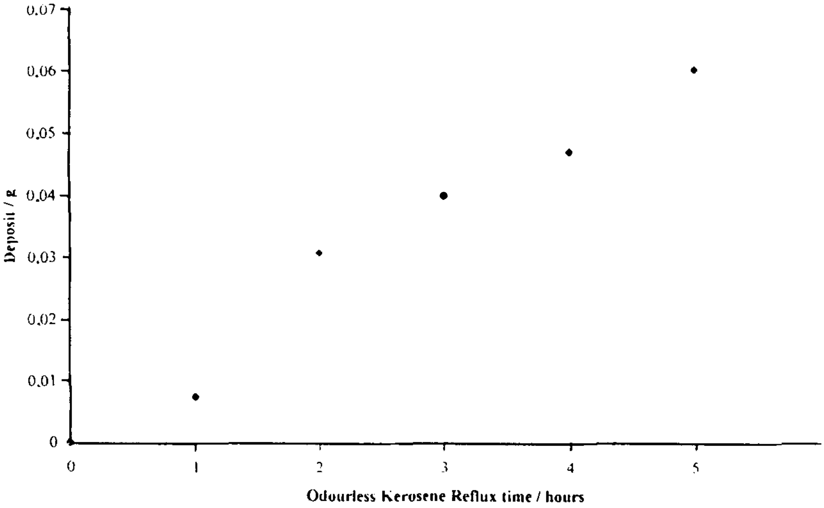


FIG. 10 Experiment F: The yield of Type II interfacial deposit.

Experiment E

Results of Experiment E are summarized in Table 5. In none of the batch tests did the presence of fines result in the formation of an interfacial deposit similar to Type II crud. In tests 8 and 9 with degraded OK, sodium laurate fines were found to be unstable in contact with the aqueous phase

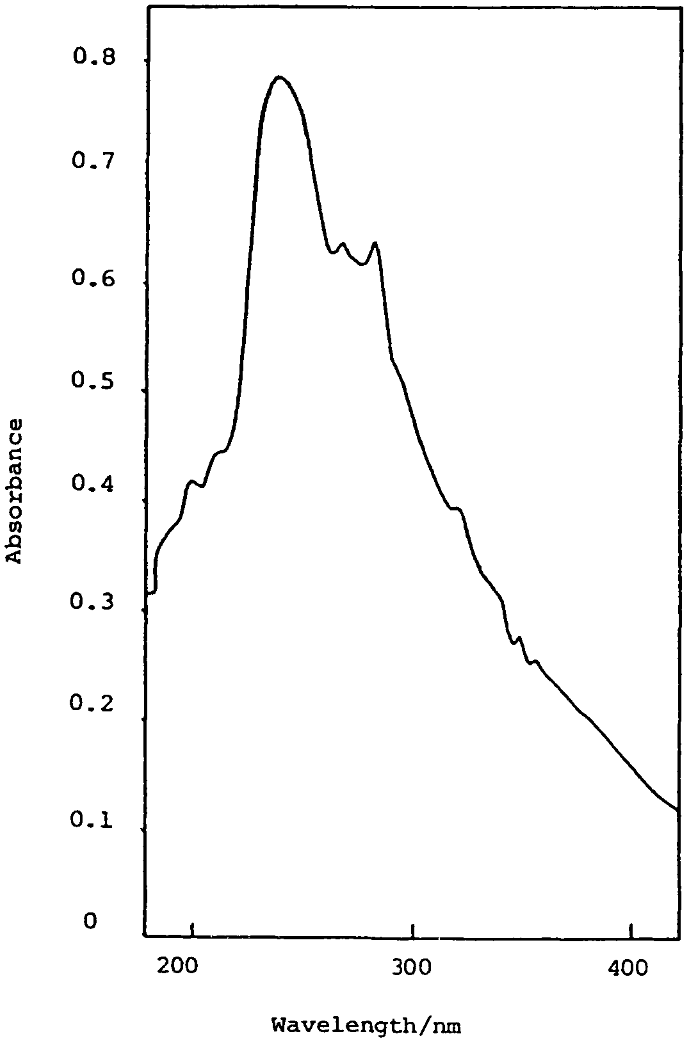


FIG. 11 Ultraviolet spectrum of interfacial deposit Type II dissolved in 30%TBP/OK (path-length = 1 cm, reference = 30% TBP/OK).

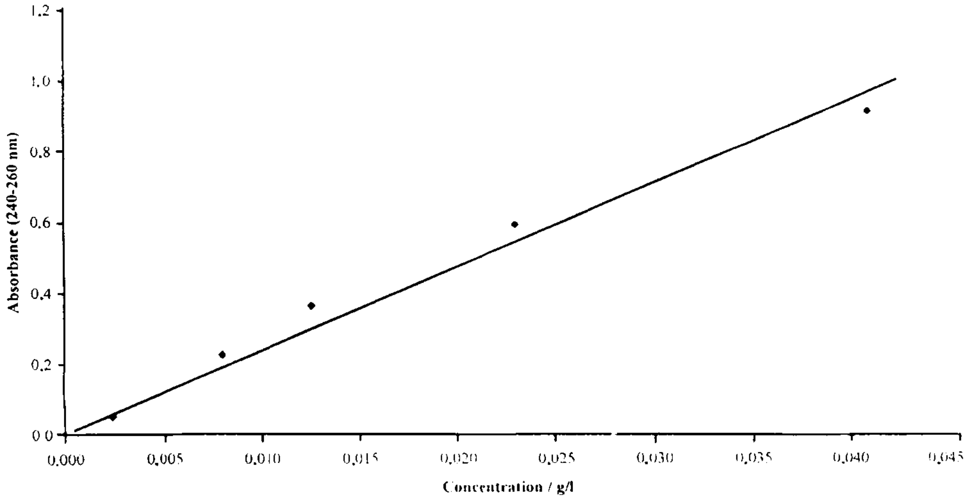


FIG. 12 Beer–Lambert plot for Type II interfacial deposit in 30% TBP/OK.

and dissolved on standing. Carbon fines suspended in the organic phase and adhered to the glass of the test tube, and silica fines settled in the aqueous phase on standing.

Experiment F

A plot of filtration residue after contacting for 1 month against the OK reflux time (extent of chemical degradation) is shown in Fig. 10. Figure 11, the ultraviolet spectra of the filtrate residue (Type II crud) dissolved in 30% TBP/OK, is very similar to those obtained earlier for chemically degraded OK (Fig. 1). A Beer–Lambert plot of absorption intensity against concentration of interfacial deposit is shown in Fig. 12.

DISCUSSION AND CONCLUSIONS

PUREX solvent wash crud formers may be generated by diluent degradation; interfacial deposits similar to those observed in the THORP pilot plant were generated when chemically degraded diluent (OK or nDD) or process solvent prepared with degraded OK was contacted with sodium carbonate solution. The failure of solvent prepared with degraded nDD to form cruds may be due to the increased chemical stability of nDD relative to OK (24). Similarly, the failure of tests with chemically degraded solvent to produce interfacial deposits may be due to increased chemical stability of the diluent in the presence of TBP or, alternatively, greater solubility of crud formers in the more polar organic phase (30% TBP/OK).

Odorless kerosene is susceptible to chemical degradation through reaction with nitric acid at elevated temperatures; pH-sensitive chromophores, surface-active species, and crud-formers were generated within the first hour of reflux. Spectroscopic investigations indicated the presence of a range of functional groups consistent with theories of chemical nitration and oxidation (13, 14, 18). The infrared and ultraviolet/visible spectroscopic reaction profiles may be explained by establishment of equilibria between the degradation products through reactions including those listed earlier. In the degradation of OK, the nitroalkane concentration (1555 cm^{-1} IR absorption) increased through reactions such as (4a) before stabilizing, while carbonyl compounds (1715–1720 cm^{-1} IR absorption) and alkyl nitrates or nitrites (1644 cm^{-1} absorption) built up throughout the reflux through reactions such as (6) and (4b), respectively.

It is not possible to compare the relative concentrations of degradation products since the molar extinction coefficients are unknown. However, by reference to known compounds the sample contents of degradation products were estimated to be no more than 2% of the sample in even the most highly degraded samples prepared. The rapid decline in interfacial tension in the system degraded with OK/nitric acid (6 M) is consistent with the generation of surface-active species through the introduction of functional groups into the hydrocarbon molecules of the diluent. Brown (29) suggested that the presence of surface-active species may have a detrimental effect upon mass transfer across the liquid–liquid interface in the PUREX process.

In the batch tests with degraded OK and sodium carbonate solution (0.25 M), the first indication of diluent degradation was given by the shape of the aqueous/organic interface. This has been reported as the basis of a test of solvent quality known as the D and M test, a flat meniscus with sodium carbonate solution (0.25 M) being indicative of excess cationic surfactants (26). More highly degraded diluent formed interfacial deposits and emulsions which were classified according to their appearance:

Type I crud: interfacial fines/emulsion
Type II crud: amorphous interfacial deposits
Type III crud: multilayers of interfacial film

Type I interfacial deposits were formed in tests with chemically degraded nDD, contacted with sodium carbonate solution (0.25 M), although no other types of interfacial deposit were observed.

On the basis of the experiments reported here and in previous work (20, 26), it is possible to propose mechanisms for the formation of the interfacial deposits obtained.

Type I Crud (interfacial fines/emulsion)

Tallent, Mailen, and Dobson of Oak Ridge National Laboratory (20) identified long-chain carboxylic acids in degraded solvent by potentiometric titrations and infrared spectroscopy, and suggested that sodium salts of such species might be involved in problems with phase separation in the PUREX alkaline solvent wash because of their inherent surface-active properties.

The formation of interfacial lines on transfer from the acid conditions of the solvent reflux (primary extraction stage) to the alkaline conditions of the batch test (solvent wash) may be explained if Type I crud formation were initiated by the precipitation of a salt; both carboxylic acids and nitroalkanes (30) might be expected to form sodium salts under the conditions encountered in the alkaline solvent wash. As the concentration of such species increases, micellization or precipitation may occur to give the interfacial fines.

Type I crud formation through precipitation is consistent with the observed solubility of the fines in fresh odorless kerosene (Experiment B) and the crystalline nature of the interfacial deposits observed in preliminary experiments (7). Absorption peaks characteristic of both carbonyl species (1715–1720 cm^{-1}) and nitroalkanes (1555 cm^{-1}) have been recorded in the infrared spectra of both degraded process solvent (7) and radiochemically and chemically degraded diluents.

The effect of aqueous phase composition on the occurrence and nature of the interfacial deposits formed in Experiment C may also be explained by reference to the above mechanism. Sodium hydroxide is a stronger alkali than carbonate or bicarbonate; therefore, the equilibrium between undissociated acid and salt will be further over toward salt. Hence, more Type I crud will be formed. Carbonyl and nitroalkane degradation products are also constituents of Type II crud (Fig. 2c). If a greater proportion of them were precipitated as Type I crud, then less would be present in solution to contribute to Type II crud, and hence less Type II crud might be expected to be formed.

Further support for this mechanism comes from Experiment D in which interfacial deposits visually similar to Type I crud were generated in tests with lightly degraded, noncrud-forming odorless kerosene doped with carboxylic acids. As might be expected from experience with soaps, the carbon chain length of the acid molecule governs its behavior at the liquid–liquid interface (31). In tests with fresh OK, short-chain acids (C_6–C_8) were extracted to the aqueous phase and precipitated on standing, whereas longer-chain acids (C_{11}–C_{12}) were surface active, lowering the interfacial tension and producing emulsions. This observation is consistent with the findings of Adamov (9) who reported the sodium carbonate solvent wash to be only effective at removing carboxylic acids with carbon chain lengths of C_{11} or less. Tests with lightly degraded OK doped with short to medium chain (C_6–C_{10}) acids produced interfacial deposits visually similar to Type I crud, whereas longer chain acids (C_{10}–C_{12}) produced emulsions. Thus, it appears that not only is the occurrence of cruds dependent upon the balance between the hydrophobic and hydrophilic properties of the acid, but also involves interactions with other degradation products.

The concentration of lauric acid required for emulsion formation in the sodium carbonate (0.25 M) solvent wash was determined to be between 0.01 and 0.001 M for both fresh and degraded OK. This value is below the detection limits of the FT-IR instrument used but is consistent with the results of Tallent et al. (20) who reported carboxylic acid concentrations of 0.0015 M in degraded solvent.

Type II Crud (amorphous dark brown deposits)

The average chain length of the alkanes in OK is C_{10}–C_{16}. Therefore, unless chemical degradation caused extensive chain cleavage, the primary degradation products would consist of long-chain hydrophobic hydrocarbon molecules with hydrophilic functional groups. Such species would be expected to be surface active and accumulate at the liquid interface, resulting in the decrease in interfacial tension observed in Fig. 9 (32).

It is proposed that Type II crud is a nonstoichiometric agglomerate of degradation products (nitroalkanes, alkylnitrates, alkylnitrites, carbonyls, etc) which concentrate at the liquid interface due to their surface-active nature. Type II crud was only observed in batch tests with more highly degraded odorless kerosene which formed Type I crud on contact with the alkaline solution; thus the presence of Type I crud at the interface may act as a nucleating agent for the formation of Type II crud. The precipitation of deposits in the aqueous phase on standing for prolonged periods may be the result of slow reactions which increase the hydrophilic character of the deposits' surface.

The mechanism proposed is supported by the infrared spectra of Type II crud (Fig. 2c) which show an increase in absorption intensity of all types of degradation products relative to the parent degraded OK, and a broad absorption between 3200 and 3600 cm^{-1} characteristic of coordinated water molecules. Experiments to try and induce the formation of Type II crud through the addition of fines (Experiment E, Table 5) were unsuccessful, although the silica fines did take on a dark brown color, indicative of degradation product adsorption in tests with lightly degraded (Type I crud-forming) OK.

The linear shape of the graph of Type II crud yield against the extent of chemical degradation of OK (Fig. 10) is consistent with the mechanism and composition proposed for Type II crud. The total concentration of degradation products increases with reflux time, whereas the concentrations of specific degradation products may stabilize (Figs. 5–8). It should be noted that further crud formed following filtration, thus the yield obtained does not represent the total "crud-potential" of the system. However, the results may be extrapolated to indicate yields of (dry) crud of the order of grams/liter.

Because of the small amount of Type II crud available from Experiment F, it was only possible to prepare 30% TBP/OK solutions over a limited concentration range. However, within the range examined (0–0.4 g/L) the concentration/absorbance data give a reasonable straight line ($R^2 = 0.98$) with only a slight deviation from the Beer–Lambert law at the highest concentration (Fig. 12). The fact that the plot approaches a straight line despite the crud being composed of a variety of different compounds is perhaps surprising, and may be taken to indicate that the range of compounds involved is actually quite limited. The extinction coefficient E was determined as 26.21 $g^{-1} \cdot dm^3 \cdot cm^{-1}$.

Knowledge of the extinction coefficient allows the estimation of diluent degradation product concentrations in degraded solvents. If the solubilities of crud-formers could be determined, it might be possible to predict the occurrence of such deposits from on-line UV spectral monitoring of process solvent. In this work degraded OK becomes Type II crud-forming after a reflux of about 1 hour, corresponding to a degradation product concentration of 0.012 g/L.

The failure of tests with chemically degraded nDD to form interfacial deposits analogous to Type II crud may have several explanations.

1. The increased chemical stability of nDD relative to OK may result in insufficient concentrations of degradation products being formed within the period of reflux.
2. The chemical composition of nDD may be such that the degradation products responsible for Type II crud are not formed.
3. The solubility of Type II crud-forming degradation products may be greater in nDD than in OK.

Of these possible explanations, the third seems the least likely.

Type III Crud (interfacial film)

It was more difficult to propose a mechanism for formation of this type of interfacial deposit as its occurrence was unpredictable. However, it was observed that batch tests that formed Type I crud never formed Type III crud. Other work (7) has examined the destabilization of interfacial deposits formed in the system-degraded OK/sodium carbonate solution by subsequent solvent washes and found that when the organic phase and interfacial deposits were transferred to a dilute nitric acid (0.1 M) aqueous phase, the interfacial fines of Type I crud were replaced by multilayers of interfacial films, Type III crud. Lightly degraded OK with added lauric acid behaved similarly, forming multilayers of diffuse interfacial film. Thus, it is proposed that as with Type I crud, long-chain carboxylic acids and other degradation products may be involved in the formation of Type III crud, the physical form of the crud formed being pH dependent. The unpredictable occurrence of Type III crud observed throughout this series of experiments might be explained by entrainment of nitric acid (6 M) in the OK during its chemical degradation and subsequent transfer to the alkaline solvent wash batch tests.

Neace (26) suggested that surfactants present in degraded solvent are involved in PUREX crud formation. Type II crud often had a high affinity for the glass walls of the test tube, which carry a negative charge under the solvent wash conditions. Therefore, the degradation products involved may possess a positive charge, i.e., be cationic surfactants. Batch tests (7) with fresh and lightly degraded OK doped with various surfactants produced emulsions and interfacial deposits visually similar to Type III crud. It is therefore proposed that Type III crud consists of lamellae of oriented surface-active diluent degradation products. Attempts to determine the presence of anionic or cationic surfactants in degraded OK using the bromophenol blue and methylene blue spot-tests previously used by Neace (26, 36) were unsuccessful as the tests were found to be unsuitable for use with degraded OK.

SUMMARY

Radiochemical degradation of the organic phase diluent may be a cause of interfacial deposits in the alkaline solvent wash, a stage introduced to lower the concentration of acidic degradation products such as dibutyl phosphate. Although diluent degradation products have previously been reported to be fission product complexing agents (11, 23, 37–39), they have not been implicated in crud formation before.

Experiments have demonstrated that interfacial deposits similar in appearance to process cruds may be generated by contacting chemically degraded diluents with aqueous alkaline solutions. Using the system chemically degraded OK/$Na_2CO_{3(aq)}$ (0.25 M), three distinct types of interfacial deposit were generated:

Type I crud: interfacial fines and or stable emulsions
Type II crud: dark brown/black amorphous interfacial deposits
Type III crud: multilayers of interfacial film

On the basis of the results obtained, it is proposed that these are due to precipitation of salts of diluent degradation species such as long-chain carboxylic acids, nonstoichiometric agglomerates of surface-active diluent degradation products, and an alternative pH-sensitive manifestation of the surface-active degradation products responsible for Type I crud, respectively.

Although this work concentrates on the chemical degradation and subsequent solvent wash behavior of diluent (OK and nDD) rather than process solvent (30% TBP/OK or 30% TBP/nDD), it is believed that the observations and conclusions drawn are largely applicable to the more complicated solvent system. Indeed, experiments (7) with process solvent prepared with more highly degraded (5 hour reflux with nitric acid) OK contacted with various alkaline and acidic aqueous phases produced interfacial phenomena analogous to that obtained with radiolytically degraded process solvent under equivalent conditions, i.e., Types I and III cruds. Interfacial deposits visually similar to Type II crud were observed in the TMAPP although their highly radioactive nature prevented detailed analysis.

OK is used as the organic phase diluent at Sellafield and many other PUREX processes throughout the world. However, other more chemically stable diluents such as nDD are also used. The choice of diluent depends mainly on cost and degradation behavior (40, 41). Diluent composition influences radiochemical solvent degradation through the distribution of radiation energy between molecules of TBP and the diluent (19, 38, 42). Napthenes and aromatics act as energy sinks, absorbing energy and giving rise to aliphatic and aromatic degradation products such as those suspected of involvement in solvent wash Type II crud formation, but in doing so reducing the energy available to degrade TBP, the primary degradation product of which, DBP, has been implicated in first contactor stage crud formation, whereas more stable diluents are less effective energy sinks with consequently proportionally higher TBP degradation. Thus, a delicate balance is obtained: the degradation of diluent is undesirable, but the degradation of TBP may be even more so.

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