Investigation of red oil decomposition by simulated Hanford tank wastes

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Abstract

Samples of 'red oil' have been placed in contact with simulated Hanford tank wastes, and Differential Scanning Calorimetry used to compare energetic content both before and after exposure to these waste simulants. Of the 85 samples studied, 44 samples had their energy content reduced by 90% or more following contact with waste simulant, while 77 of the 85 samples showed at least a 50% fall in energy content. All 85 samples showed at least some reduction in energetic content. The duration of contact between red oil and waste simulant was generally a few hours or days, and the overwhelming majority of the data suggest that contact times of several years, as would be typical in Hanford waste tanks, would further reduce the energy content of red oil to negligible quantities.

1. Introduction

A number of destructive so-called red oil incidents have taken place at uranium processing facilities following inadvertent overheating of organic materials with uranyl nitrate/nitric acid [1–10]. These incidents occurred under highly acidic processing conditions, and no such red oil incidents have been documented within nuclear waste storage facilities, where materials are usually stored in highly alkaline media. However, questions concerning possible long-term survival of a red oil-type material within the Hanford waste tanks have recently been raised. Scenarios have been proposed in which red oil material was inadvertently formed during uranium processing operations at the Hanford site, and subsequently routed to the waste tanks.

From first principles, it would be expected that the energetic components within red oil would be decomposed and rendered non-energetic within a very short period

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following contact with a high pH medium [11]. However, virtually no experimental results were available with respect to the behavior of red oil in alkaline systems such as the Hanford waste tanks. Therefore, a research program was initiated to investigate the behavior of red oil under simulated high-level radioactive waste tank conditions.

Bounding conditions were employed throughout the work to create a worst-case scenario with respect to the decomposition environments which were applied to the red oil samples. For example, many decomposition reactions were carried out by placing red oil samples onto the surface of a waste simulant and leaving them undisturbed. This worst-case model is somewhat unrepresentative of actual conditions at Hanford in that it assumes both that red oil could reach a waste tank after traveling through transfer pipes together with the alkaline waste without mixing taking place, and also that it was not involved in any tank-to-tank transfer operations which would have resulted in mixing with the alkaline waste. Thus, to model more realistic conditions, samples of red oil were also stirred for varying periods with the simulant materials. Additionally, the volume ratios of red oil: simulant in our laboratory reactions were typically 1:20. This model approximates a 500 000 gallon tank containing 25 000 gallons of red oil and, to say the least, represents a bounding worst-case scenario.

The waste simulants did not contain radioactive components, and thus the effects of the intense radiolytic environments within the waste tanks were not taken into account. However, chemical decomposition of red oil in an alkaline environment was expected to be the predominant mechanism and to greatly outweigh radiolytic effects over a time period of hours or days.

2. Decomposition studies

2.1. Introduction

Decomposition studies involved a number of variable parameters: (i) pH of the waste simulant; (ii) decomposition temperature; (iii) contact time between simulant and red oil; (iv) use of static (non-stirred) or stirred contact; (v) changing from hydroxide to carbonate as the predominant basic species in the simulant; (vi) surface/volume ratio of contact.

Removal of energetic content from red oil may be accomplished in one of two ways, depending upon whether a metal complex or a purely organic molecule is being considered. The energetic content of the adduct $UO_2(NO_3)_2(TBP)_2$ arises from the presence of both oxidizing nitrate groups and organic butyl groups (potential fuel) coordinated to a uranium metal center. Contact of $UO_2(NO_3)_2(TBP)_2$ with an alkaline waste material (containing sodium hydroxide and sodium carbonate, among other salts) results in uranyl ion (UO_2^{2+}) being strongly complexed by hydroxide and/or carbonate ion, displacing both nitrate and TBP from the coordination sphere of uranium. Nitrate ion enters the aqueous phase as sodium nitrate, and TBP remains in the organic layer floating on the aqueous phase. Contact between nitrate groups

and organic material (discounting emulsion formation) is now limited to the organic/aqueous interface.

In the case of energetic organic molecules such as nitrated hydrocarbons or organo-nitrate compounds, removal of the oxidizing group requires cleavage of a carbon–nitrogen or carbon–oxygen bond, which would not be expected to occur as rapidly as the displacement reaction discussed above. In a waste tank environment, there are two principal decomposition routes: (a) replacement of the oxidizing group by a hydroxyl group in a hydrolysis reaction; (b) direct cleavage of the C–N or C–O bond by radiolysis. Our studies modeled only the first of these reactions.

2.2. *Experimental procedures*

The principal components of Hanford waste tank material are sodium hydroxide, sodium nitrate, sodium nitrite, sodium aluminate and sodium carbonate, together with other metal salts and organic complexants. The experimental studies employed several simulant compositions (Tables 1 and 2) [12] which are representative of the majority of both single-shell and double-shell tank wastes.

In a typical static (non-stirred) decomposition reaction, 5 ml of red oil was layered on top of either 100 ml or 200 ml of the waste simulant contained in a volumetric flask (contact area $1.2\,cm^2$), a measuring cylinder ($4.9\,cm^2$) or an Erlenmeyer flask

Table 1
Summary of waste simulants used in degradation studies

	1-36-1 (101-SY simulant)	1-37-2	1-37-3	1-38-1	1-41-2
NaOH	27.50[a]	80.0	40.0	2.00	10.0
$NaNO_3$	52.2	221	110.5	297.5	170
$NaNO_2$	63.0	151.8	75.5	55.2	138
Na_2CO_3	22.3	42.4	21.2	116.6	21.2
$NaAlO_2$	39.1	123	61.5	12.3	41.0
KNO_3	3.37	–	–	–	–
Na_4EDTA	21.2	58.4	29.0	159.4	58.0
$Na_3PO_4 \cdot 12H_2O$	10.25	–	–	7.6	–
KCl	5.2	–	–	–	–
Na_2SO_4	2.37	–	–	14.2	–
NaF	0.25	–	–	2.1	–
$NaCOOCH_3$	–	–	–	–	–
$Na_2C_2O_4$	–	–	–	–	–
NaCOOH	–	–	–	–	–
$Fe(NO_3)_3 \cdot 9H_2O$	0.81	–	–	–	–
$Cr(NO_3)_3 \cdot 9H_2O$	12.6	–	–	–	–
pH	13.75	13.90		13.15	13.15
Density (g cm^{-3})		1.42		1.32	1.26

[a] Figures reported are grams of constituent per liter of simulant.

Table 2
Summary of waste simulants used in degradation studies

	1-44-1	1-44-2/1-45-1/ 1-48-1 (titrated with HNO_3 to desired pH)	1-55-1 (107-AN simulant)	1-57-1 (103-C simulant)
NaOH	–	2.00	40.0	–
$NaNO_3$	170[a]	297.5	325.5	11.9
$NaNO_2$	103.5	55.2	73.85	45.6
Na_2CO_3	70	116.6	132.5	42.4
$NaAlO_2$	82	12.3	3.89	–
KNO_3	–	–	5.45	–
Na_4EDTA	80	159.4	37.7	12.8
$Na_3PO_4 \cdot 12H_2O$	21	7.6	1.90	7.6
KCl	–	–	–	–
Na_2SO_4	–	14.2	20.0	41.2
NaF	–	2.1	–	–
$NaCOOCH_3$	–	–	60.6	–
$Na_2C_2O_4$	–	–	59.9	20.7
NaCOOH	–	–	60.6	–
$Fe(NO_3)_3 \cdot 9H_2O$	–	–	10.9	0.81
$Cr(NO_3)_3 \cdot 9H_2O$	–	–	–	–
NaCl	–	–	5.85	–
$NiNO_3 \cdot 6H_2O$	–	–	–	0.58
pH	13.20	1-44-2 = 10.29 1-45-1 = 8.35 1-48-1 = 7.12	11.36	9.27
Density (g cm^{-3})	1.33	1.32	1.46	1.12

[a] Figures reported are grams of constituent per liter of simulant.

(30.5 cm^2), and left undisturbed either at room temperature or on a hot plate at elevated temperature. The colors of the decomposed organic materials spanned a wide range from almost colorless, through yellow and orange, to an intensely deep red, although no correlation exists between the color of the decomposed sample and its energetic content.

In a stirred decomposition reaction, 5 ml of red oil was added to 100 ml of vigorously stirred waste simulant. After a suitable time period the organic material was extracted from the aqueous phase by means of a hexane extraction, and the hexane removed to leave an oil which was typically yellow or orange in color.

2.3. Observations

Initial studies employed waste simulant 1-37-2 (see Table 1 for composition). Under static conditions, contact of red oil with this simulant produced an immediate orange/yellow gelatinous precipitate at the organic/aqueous interface, which was

formed by reaction of uranyl species in the organic phase with sodium hydroxide in the aqueous phase. The quantity of gelatinous material gradually increased as more uranium was precipitated, and the organic/aqueous interface eventually became clogged with precipitate. The aqueous simulant phase often took on a deep orange or red color during contact with the red oil.

A second simulant closely matched recent analysis results for the supernatant liquid in tank 107-AN (simulant 1-55-1, Table 2). Contact of red oil with this simulant produced very little precipitate due to the low hydroxide concentration. In this case, uranium is complexed by carbonate ion as soluble uranyl carbonate species, rather than insoluble uranyl hydroxide, and is subsequently transported into the aqueous phase.

Another simulant approximated the composition of the supernatant liquid in tank 103-C (sample 1-57-1, Table 2). Due to the low density of this simulant ($1.12 \, \text{g cm}^{-3}$), many red oil samples sank beneath the aqueous phase and began to decompose as they sat at the bottom of the flask. After 24 h at room temperature approximately one third of the organic phase had risen to the surface and was floating on the simulant whilst the remainder was at the bottom of the flask in the form of oily orange globules covered in a thin yellow crust. It is proposed that removal of uranium from the organic phase as soluble uranyl carbonate species decreases the density of the organic material until it becomes less dense than the aqueous phase, at which point it floats to the surface. Use of the same simulant at higher temperature (65 °C) resulted in the red oil initially sinking beneath the simulant, but thermal currents continually carried globules of the organic phase up to the surface of the liquid and back down again. All of the organic phase was floating on the aqueous phase after a period of 24 h.

2.4. NMR studies

The decomposed organic samples were subjected to ^{1}H, ^{13}C and ^{31}P NMR analysis. Many of the samples showed resonances in their ^{13}C NMR spectra which could not be assigned to either TBP or diluent. The position of these resonances in the region 82–92 ppm, together with the significant nitrogen content found by elemental analysis and the absorptions seen in their infra-red spectra, led to assignment of the resonances to the same classes of nitrogen-containing organic compounds (nitro, nitrite, nitroso and/or nitrate) as seen in the original red oil samples. A resonance at ca. 179 ppm in the samples is assigned to a carboxylic acid (the corresponding resonance is seen at 180.35 ppm in lauric acid, $CH_3(CH_2)_{10}COOH$, and at 180.55 ppm in butyric acid, $CH_3(CH_2)_2COOH$ [13]). The relative intensity of the ^{13}C resonances assigned to degraded solvent components, compared with those due to TBP and diluent, suggested that the degradation products were present only in low concentration.

2.5. IR studies

Neither TBP nor the hydrocarbon diluents show any absorptions in their infra-red spectra between 1465 and ca. $2800 \, \text{cm}^{-1}$, and thus any bands seen in this region for the decomposed samples may be assigned to either degraded diluent products or residual nitrate ion. In all decomposed organic samples, absorptions due to diluent

degradation products were observed at ca. 1715, 1627 and 1550 cm^{-1}, and were assigned to carboxylic acids (1715 cm^{-1}), nitrates or nitrites (1627 cm^{-1}) and nitro compounds (1550 cm^{-1}).

2.6. Elemental analysis

Combustion analyses were obtained for carbon, hydrogen and nitrogen for all of the decomposed samples, and these analyses revealed the presence of nitrogen in quantities ranging from 0.35 to 5.0%. Using the arguments put forward for the nitrogen content of red oils themselves [14], the majority of nitrogen present in the decomposed materials is expected to be present either as nitrate ion coordinated to an organic-soluble metal complex such as $UO_2(NO_3)_2(TBP)_2$, or within an organic molecule formed by solvent nitration.

During one series of decomposition experiments, samples of one red oil material were stirred at room temperature with portions of the same waste simulant for varying periods of time. Each decomposed sample was analyzed for nitrogen content and this value plotted versus $\log_e$(decomposition period). This plot indicated that the nitrogen content of the red oil would be reduced to zero after approximately 1050 h (45 d) of continuous stirring. Thus although the hydrolysis of nitrated hydrocarbon components by alkaline waste requires a considerable period of time, this period is relatively short compared to the contact times of many years expected within a waste tank environment.

In the case of static decompositions, removal of nitrogen-containing components is somewhat slower. Thus after 30 d of undisturbed contact with a waste simulant containing 2 M sodium hydroxide, the nitrogen content of a decalin-containing red oil sample had dropped from 1.88% to 0.49%, while 12 d of contact with a pH 10.29 simulant reduced the nitrogen content of a Spray Base red oil from 3.65% to 1.65%.

2.7. ICP studies

ICP spectroscopy was used to examine aqueous phases for uranium content after contact with red oil materials. Analyses showed that for hydroxide-rich waste simulants the aqueous phase contained < 1 ppm soluble uranium, indicating that uranium was precipitated as insoluble species. Aqueous phases with high carbonate concentration contained several hundred ppm of soluble uranium, confirming that uranyl ion is efficiently transferred across the organic/aqueous interface as soluble carbonate species even in non-stirred systems.

3. Energetic studies

3.1. Experimental results

After exposure to waste simulant, the 85 decomposed organic samples were subjected to DSC analysis in the temperature range from 25 °C to 350 °C under an

Table 3
Summary of degradation experiments

Sample	Initial energy ($J\,g^{-1}$)	Final energy ($J\,g^{-1}$)	Percentage of initial energy lost	Stirring	pH of simulant	Contact time (h)	Surface area of contact
1-33-1	125	0	100	Yes	13.90	17	–
1-34-1	83	0	100	Yes	13.90	18	–
1-35-4	81	0	100	No	13.90	96	High
1-37-1	61	0	100	Yes	13.75	72	–
1-38-1	125	0	100	Yes	13.90	216	–
1-38-4	125	1	99	Yes	13.15	48	–
1-39-1	103	0	100	Yes	13.90	216	–
1-39-2	103	10	90	Yes	13.15	120	–
1-40-2	217	46	79	Yes	13.15	24	–
1-41-1	217	0	100	No	13.90	720	High
1-41-2	217	0	100	Yes	13.15	24	–
1-42-1	83	5	94	No	13.90	912	High
1-42-2	217	47	78	No	13.15	168	Low
1-42-3	190	8	96	Yes	13.15	5	–
1-43-2	190	2	99	Yes	13.15	1	–
1-43-3	190	0	100	Yes	13.15	0.25	–
1-43-4	190	4	98	Yes	13.15	65	–
1-44-1	190	14	93	No	13.15	29.5	High
1-44-2	220	0	100	Yes	13.15	5.5	–
1-44-3	186	17	91	Yes	10.29	18	–
1-44-4	220	0	100	No	13.15	6	High
1-44-5	220	0	100	Yes	13.15	30	–
1-45-1	186	4	98	Yes	8.35	2	–
1-45-2	220	16	93	Yes	8.35	3	–
1-45-3	190	9	95	Yes	8.35	2	–
1-45-4	186	106	43	No	13.15	96	Low
1-46-1	186	0	100	No	8.35	96	Low
1-46-2	220	31	86	No	8.35	96	Low
1-46-3	190	41	78	No	8.35	96	Low
1-46-4	190	20 (av.)	89	No	8.35	161	Low
1-46-5	220	0	100	No	10.29	166	Medium
1-47-1	186	18	90	No	10.29	94	Medium
1-47-2	186	68	63	No	13.90	144	Low
1-47-3	220	0	100	No	13.15	144	Low
1-49-1	186	67	64	No	8.35	244	Low
1-49-2	190	2	99	No	8.35	244	Low
1-49-3	186	99	47	No	7.12	69	Low
1-49-4	220	0	100	No	7.12	69	Low
1-49-5	220	0	100	No	7.12	69	Low
1-49-6	190	88	54	No	7.12	69	Low
1-50-1	197	10	95	No	7.12	69	Low
1-50-2	197	76	61	No	7.12	69	Low
1-50-3	186	48	74	No	8.35	244	Medium
1-50-4	186	56	70	No	8.35	168	Medium
1-50-5	197	0	100	Yes	7.12	96	–
1-51-1	186	24	87	No	7.12	95	High
1-51-2	197	3	98	No	7.12	96	High

Table 3 (continued)

Sample	Initial energy (J g⁻¹)	Final energy (J g⁻¹)	Percentage of initial energy lost	Stirring	pH of simulant	Contact time (h)	Surface area of contact
1-51-3	197	34	83	No	7.12	96	Medium
1-51-4	186	12	94	No	10.29	287	High
1-51-5	103	0	100	Yes	7.12	0.16	–
1-52-1	160	0	100	Yes	7.12	0.08	–
1-53-1	197	87	56	No	13.90	111	Low
1-53-2	197	59	70	No	13.15	42	Low
1-53-3	83	29	65	No	7.12	91	Medium
1-53-4	197	123	38	No	13.90	110	Low
1-53-5	186	56	70	No	13.15	91	Low
1-54-1	197	95	52	No	13.15	111	Low
1-54-2	197	107	46	No	7.12	110	Low
1-54-3	83	38	54	No	13.90	91	Medium
1-54-4	331	236	29	No	13.90	96	Low
1-54-5	125	123	1	No	13.90	96	Low
1-55-1	186	59	68	No	11.36	90	Medium
1-55-2	217	0	100	No	7.12	89	Low
1-55-3	190	56	71	No	11.36	90	Medium
1-56-1	81	32	60	No	11.36	108	Low
1-56-2	30	0	100	No	11.36	108	Low
1-56-3	217	0	100	No	11.36	89	Low
1-56-4	217	0	100	No	11.36	108	Low
1-56-5	217	0	100	No	7.12	89	Low
1-56-6	331	248	25	No	11.36	108	Low
1-57-1	125	0	100	No	11.36	108	Low
1-57-2	186	68	73	Yes	11.36	94	–
1-57-3	217	80	63	Yes	11.36	94	–
1-58-1	186	90 (av.)	54	No	9.27	34	Low
1-58-2	217	9	96	No	9.27	34	Low
1-58-3	190	40	79	Yes	9.27	29	–
1-59-1	186	52	72	Yes	9.27	29	–
1-59-2	190	51	73	No	9.27	46	Low
1-59-3	220	58	74	No	9.27	46	Low
1-59-4	220	63	71	No	9.27	46	Low
1-60-1	190	61	68	No	9.27	46	Low
1-60-2	217	159	27	Yes	13.75	1	–
1-60-3	217	158	27	No	13.75	25	High
1-60-4	217	17	92	Yes	13.75	0.25	–
1-60-5	217	34	84	Yes	13.75	2	–

atmosphere of air. Taking the results as a whole, the exposure of red oil to the simulated waste materials significantly reduced or completely removed the initial energy content in the vast majority of cases, leaving predominantly endothermic events caused by vaporization of water, diluent and TBP, or the thermal decomposition of complexes containing butylphosphate groups (results are summarized in Table 3).

In a small number of cases the decomposed samples still showed significant energy content after contact with waste simulant. Thus after a static 111 h contact at 55 °C, sample 1-54-1 (Table 3) showed an exotherm of 95 J g^{-1} at 248 °C, compared with an initial energy content of 197 J g^{-1}, and a static 69 h contact at 55 °C reduced the energy content of sample 1-49-6 (Table 3) from 190 to 88 J g^{-1}. Several factors should be borne in mind when considering these results: (a) The energy remaining within these samples is well below the level recognized as safe for interim storage within a waste tank; (b) As well as exothermic events, the samples showed endotherms which were often of greater magnitude and occurred at lower temperatures than the exothermic excursions; (c) The exotherms in the decomposed materials were usually high-temperature events (> 200 °C), and those at lower temperatures were of small magnitude (< 20 J g^{-1}); (d) Repeated DSC measurements of the decomposed samples strongly suggest that energy content continues to fall with time, even after removal from contact with the waste simulant. This is highly significant with respect to the Hanford waste tanks, where many years have already elapsed since the last addition of waste to many of the tanks.

In two of the cases studied, it was initially found that the decomposed material appeared to possess a higher energy content than the original red oil sample. In the first case, the decomposed organic material (referred to as sample A in the discussion below) showed an exotherm of 11 J g^{-1} at 24 °C, an exotherm at 72 °C (246 J g^{-1}), and an exotherm at 246 °C (205 J g^{-1}) giving a total of 462 J g^{-1}, whereas the original red oil sample showed a total energy release of 200 J g^{-1}. In the second example, the decomposed material (referred to as sample B below) showed an exotherm of 201 J g^{-1} at 78 °C and an exotherm of 40 J g^{-1} at 252 °C (total 241 J g^{-1}), compared with 186 J g^{-1} for the original red oil sample. Analytical data for these two samples did not reveal any significant differences when compared to results for samples showing much lower energetic events. Nitrogen content of the two samples (1.58% for sample A and 2.23% for sample B) was on a par with many other decomposed materials, and the quantity of nitrated diluent components observed by NMR and IR spectroscopy was in line with many other less energetic samples. Since the apparent increase in energy content of these two samples was out of line with all of the other decomposition experiments, a more detailed investigation of these samples was warranted.

DSC analysis of further portions of samples A and B gave results which were totally different from the initial measurements: an exotherm of magnitude 23 J g^{-1} (at 257 °C) for sample A and an exotherm of 23 J g^{-1} (at 255 °C) for sample B. The discrepancy between measurements raised the question of whether the original DSC measurement had been in error or whether the samples had continued to undergo decomposition in the time period between the two DSC analyses (this interval was 66 d for sample A and 53 d for sample B). To provide additional data, 16 of the other 83 decomposed samples were randomly selected and re-submitted for DSC analysis. Of these 16 samples, 15 showed significant reductions in energy content compared with their initial measurement. Thus even after removal from direct contact with the waste simulant, the organic materials appear to undergo decomposition reactions which reduce their energy content.

Next, the experimental procedures which led to the formation of samples A and B were repeated. In the case of sample A, the decomposition was repeated under identical conditions on eight occasions, after which DSC analysis of the organic materials showed exotherms totaling 0, 35, 28, 38, 28, 8, 17 and 9 J g^{-1}, respectively (average 20 J g^{-1}). These results are in complete contrast to that obtained for sample A above, which showed total exotherms of 462 J g^{-1}. The experimental procedure which produced sample B was also repeated on eight occasions and DSC results showed exotherms totaling 9, 123, 6, 168, 160, 74, 107 and 72 J g^{-1}, respectively (average 90 J g^{-1}), although none of the samples exhibited the large (201 J g^{-1}) exotherm seen at 78 °C in sample B above. It is difficult to propose an explanation as to why the results from eight identical experiments are in such wide variance, since the reproducibility of the DSC instrument in duplicate runs is generally within ± 10%, but it can clearly be seen from these experiments, and from those described above for sample A, that the significant *increase* in energy content which was of initial concern does *not* appear to be a reproducible phenomenon.

3.2. Summary of results

From first principles, the following variable conditions would be expected to have an influence upon the decomposition of red oil in contact with waste simulant:

% of initial energy lost during contact
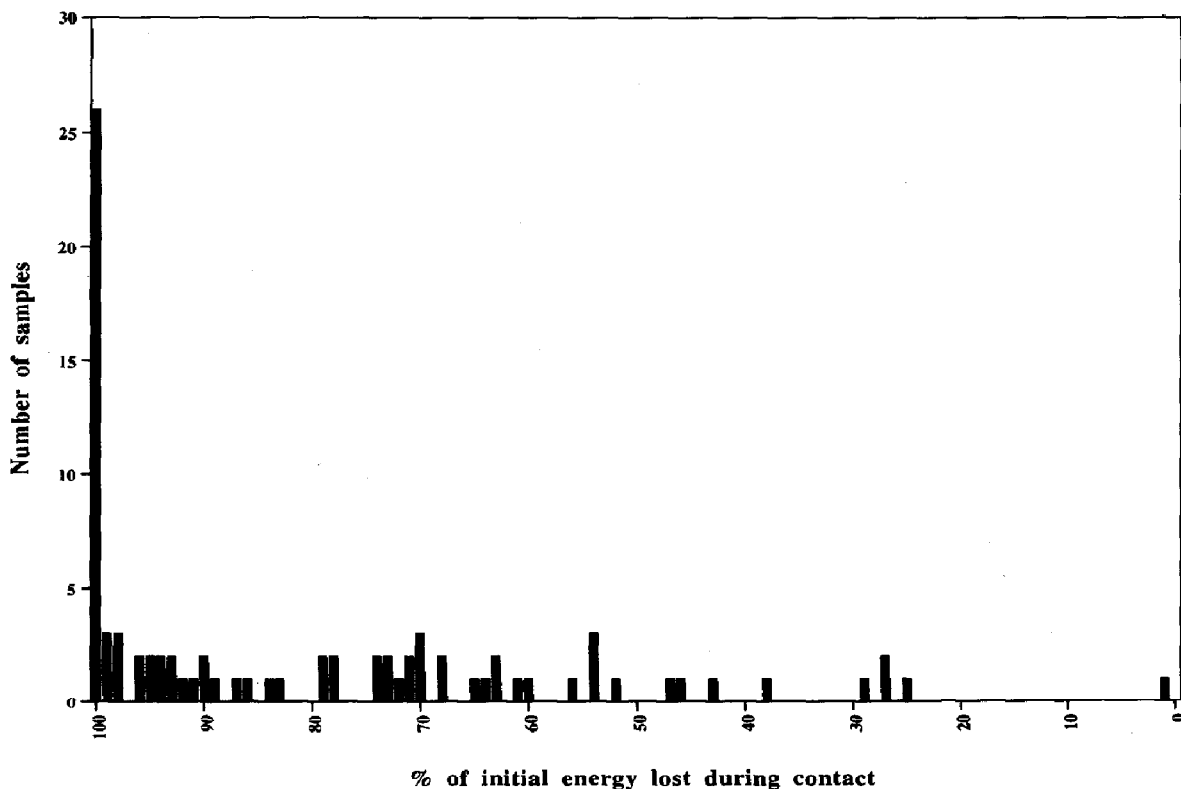
Fig. 1. Summary of percentage energy loss in decomposition experiments.
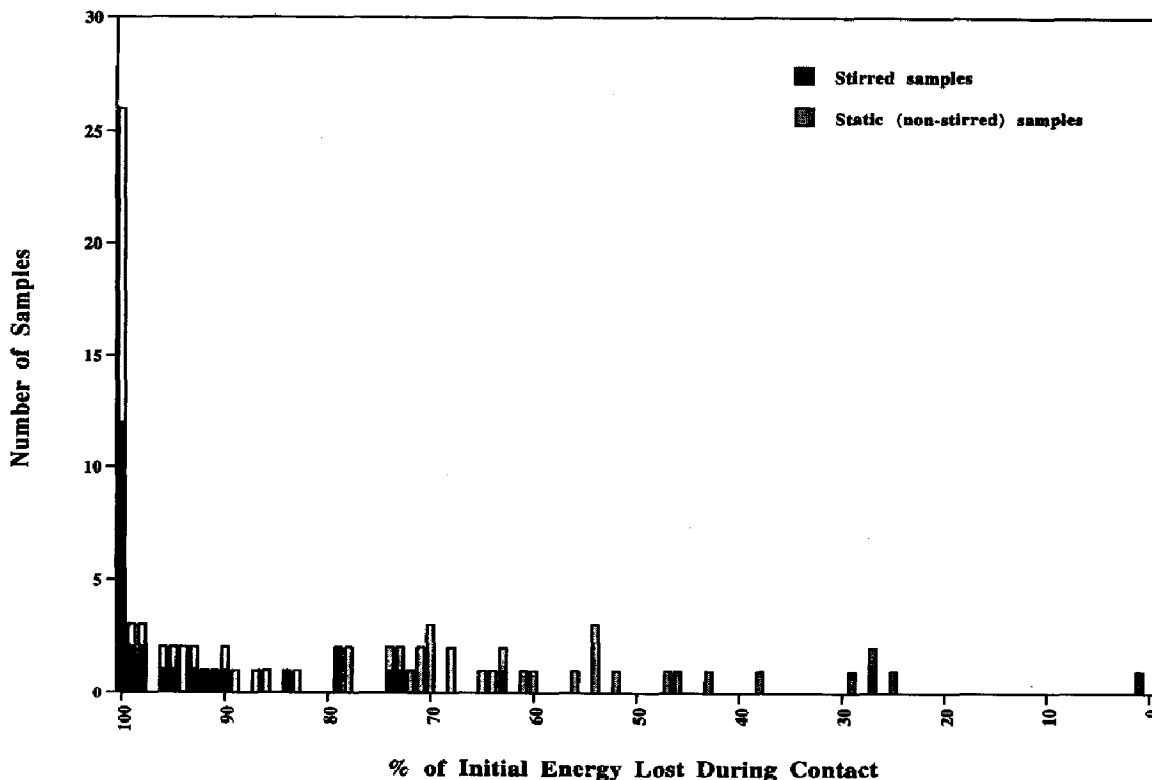
Fig. 2. Summary of decomposition experiments: stirred versus static contacts.

(1) *Temperature.* Increased temperatures should lead to more rapid hydrolysis of energetic organic components and more rapid decomposition of red oil samples.

(2) *Agitation.* Stirring the red oil sample into the waste simulant should assist decomposition by bringing the aqueous phase into intimate contact with small droplets of red oil.

(3) *Surface/volume ratio* (for non-stirred samples) – For a constant simulant volume, increasing the surface area of contact should lead to more rapid decomposition.

(4) *pH* – An aqueous phase of high pH (high OH^- concentration) should produce more rapid decomposition than a low pH aqueous phase, other conditions being equal.

A graphical representation of all 85 decomposition experiments is shown in Fig. 1, and the results are broken down further to show the effects of agitation (Fig. 2), surface area (Fig. 3) and pH (Fig. 4) upon decomposition.

(1) *Temperature.* The expected observation that higher temperatures should produce more rapid decomposition of red oil was not entirely supported by experimental results. The data suggest that the relationship between removal of energy content and temperature in these complex systems is not as straightforward as might have been expected.

(2) *Agitation.* Stirring the red oil sample into the waste simulant clearly resulted in more effective decomposition than for undisturbed reactions. From Fig. 2 it can be

seen that, of the 27 degraded samples which showed the smallest energy loss following contact with waste simulant, 25 resulted from static (non-stirred) contacts.

(3) *Surface area.* The expected observation that low surface area contacts produce less effective decomposition appeared to be borne out by the results. Fig. 3 reveals that, of the 17 non-stirred samples which showed the smallest energy loss on contact with waste simulant, 15 resulted from contacts in vessels of lowest cross-sectional area.

(4) *pH.* Any correlation between pH of a waste simulant and effectiveness of decomposition appeared tenuous at best (Fig. 4). While hydroxide ion is more effective than carbonate ion for decomposition of energetic organic molecules, carbonate ion is at least as good as, if not better than, hydroxide for decomposition of energetic uranyl-based complexes since it does not lead to precipitate formation. The presence of a high concentration of hydroxide ion (high pH) can produce gelatinous precipitates which can clog the organic/aqueous interface. Thus the balance between hydroxide and carbonate concentrations appears more important than simply the measured pH of a waste material.
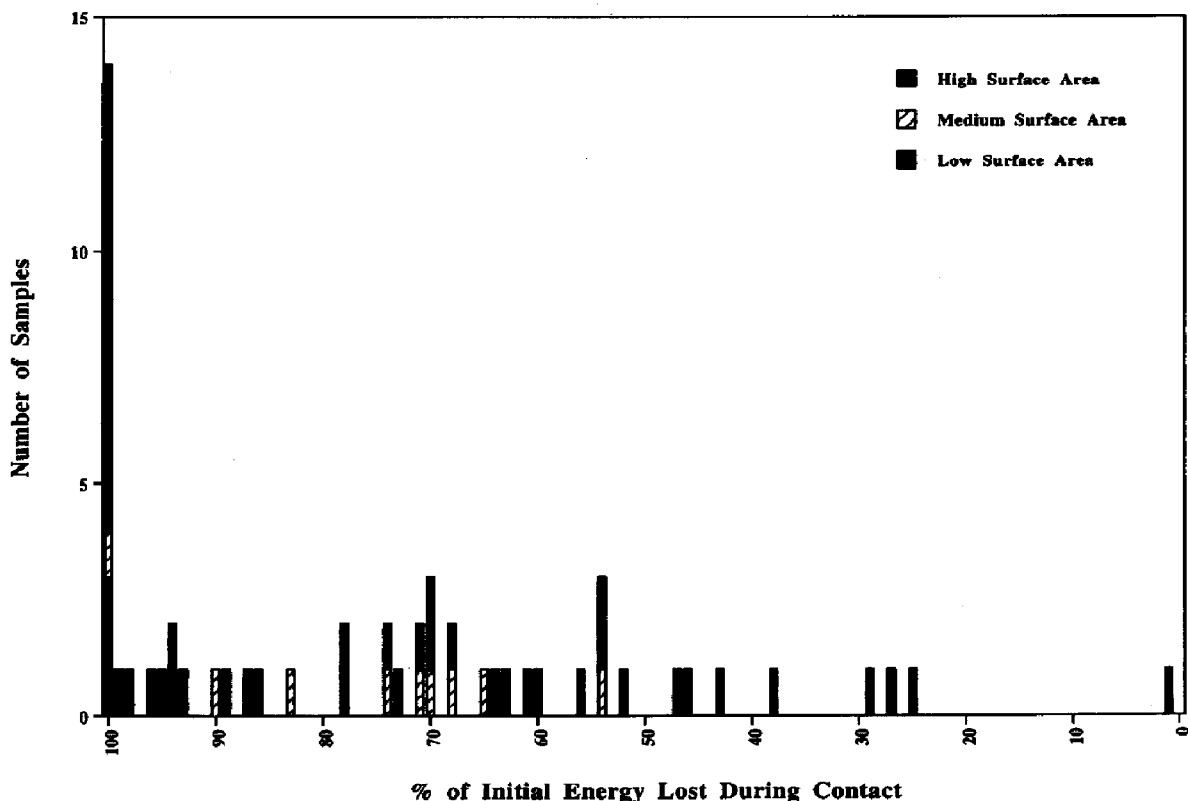

Fig. 3. Summary of decomposition experiments: influence of surface area of contact.
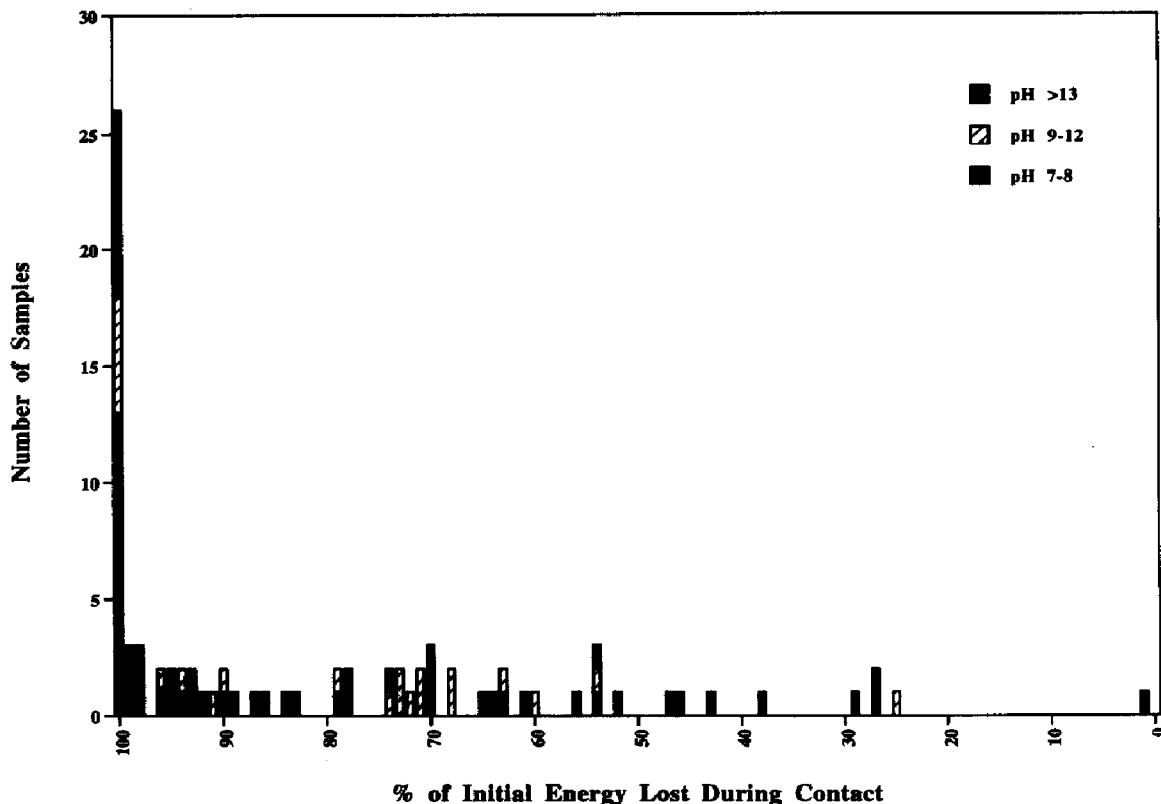
Fig. 4. Summary of decomposition experiments: influence of pH of waste simulant.

4. Discussion

4.1. Introduction

Previous workers investigating the degradation of hydrocarbon diluents by nitric acid and/or radiolysis [16–21] have identified organic nitro (RNO_2), nitroso (RNO), nitrite (RONO) and nitrate ($RONO_2$) complexes, carboxylic acids (RCOOH), hydroxamic acids (RCONHOH), alcohols (ROH) and ketones ($RR'C=O$), and similar components are also expected to be present within typical red oil samples. Of these compounds, the nitrogen-containing organic materials would be the most undesirable waste tank components, since they are energetic species in their own right [15]. Therefore, the fate of these species in a typical waste material must be considered.

4.2. Decomposition within waste tanks

Previously, mention has been made of 'possible deposit of potentially explosive nitro compounds in the underground storage tanks [22]' and Brown [23] has stated that organic nitrites and nitrates are easily hydrolyzed by acids or alkalis whereas nitro compounds cannot be hydrolyzed. Borsheim [11] states that 'the small quantity

of nitrated diluent constituents (in red oil) are likely hydrolyzed' by the waste tank contents, and 'any nitrogen-containing diluent components are expected to slowly hydrolyze to the corresponding alcohol when exposed to dilute base'. Martin [24] reports that 'if (nitrate esters) were formed in the separation process cycle they would not survive the alkalinity of the tank waste', and that the 'possibility for (nitrate ester) survival and concentration in the waste is negligible'.

Alkyl nitrates within the waste material are expected to decompose through a hydrolysis reaction with hydroxide ion to produce the corresponding alcohol (Eq. (1)):
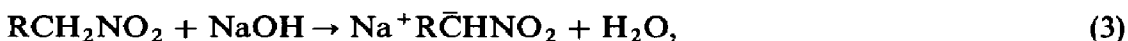
$$RONO_2 + OH^- \rightarrow R-OH + NO_3^-. \tag{1}$$

Literature data are available for the rates of both hydrolysis and thermal decomposition of alkyl nitrates [25–35].

Alkyl nitrites are relatively easily decomposed to form carbonyl compounds, alcohols and carboxylic acids, and can also react with water in an equilibrium reaction (Eq. (2)):

$$RONO + H_2O \rightleftharpoons ROH + HNO_2. \tag{2}$$

This reaction would be expected to be driven to the right in an alkaline environment, due to the neutralization of nitrous acid. Rates of hydrolysis of alkyl nitrites in both acidic and basic media are also available in the literature [36–40].

Contact of primary and secondary nitroalkanes with a high pH waste material is likely to result in deprotonation rather than hydrolysis. The product of this reaction is a nitronate salt (Eqs. (3) and (4)):

$$RCH_2NO_2 + NaOH \rightarrow Na^+R\bar{C}HNO_2 + H_2O, \tag{3}$$

$$RR'CHNO_2 + NaOH \rightarrow Na^+RR'\bar{C}NO_2 + H_2O. \tag{4}$$
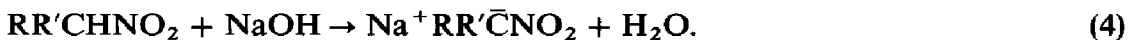
Tertiary nitro compounds cannot undergo this reaction owing to their lack of an α-hydrogen atom. Salts of the nitroparaffins (nitronate salts) are highly colored, and the colors are reported to transfer into the aqueous phase upon contact with a sodium carbonate wash solution [41]. The nitronate salt may subsequently enter into a number of reactions:

(i) The nitronate anion may coordinate to a metal center [42, 43] although this reaction is unlikely to occur in the waste tanks since virtually all metal ions (except sodium) are in the form of an oxide/hydroxide sludge;

(ii) If the nitronate anion enters an environment of low pH (i.e. if the waste were to be re-acidified), it may enter into a Nef reaction [44], with the formation of a ketone (Eq. (5)).

$$Na^+RR'\bar{C}NO_2 + H^+ \rightarrow RR'C=O + H_2O + N_2O. \tag{5}$$
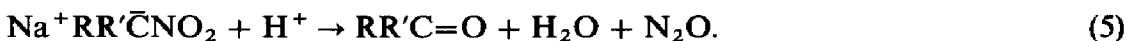
The Nef reaction also occurs under entirely basic conditions [45], but the required conditions do not exist in a typical waste tank;

(iii) Further nitration of the nitronate anion may occur. A primary or secondary nitro compound treated with aqueous sodium hydroxide and aqueous sodium nitrite

in the presence of a mild oxidant [such as iron(III) or silver(I)] can undergo nitration to produce a gem-dinitro compound [RCH(NO$_2$)$_2$ or RR'C(NO$_2$)$_2$] [46, 47]. However, no evidence exists to suggest that this reaction has taken place within an actual waste tank. The hydrolysis rates of such highly-nitrated materials exposed to aqueous sodium hydroxide have also been studied [48].

Experimental data available for radiolysis of organic materials suggest that bond cleavage reactions are common, and that radiolysis will perform a function similar to hydrolysis in the decomposition of energetic organic molecules. The effects of radiolysis upon nitroalkanes has been the subject of a limited amount of experimental study. Reactions such as oxidative denitration, which result in cleavage of the carbon–nitrogen bond and thus substantial lowering of energetic content, have been reported (Eq. (6)):

$$RNO_2 + \dot{O}H \rightarrow \dot{R}(OH)NO_2 \rightarrow R\dot{O} + HNO_2 \tag{6}$$

and the rate of reaction of solvated electrons (e_{aq}^-), hydrogen radicals (H$^{\bullet}$) and hydroxyl radicals (OH$^{\bullet}$) with some nitro and nitroso compounds have been studied [49–55]. As reported recently, however [21], the literature does not contain sufficient information to make detailed analyses of the effects of radiolysis upon a system as complicated as a waste simulant/red oil mixture.

The results of the decomposition studies suggest that although hydrolysis of nitrogen-containing species within red oil takes a considerable period of time, certainly many weeks and possibly several months, the concentration of these species is continually falling as contact time increases. Following a contact period of many years in a typical waste tank, and if the effects of radiolysis (which tends to fragment organic materials) are also included, it would be difficult to propose that concentrations of nitrated hydrocarbons sufficient to produce any type of energetic event could still exist.

5. Conclusions

A total of 85 samples of red oil were subjected to decomposition by contact with waste simulant materials, using a wide range of conditions: (a) pH ranging from 13.90 to 7.12; (b) temperatures from 20 °C to 65 °C; (c) stirred and non-stirred (static) contact periods; (d) low, medium and high surface area contacts; (e) contact periods ranging from 5 min to 38 d. In the vast majority of cases, the energetic content following contact with the waste simulant was *substantially* lower than the energy content of the original red oil material, and in many cases the energy content had been reduced to zero after contact periods of only a few hours.

The majority of the decomposition studies involved contact between red oil and waste simulant materials for a period of a few hours or days, and thus provide a 'snapshot' picture of the initial steps in the decomposition process. When applying these short-term results to actual waste tank environments, consideration should be given to the fact that materials have been in contact with one another in the tanks for many years or even decades. Since contact times of a few hours or days result in

a significant reduction in energy content of the red oils , it would only be logical to conclude that extending the contact period to weeks, months and years would result in further reductions in energy content until the materials no longer showed any exothermic behavior.

6. Experimental details

Infra-red spectra were recorded on a Bio-Rad FTS40 instrument between KBr plates. Elemental analyses were performed by combustion in a Perkin-Elmer 2400 CHN analyzer. Differential Scanning Calorimetry and Gas Chromatography/Mass Spectrometry results were obtained by Monarch Analytical Laboratories, Maumee, OH. DSC results were obtained between room temperature and 350 °C at a heating rate of 10 °C/min under an atmosphere of air or nitrogen as required. In all cases the temperatures given for exothermic or endothermic reactions are the values for peak energy output, and not the onset temperature of reaction. Red oil samples were prepared as described previously [14].

6.1. Decomposition studies

Procedure A (Stirred, room temperature decomposition). One hundred millilitres of simulant was placed into a 250 ml Erlenmeyer flask together with a Teflon-coated stir bar. Vigorous stirring was begun and 5 ml of a red oil material was added using a teat pipette. After stirring for the required amount of time, the simulant/organic mixture was poured into a separating funnel containing 150 ml of hexane. The funnel was stoppered and shaken vigorously, at which point the hexane layer became pale yellow. The hexane layer was separated from the aqueous layer and hexane removed to leave a liquid which ranged in color from yellow to deep orange.

Procedure B (Static decomposition). One hundred millilitres of simulant was placed into a vessel of suitable cross-sectional area, to provide differing surface-to-volume ratios. 5 ml of red oil was added to form an even layer on the surface of the simulant. After standing for the required amount of time, the organic layer was carefully removed using a teat pipette.

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