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THIS TEST PLAN IS A CONTINUATION OF THE INVESTIGATIONS OF WET OXIDATION OF ORGANICS IN BASIN F. THE BROAD OBJECTIVE OF THIS TEXT PROGRAM IS TO ESTIMATE THE DEGREE TO WHICH WET OXIDATION UNDER VARIOUS REACTION CONDITIONS WILL DETOXIFY THE WASTEWATER IN BASIN F, AND THUS SIMPLIFY ITS ULTIMATE DISPOSAL. SPECIFICALLY, THE FIRST OBJECTIVE WILL BE TO MEASURE THE DEPENDENT VARIABLE AND TO ASSOCIATE CHANGES IN THEM WITH THE VARIOUS WET OXIDATION REACTION CONDITION. THE SECOND OBJECTIVE WILL BE TO OBTAIN A PRELIMINARY ESTIMATE OF THE COST FOR COMMERCIAL EQUIPMENT AS A FUNCTION OF CONVERSION LEVEL AND THROUGH-PUT RATES.

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AT

ROCKY MOUNTAIN ARSENAL

Supporting Program Under ITARMS 1.05.57

By

Process Development and Evaluation Division of
The Contamination Control Directorate

ROCKY MOUNTAIN ARSENAL
Commerce City, Colorado 80022

REPORT NO. 10557-4

JULY 1978

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INTRODUCTION

This test plan is a continuation of the investigation of wet oxidation of organics in Basin F, in accordance with instructions from Colonel Damon D. Wingfield, Assistant Project Manager for Installation Restoration, dated 24 April 1978.

The term "wet oxidation" describes oxidation that occurs when oxygen (air), organic matter, and liquid water are brought into contact at temperatures between about 400°F and 700°F. Above 700°F (its critical temperature) water is a gas regardless of pressure, and the wet oxidation reaction mechanism becomes inoperative.

Different organic compounds vary widely in their rates of oxidation but in principle all the carbon can be oxidized to CO_2; halogen atoms in the organic compounds become the corresponding halogen acids or salts thereof, depending on pH. In practice, total oxidation is prevented by the decreasing reaction rates associated with low organics concentrations.

Basin F waste water at Rocky Mountain Arsenal (RMA) has been characterized in detail in Reference 3. It contains about 16 percent total dissolved solids in a solution measuring 25,000 ppm Chemical Oxygen Demand (COD) and 22,000 ppm Total Oxidizable Carbon (TOC). The oxidizable carbon is present in compounds that were discarded during the manufacture and handling of pesticides, nerve gas, and various other chemicals. As a class, the organic residues are considered to be toxic at part-per-billion levels, although there is considerable variance among individual compounds.

Because of the comparatively high concentration of organics present, a gallon of Basin F waste potentially can contaminate a large volume of pure groundwater in the aquifer underlying the Basin. For example, the dissolved

TOC level of groundwater averages .7 ppm (based on a study of 50 samples, Reference 4); if 1.4 ppm TOC were allowed, one gallon of Basin F water would contaminate 31,000 gallons of groundwater. If individual contaminating compounds are chosen, a different groundwater contamination ratio would be obtained for each compound.

The dissolved solids are made up primarily of inorganic compounds of sodium, calcium, magnesium, iron, and manganese which are present as chlorides, carbonates, phosphates, and sulfates. Smaller amounts of many other inorganic compounds are present (Reference 3).

Broadly, the alternatives for managing Basin F are either the indefinite containment of water in Basin F or its permanent disposal. At the present time, it seems necessary to investigate both of the alternatives, as a means of increasing reliability of the overall decontamination program. Recommendation e., Reference 3, supports study of ultimate disposal methods for Basin F waste.

Full reliance on the total containment approach would place RMA in an indefinite care-taking position where it would be responsible for monitoring a barrier surrounding Basin F and where it would have the burden of proof that there was no leakage downward through undiscovered faults or voids in the floor of the contained area, in the contact area at the bottom of the barrier, or in the barrier itself. This proof would be challenged every time contaminants were detected at a new location and would be a continuing source of friction between RMA and the surrounding communities. Because of these uncertainties, a small-scale investigation of the disposal alternative via wet oxidation has been underway (Reference 2) and because of encouraging results, the investigation has been recommended for continuation to the point where moderately accurate estimates of large-scale performance and the associated costs can be made (Reference 7). The cost of this test program is not expected to exceed $5,000.

Disposal of the Basin F waste water involves:

(1) Destruction of the organic compounds.

(2) Separation of the inorganic compounds from solution and their disposal.

(3) Disposal of the water.

All the above steps must be accomplished without releasing toxic levels of any of the compounds present. Wet oxidation is a well established procedure that appears to be promising because its rate is highest at high organics concentration, because it oxidizes compounds insitu without requiring their preliminary isolation from solution, and because subsequent separation of the inorganic compounds will be simplified. Solution entrained by the separated inorganic compounds is expected to be comparatively free of organics, even if there has been no treatment beyond wet oxidation.

These considerations, in addition to considerable evidence of current leakage from Basin F, constitute the basis for study of the decontamination alternative.

OBJECTIVES

The broad objective of this test program is to estimate the degree to which wet oxidation under various reaction conditions will detoxify the wastewater in Basin F, and thus simplify its ultimate disposal. The primary improvement is expected to be a substantial reduction in quantity of the organic compounds, through oxidation; the inorganic compounds that comprise about 16% of the waste solution will be largely unaffected by oxidation although there will be some minor effects such as the precipitation of iron oxides. Disposal of these compounds is expected to be simplified, however, because the entrained solution will contain comparatively low organic levels.

Specifically, the first objective will be to measure the following dependent variables and to associate changes in them with the various wet oxidation reaction conditions discussed later.

Dependent Variables

Y_1 -- Total organic carbon (TOC).
Y_2 -- Using TOC data, calculate rate constants for fast and slow stages of the oxidation.
Y_3 -- Analyze product for a number of specific organic compounds (from Table 17, Reference 3).

1. Aldrin
2. Isodrin
3. Dieldrin
4. Endrin
5. Dithiane
6. DIMP
7. DMMP
8. Sulfoxide
9. Sulfone

Y_4 -- pH of effluent.
Y_5 -- Analyze precipitate formed during run for inorganic content.
Y_6 -- Compare toxicity of products with the original Basin F wastewater using an aquatic bioassay.

The above analyses will be carried out by MALD at RMA except that Y_6, the bioassay, will be carried out at either Ft. Detrick or Aberdeen. Some analyses may be duplicated by contractor for process-control purposes.

The reaction conditions below may be changed at will and are therefore regarded as independent variables. The chosen levels are described later.

Independent Variables

X_1 -- Catalyst (none used in initial test). Potential for catalysis will be estimated from results of one type, to be selected by contractor. Test catalyst will not necessarily be economical.
X_2 -- pH of feed stock. This variable will cause formation of a precipitate at some of its values. The clear solution remaining after removal of the precipitate will be used as feed stock. Trials at three pH levels are planned.

Independent Variables (conc'l)

X_3 -- Feed rate. This variable will be fixed at three levels to provide estimates of the connection between residence time and TOC removal in the continuous reactor.

Reaction temperature will be fixed at one level (600^{O}F) to obtain maximum reaction rate. This temperature is a practical maximum for commercial use. The other parameter is the feed stock source.

Parameters

P_1 -- Reaction temperature of 600^{O}F.
P_2 -- Feed stock will be Basin F waste.

The second objective will be to obtain a preliminary estimate of the cost for commercial equipment as a function of conversion level and throughput rates. This information is expected to be furnished by contractor from correlations previously developed for the test apparatus.

APPROACH

The approach to wet oxidation testing is partly defined by the equipment known to be available. ASTRO METALLURGICAL CORPORATION conducted the initial wet oxidation test (Reference 2) gratis in a small batch reactor; they also have a small continuous unit capable of 0.3 gpm which they operate for a charge of $40.00 per hour ($1,000.00 minimum). The reactor volume is 2 gallons; at the maximum flow of 0.3 gpm, the minimum residence time is about seven minutes. Longer residence times are obtained by adjusting the feed rate to lower values. The preliminary testing indicated that a residence time of one or two hours would be necessary to obtain eighty to ninety percent oxidation of the initial oxidizable carbon; tests will be designed to encompass these reaction times.

Platinum black may be used to predict the wet-oxidation reaction response to catalysis in general; a positive result would lead to trials of economically feasible catalysts at a later date, if otherwise warranted activated carbon is an alternative (Reference 5).

The pH levels are not expected to have a major effect on the rate, but they could conceivably affect the wet oxidation mechanism and hence the toxicity of the products. Control of pH is also a possible means of corrosion control.

Residence time in a continuously fed-stirred reactor is defined as the reactor volume divided by the flow rate. For a two gallon reactor, the residence times and corresponding flow rates are tabulated below:

TABLE VI

FEED VOLUME AND RESIDENCE TIME CALCULATIONS - 2 GALLON REACTOR

Desired Residence (Min)	Required Feed Rate (gpm)	Volume* Feed (Gals)	** Estimated Oxidation (% of Slow Oxidation) (Steady State) If K=.005	If K=.015
6	.33	200	3	8
15	.133	80	7	18
30	.067	40	13	31
60	.033	20	23	48
120	.017	10	37	64
600	.0033	2	74	90

* - Steady state can be (practically) reached at 5 hrs. (300 mins.) run time over wide ranges of flow rate and allowing for a large uncertainty in the rate constant (Table II). The "Volume Feed" requirement is accordingly calculated for 5 hours. The final reactor content of 2 gallons will approach steady-state composition. Additional run time may be needed to produce sufficient product for all analytical tests; additional feed will be necessary in accordance with the additional product.

** - The oxidation conversion level estimate is for the secondary, slower oxidation rate. The total conversion percentages will be considerably higher than those in Table VI because the fast oxidation is about ten times as fast as the slow oxidation. See Table I for the total conversion estimates and Table IV for the total feed estimates. Formulas are given in the Appendix.

METHODOLOGY

Figure I is a representation of the experimental design adopted to investigate the three independent reaction variables listed previously as X_1, X_2, and X_3. The design calls for running ten of the total 18 possible combinations of reaction variables and levels. There are two levels for catalyst, three feed rates, and three pH levels. The design has not been entirely randomized because of the operational complexities associated with full randomization; the run sequence was designed to minimize changes in feed stock and in the number of catalyst changes.

Assumptions for the design are that each run starts with a full 2-gallon reactor agitating at 600°F. Feed and air input start at time zero and the continuous reaction proceeds until the product composition stabilizes. After this point, three gallons of product are collected; considering the two gallons left in the reactor, five gallons product from each of the ten runs will be available for analyses and bioassay tests.

These runs vary considerably in their run-times and wastewater throughput. Estimates of these quantities are developed in the Appendix and listed in Tables III through V.

The total run time for ten runs under ideal conditions is estimated at 115 hours. Current charges are $40.00 per reactor-hour. Discussions with the potential contractor will be held after their examination of this program, prior to writing a contract. An estimated schedule for all activities is attached.

A Gantt Chart showing estimated schedule for completion of this program is attached.

REFERENCES

1. H. L. LAWLESS, "Proposed Research/Development Strategy for Treatment of Subsurface Water," Report No. 1, 14 Sept 1977.

2. H. L. LAWLESS, "Preliminary Test of the Wet Oxidation of Organics in Basin F Wastewater," Supporting ITARMS 1.05.07 (Recent reorganization has brought this under ITARMS 1.05.57).

3. "Interim Report, Basin F Investigative Studies (Phase I)" by R. Buhts, Waterways Experiment Station, Vicksburg, Mississippi 39180.

4. TOC in Groundwater, USGS JOUR. RES., Vol 2, No 3, May-June 1974 p361-369 "Occurrence of Dissolved Organic Carbon in Selected Ground-Waters in the U.S.", I. A. Leenheer et. al.

5. Pilot-Plant Demonstration of Wet Oxidation for Treatment of Shipboard Wastewaters, USCG Report No. CG-D-34-76.

6. R. E. BUHTS, P. G. MALONE, D. W. THOMPSON, "Evaluation of Ultra-Violet Ozone Treatment of Rocky Mountain Arsenal (RMA) Groundwater (Treatability Study)".

7. Colonel Damon D. Wingfield, letter to Commander, RMA, 24 April 78, Subject "Preliminary Test of Wet Oxidation of Organics in Basin F Wastewater at RMA".

FIGURE I

Factorial Design - Basin F Wet Oxidation Runs.

All runs on Basin F waste at 600°F
Continuous feed to stirred reactor
Run conditions are nominal values

		No Catalyst			Trial Catalyst		
		pH=3	pH=7	pH=11	pH=3	pH=7	pH=11
Feed Rates to Two Gallon Reactor	G=.4 gph		1			8	
	G=1 gph	4	2	5	10	7	9
	G=4 gph		3			6	

A) Make runs in sequence as numbered.

B) Sample Schedule: Empty the reactor contents (2 gal) after the following run times. For each sample, the run time is measured from the point where air starts into a reactor containing unmodified charge material at 600°F.

SAMPLE NO.	RUN TIME (HRS.)	TOTAL REACTOR TIME (HRS.)	SAMPLE (GAL.)
1	0.5	.5	2
2	1.0	1.5	2
3	1.5	3.0	2
4	5.0 PLUS*	8.0 PLUS*	5
			11

* - Plus time to make 3 gals.

C) Sample shipment: Return samples to Rocky Mountain Arsenal, Bldg. 831, Commerce City, Colorado 80022, ATTN: Harold Lawless. Label for complete identification.

APPENDIX

For a first order reaction conducted in a continuously fed, stirred reactor, the ratio of the reactant concentration in the product stream to that in the feed is given by Equation I:

$$(I)\qquad \frac{C}{C_o} = \frac{G + K_p V_r e^{-\left(K_p + \frac{G}{V_r}\right)t}}{G + K_p V_r}$$

Where: C = Concentration in product stream (lb.-M/Gal)
C_o = Concentration in feed stream (lb.-M/Gal)
G = Throughput rate (gpm)
K_p = Pseudo first order rate constant (min-1)
V_r = Reactor volume (gal)
t = Time since start of reaction=run time (Min)

As run time (t) increases, Equation I reflects the fact that C/C_o reaches a stable minimum corresponding to the maximum conversion obtainable at the given run conditions. The run time necessary to reach stable conditions is about five hours over a wide range of conditions, as indicated by the solutions for Equation I tabulated in Table II.

From 1, after long run times:

$$(II)\qquad \frac{C}{C_o} \doteq \frac{G}{G + K_p V_r} \doteq \frac{100 - \%CONV.}{100}$$

$$\text{note: } \frac{C_o - C}{C_o} \doteq \frac{\%CONV}{100}$$

Equation II represents the conversion due to a single first order reaction; in fact, wet oxidation experimental results indicate that two simultaneous first order reactions are involved and that one is about ten times the rate of the other.

Total oxidizable carbon (TOC) measures the combined effect of both reactions, and this combined, steady state conversion level, as measured by TOC, can be estimated from the two rate constants.

For two reactions:

$$(III\text{-}A)\qquad \frac{\%CONV.}{100} \doteq \frac{TOC_o - TOC}{TOC_o} \doteq \frac{C_o - (C_1 + C_2)}{C_o}$$

If the initial concentrations of the fast-oxidizing and the slow-oxidizing compounds are respectively X C_o and $(1-X)C_o$ then, from II

$$\text{III} \quad \%\text{Conv} = 100\left[1-\left(\frac{X}{1+\frac{K_1V_H}{G}}+\frac{(1-X)}{1+\frac{K_2V_H}{G}}\right)\right]$$

Conversion estimates from Equation II for the experimental 2-gallon reactor are listed in Table I, attached, for a series of feed rates and for two approximate X values. In order to obtain 80% conversion or better, the feed rate (G) estimate is 1 gph (.016 gpm) or less; 90% conversion requires a slower feed rate of 0.4 gph (.007 gpm). The residence times corresponding to these feed rates are 2 hours and five hours (2 gallon reactor).

As indicated by trends in the calculations in Table II (Equation I), both feed rates are expected to allow a stable product composition to be reached in five hours or less; some additional time to produce three gallons of product (of constant composition) will be necessary. Each run is designed to yield five gallons of product for testing; the reactor contents (2 gallons) and the product (3 gallons produced after steady state composition has been reached) will be containerized separately after each run for subsequent TOC analysis, but the two containers will be combined for organics analysis and bioassay if the TOC analyses are comparable.

The total feed volume requirements (10 runs) are estimated in Tables III and IV. The total reactor-hours that will be required to produce five gallons of product for each of ten runs have been estimated in Table V (115 Hours).

TABLE I

ESTIMATE* OF TOTAL CONVERSION AT STEADY STATE CONDITIONS FOR WET OXIDATION CONDUCTED BY CONTINUOUS FEED TO A TWO-GALLON STIRRED REACTOR AT FEED RATES (gpm) SHOWN. RATE CONSTANTS FOR THE FAST AND SLOW REACTION ASSUMED TO BE 0.15 AND 0.015 MIN^{-1} RESPECTIVELY.

FEED RATE (G)		CALCULATED CONVERSION*		RESIDENCE TIME
gph	gpm	X=.5	X=.6	MIN.
.2	.003	95%	96%	606
.4**	.006	91	92	303
.5	.008	88	90	241
1.0**	.016	80	83	121
2.0	.033	69	73	60
4.0**	.066	57	62	30
20.0	.33	28	32	6

** - FEED RATES FOR TEST RUN (FIGURE 1)

* - (EQN III) CALCULATED CONVERSION = $100\left[1-\left(\frac{X}{1+\frac{K_1V_R}{G}}+\frac{(1-X)}{1+\frac{K_2V_R}{G}}\right)\right]$

Where X = fraction TOC due to fast oxidation rate
(X values in Table are assumptions that seem reasonable)

Measured Conversion = $100\left[1-\frac{\text{PRODUCT TOC AT STEADY STATE}}{\text{TOC OF FEED}}\right]$

Rate constant estimates were obtained from measured conversion, Reference 2, at the beginning and end of the reaction.

TABLE II

PRELIMINARY ESTIMATE FOR RATIO [C (Effluent)/Co (Feed)] IN TWO GALLON WET OXIDATION REACTOR

Run Time Elapsed (Min.)	Case 1 (K=.001)			Case 2 (K=.005)			Case 3 (K=.015)		
	tr=6 G=.33	tr=60 G=.033	tr=600 G=.0033	tr=6 G=.33	tr=60 G=.033	tr=600 G=.0033	tr=6 G=.33	tr=60 G=.033	tr=600 G=.0033
15	.99448	.98681	.98529	.97288	.93589	.92862	.92227	.82069	.80090
30	.99402	.97666	.97116	.97077	.88946	.86402	.91704	.70890	.64580
100	.99398	.95279	.91215	.97059	.79453	.63479	.91667	.54422	.26954
300	.99398	.94316	.79305	.97059	.76781	.35039	.91667	.52385	.10520
600	.99398	.94286	.69959	.97059	.76744	.26203	.91667	.52381	.09914
1200	.99398	.94286	.63833	.97059	.76744	.24838	.91667	.52381	.09910
2400	.99398	.94286	.62329	.97059	.76744	.24812	.91667	.52381	.09910
4800	.99398	.94286	.62264	.97059	.76744	.24812	.91667	.52381	.09910

NOTES: (1) $tr = \frac{\text{REACTOR VOL.}}{\text{FEED RATE}}$

(2) % conversion = (1-tabulated value)100

EQN.(I) $$\frac{C}{C_0} = \frac{G + K_p V_r e^{-\left(K_p + \frac{G}{V_r}\right)t}}{G + K_p V_r}$$

Where: C_0 = Concentration of reactant in feed (lb-mole/gal)
C = Concentration of reactant in effluent (lb-mole/gal)
G = Feed rate (gallon/min)
V_r = Reactor volume (gal)
K_p = Reaction rate constant (min^{-1})
t = Running time (min)

TABLE III

GALLONS FEED STOCK FOR TEST PLAN

RUN NO.	1	2	3	4	5	6	7	8	9	10
Feed pH	7	7	7	3	11	7	7	7	11	3
Feed Rate, gph	.4	1	4	1	1	4	1	.4	1	1
Run 8 hrs. (Fig. I)	5.2	8	32	8	8	32	8	3.2	8	8
ALL SAMPLES	11	11	11	11	11	11	11	11	11	11

TABLE IV

SUMMARY OF FEED BY pH - GALLONS

	pH=3	pH=7	pH=11
THEORY	38	156	38
RMA TO FURNISH	100	300	100

TABLE V

ESTIMATED RUN TIMES - HOURS

RUN NO.	1	2	3	4	5	6	7	8	9	10
See Figure 1*	8	8	8	8	8	8	8	8	8	8
For 3 Gal. Product	7.5	3	.8	3	3	.8	3	7.5	3	3
TOTAL RUN TIME	15.5	11	8.8	11	11	8.8	11	15.5	11	11

TOTAL REACTOR TIME ESTIMATE IS 115 HOURS RUN TIME

* - Times given are explained in Footnote to Figure 1.

WET OXIDATION OF ORGANICS IN BASIN F WASTEWATER

Progress as of 15 July 1978 and Future Schedule

		1978					1979							
	COMPLETED	AUG	SEP	OCT	NOV	DEC	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG
Literature search; preliminary test to evaluate sample; Internal evaluation report; Phase II test plan.	☒													
Prepare sole source contract; get approval		▨	▨											
Obtain and adjust pH feed stock for test and ship to contractor.		▨												
Run 85 hours total (est) for data on 10 runs;			▨	▨										
Return samples to RMA					▨									
Plant cost estimate from contractor					▨									
TOC Analyses					▨									
Remaining analyses					▨	▨								
Aquatic Bioassay					▨	▨								
Activated Carbon Test Lab. Scale					▨	▨								
Uv/O_3 Test, Laboratory Scale					▨	▨								
Data analysis/economical analysis					▨	▨	▨							
Final report on Phase II -- develop design criteria for on-site pilot plant								▨	▨					