

PHOTO-OXIDATION OF ORGANIC COMPOUNDS IN LIQUID  
LOW-LEVEL MIXED WASTES AT THE INEL

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## ABSTRACT

A bench-scale oxidation apparatus is implemented to study the effectiveness of using an artificial ultraviolet source, a 175-Watt medium pressure mercury vapor lamp, to enhance the destruction of organic contaminants in water with chemical oxidants. The waste streams used in this study are samples or surrogates of mixed wastes at the Idaho National Engineering Laboratory. The contaminants that are investigated include methylene chloride, 1,1,1-trichloroethane, 1,1-dichloroethane, acetone, 2-propanol, and ethylenediamine tetraacetic acid. We focus on  $H_2O_2$ -based oxidizers for our treatment scheme, which include the UV/ $H_2O_2$  system, the dark Fenton system ( $H_2O_2/Fe^{2+}$ ), and the photo-assisted Fenton system (UV/ $H_2O_2/Fe^{2+}$ ) is used in particular. Variables include concentration of the chemical oxidizer, concentration of the organic contaminant, and the elapsed reaction time.

Results indicate that the photo-assisted Fenton system provides the best overall performance of the oxidizing systems listed above, where decreases in concentrations of methylene chloride, 1,1,1-trichloroethane, 1,1-dichloroethane, 2-propanol, and ethylenediamine tetraacetic acid were seen. However, UV-oxidation treatment provided no measurable benefit for a mixed waste containing acetone in the presence of 2-propanol.

## I. INTRODUCTION

Throughout the course of routine operation the Idaho National Engineering Laboratory (INEL) has occasionally produced small amounts of liquid mixed wastes (MW) that contain toxic organic constituents together with low-level radionuclides and perhaps heavy metals. Much of the time these contaminants are contained within an aqueous medium. In recent years the focus of waste treatment has been shifting

away from traditional methods (e.g. carbon absorption, incineration, etc.) to newer methods that eliminate the toxic components to well below regulatory limits. For a treatment method to be truly valid for full-scale waste treatment it must be effective, economical, robust (can operate successfully under a variety of conditions), and safe.

Ultraviolet-enhanced oxidation (abbreviated as UV-Ox) experiments were performed at the INEL on selected mixed wastes under Resource Conservation and Recovery Act (RCRA) treatability studies. RCRA studies are done to determine the feasibility of using a given treatment method for a particular hazardous waste.

Our UV-Ox work utilized a bench-scale oxidation unit to study the effectiveness of using a UV source to enhance the destruction of organic contaminants in water with chemical oxidants. We have focused primarily on the photo-assisted Fenton system (UV/ $H_2O_2/Fe^{2+}$ ) for our treatment scheme. The waste streams investigated herein are samples from land-disposal-restricted (LDR) mixed wastes currently being stored at the INEL, where the contaminants include methylene chloride, 1,1,1-trichloroethane (TCA), 1,1-dichloroethane (DCA), acetone, 2-propanol, and ethylenediamine tetraacetic acid (EDTA). Results from our first year UV-Ox study have been discussed elsewhere,<sup>1</sup> and are summarized here together with the results from year two.

## II. UV-BASED TECHNOLOGY FOR WASTE TREATMENT

### A. Background

The field of photo-enhanced oxidation is a burgeoning area of research worldwide, where researchers have obtained very encouraging results for the destruction of organic

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compounds.<sup>1,2,3,4,5,6,7,8</sup> This technology is also being applied to real-world problems, as there were over 150 full-scale UV-Ox treatment installations in operation by 1994.<sup>9</sup>

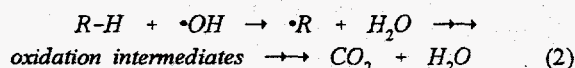
Although photo-oxidation of organic compounds can occur under natural conditions (in sunlight at ambient temperature, with no added chemicals), these natural processes are much too slow to be exploited for an effective treatment scheme. Chemical oxidizers can be used together with a concentrated UV source to greatly accelerate the oxidative reactions. Our studies utilized hydrogen peroxide-based oxidizing systems, which include the UV/H<sub>2</sub>O<sub>2</sub> system, the Fenton system (H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup>) and the photo-assisted Fenton system (UV/H<sub>2</sub>O<sub>2</sub>/Fe<sup>3+</sup>) due to the promise they have shown in oxidizing a large array of organic compounds.<sup>2,3,5,6,7,8,10,11,12,13</sup>

The reaction mechanisms for the above oxidizing systems have been discussed in an earlier paper,<sup>1</sup> and are summarized below.

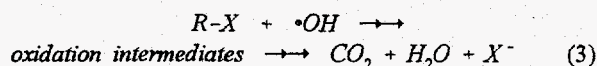
The UV/H<sub>2</sub>O<sub>2</sub> System (UV is denoted as *hν*)



General reaction between organic molecule and  $\cdot OH$ :



General reaction between halogenated organic molecule and  $\cdot OH$ :



The Fenton System:<sup>2,3,12,13</sup> H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup>

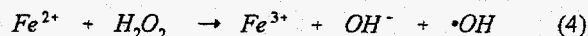
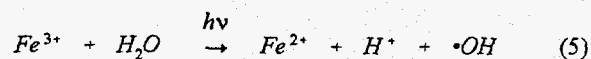


Photo-assisted Fenton system: UV/H<sub>2</sub>O<sub>2</sub>/Fe<sup>3+</sup>. The formation of hydroxy radicals in the photo-assisted Fenton system is enhanced by the addition of light having upper UV and near-UV wavelengths (300-400 nm)<sup>2,7,8,10,11</sup>



The combined contribution from Equations 1, 4, and 5 represents the net mechanism that produces hydroxy radicals for the photo-assisted Fenton system, wherein the relative contribution from Eq. 1 is small at low pH.<sup>11,12</sup> These equations imply that it crucial to maintain a relatively high concentration of  $\cdot OH$  in solution for the oxidation reactions of Eqs. 2 and 3. The oxidation/reduction cycle of iron is summarized in Eqs. 4 and 5, where fresh Fe<sup>2+</sup> is continuously being generated from Fe<sup>3+</sup>. This iron cycle proceeds as long as there is available H<sub>2</sub>O<sub>2</sub>. Literature values of the molar ratio of H<sub>2</sub>O<sub>2</sub> to total Fe ions are typically between 1 and 10.<sup>2</sup> The optimal pH for the formation of  $\cdot OH$  in the photo-assisted Fenton system has been reported to be pH  $\approx$  3.<sup>7,10</sup> The source of hydrogen peroxide for this work was a 300g/kg H<sub>2</sub>O<sub>2</sub> analytical reagent (Fisher Scientific), and the iron was delivered via FeSO<sub>4</sub>·7H<sub>2</sub>O (Fisher Scientific).

## B. Description of Bench-Scale Apparatus

The bench-scale UV-Ox system designed for this study is given in Fig. 1. Novel design features satisfy the following operating criteria: operates at near-constant temperature; system is inert to reactants; semi-batch operation; lamp orientation is optimized in relation to the reaction cell, and; there is little or no head space above the reactant mixture. A detailed process description and operating conditions are given elsewhere.<sup>1</sup>

The UV source is a 175-Watt mercury vapor lamp with a spectral output that has strong emissions between 300 and 450 nm, especially around 365 nm.<sup>14</sup> These emissions are significant in that they promote the formation of hydroxy radicals via the photo-assisted Fenton system (Eq. 5),<sup>2,7,8,10,11</sup> and they mimic part of the spectra of near-UV and visible solar radiation (300-700 nm). The vendor data for the above lamp indicates that approximately 32% of the power output occurs below 375 nm, and that 58% of the power output occurs below 450 nm.<sup>14</sup>

Two reaction cells were investigated: (1) annular quartz glass, and (2) spiral wound FEP tubing (Nalgene 890 Teflon FEP, 5-mm ID). These reactors were investigated for the sake of comparing their performance under typical operating conditions. Both reactors have similar dimensions (diameter and length), but differ in the flow path. Quartz glass and FEP tubing were chosen due to their excellent transmittance to wavelengths in the UV region (below 400 nm):

### III. WASTE DESCRIPTIONS

The INEL mixed wastes that were investigated during this study are listed in Table 1, wherein the concentrations of organic compounds in the raw MW samples are given, as well as the applicable treatment standards as defined by the Environmental Protection Agency (EPA). Although EDTA is not a regulated constituent, it is a candidate for UV-Ox because it interferes with metal precipitation reactions through the formation of metal-EDTA chelates.

Generally speaking, the radioactivity of the MW samples was in the low pCi/g to low nCi/g range, where their activity was sufficiently low to allow classification as low-level mixed waste.

**Table 1.** Liquid mixed wastes used in this study.

INEL MW ID	Organic Constituent	Conc.	EPA Treatment Standard <sup>a</sup>
INEL 654 surrogate	methylene chloride	up to 1,100 mg/L	30 mg/kg
664-B	EDTA	19,250 mg/L	NA <sup>b</sup>
TCA Still Bottoms	TCA	530 mg/L	6 mg/L <sup>c</sup>
	DCA	140 mg/L	NA <sup>b</sup>
	2-propanol	2200 mg/L	NA <sup>b</sup>
	acetone	4600 mg/L	NA <sup>b</sup>

a. For total composition in non-wastewaters.

b. Treatment Standard is not applicable to shown compound.

c. Universal Treatment Standard (UTS) limit.

### IV. TREATABILITY STUDY EXPERIMENTAL PARAMETERS

#### A. Concentration of Chemical Oxidizer

The oxidizer concentration will be a limiting factor in determining the amount of hydroxy radicals that can be produced under UV and chemical initiation (see Eqs. 1 and 4). The concentration of hydroxy radicals will in turn have a profound influence on the kinetics of oxidation reactions. Each UV-Ox run utilized an initial oxidizer concentration [ $\bullet\text{OH}$ ] that was a percentage of the stoichiometric amount required to totally oxidize the available carbon (and nitrogen,

sulfur, and phosphorus, if any) from the organic compounds in solution, forming  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . Some of the experimental runs employed multiple doses of oxidizer so that the oxidizer concentration could be kept fairly constant during the run, and so that the effect of the net or cumulative oxidizer concentration could be assessed.

#### B. Concentration of Organic Constituents

In assessing the performance of a UV-oxidation system it is also useful to vary the initial concentration of the organic waste constituents. In so doing, information can be gained about the effect of initial organic concentration on reaction kinetics and whether a oxidation process is rate limited by molecular diffusion or reaction kinetics.

#### C. Elapsed Reaction Time

The time dependence of a given oxidation process is at the very heart of kinetic rate analysis of the experimental data. Information concerning the time dependence of the extent of reaction can be gained by defining the sampling schedule with respect to time. Many of the UV-Ox experiments done for this study utilized either elapsed time or total run time as a parameter.

### V. PRETREATMENT CONSIDERATIONS

MW pretreatment can have a profound effect on the ultimate success of a treatment method. For the liquid MW samples investigated herein, pretreatment usually included one or more of the following: pH adjustment, clarification, and decantation. For a UV-Ox system it is particularly important to pretreat the incoming liquid waste to remove suspensions, organic films, or particulate matter that could otherwise attenuate light in the UV region and decrease the net transmittance of UV energy into the reactor.

### VI. RESULTS

#### A. Analytical Results per Waste Code

1. Surrogate Waste for INEL 654. The non-radioactive surrogate waste for INEL 654 was composed of dichloromethane in water. A surrogate was chosen to expedite the experimental procedures and the laboratory analysis of the samples from each run. A total of seven experimental UV-Ox runs were performed on the INEL 654 surrogate at 30 °C. Each run was performed with a single

(initial) dose of oxidizer, except run 6, which received a second oxidizer dose midway through the run. Samples taken during each run were analyzed with gas chromatography-mass spectrometry, GC-MS (Hewlett-Packard 5970 Mass Selective Detector), to determine the  $\text{CH}_2\text{Cl}_2$  levels. The analytical results from UV-Ox runs involving the INEL 654 surrogate are given in Figs. 2 and 3.

Figure 2 shows the plot of  $\log [\text{CH}_2\text{Cl}_2]$  versus reaction time, which is commonly referred to as the *first order* kinetic test, as a straight line suggests that the data may represent a first order reaction mechanism. The slopes of the data plotted in Fig. 2 for UV/ $\text{H}_2\text{O}_2$  runs (runs 1-4) differ very little, implying there is not a strong dependence of  $\text{CH}_2\text{Cl}_2$  oxidation upon the initial organic concentration. A slight increase in slope is seen when 1000% stoichiometric oxidizer is used (run 4), as compared to 300% oxidizer. There is a marked increase in the slopes of the curves when the Fenton systems were used (runs 5-7), especially the photo-assisted Fenton system (runs 5 and 6). A further increase of slope is seen in the curve for run 6, where a second injection of  $\text{H}_2\text{O}_2$  at 120 minutes caused an increased rate of  $\text{CH}_2\text{Cl}_2$  oxidation. The results for the Fenton systems clearly show that the UV/ $\text{H}_2\text{O}_2$ / $\text{Fe}^{3+}$  system provides superior performance for the oxidation of  $\text{CH}_2\text{Cl}_2$  in water, using the UV source described above, where the photo-assisted Fenton runs were able to decrease the dichloromethane concentrations from initial values of about 80-85 mg/L to less than 30 mg/L (treatment standard) in less than 50 minutes. Finally, the results for runs 2 and 3 show parallel plots, indicating that the annular quartz reactor and the FEP tubular reactor provide similar overall performance for the treatment of the INEL 654 surrogate waste.

If diffusive effects or competitive reactions are present within a reactive system it is useful to define an *apparent order of reaction* that accounts for both the chemical and physical contributions to the overall reaction rate. This can be done by considering the rate expression

$$-\frac{d[C]}{dt} = k_m [C]^m \quad (6)$$

where C is the concentration of the component being oxidized, t is time,  $-d[C]/dt$  is the differential reaction rate,  $k_m$  is the reaction rate constant, and m is the apparent order of reaction. Taking the log of both sides of Eq. 6 yields

$$\log\left(-\frac{d[C]}{dt}\right) = \log k_m + m \log [C] \quad (7)$$

A plot of  $\log (-d[C]/dt)$  versus  $\log [C]$  has slope m, and constitutes the *differential test* of reaction data, where a linear plot infers that the reaction order is constant over the concentration range of C. It is desirable to obtain low values of the slope m while maintaining high values of the reaction rate. If high values of m are seen, then the reaction rate is dropping rapidly while the concentration of C is changing little.

Figure 3 shows UV-Ox data for the INEL 654 surrogate, using the differential test. The plots for runs using the Fenton systems and 1000% stoichiometric  $\text{H}_2\text{O}_2$  provide the lowest values of the slope m, whereas the UV/ $\text{H}_2\text{O}_2$  runs using  $\leq 300\%$  stoichiometric hydrogen peroxide generate the highest values of m. In general, the advantages of the photo-assisted Fenton system are confirmed in Fig. 3. The near-identical slopes of the plots for runs 2 and 3 reaffirm that the performance of the quartz glass reactor is very similar to that of the FEP tubular reactor for the oxidation of  $\text{CH}_2\text{Cl}_2$ . The higher slope values ( $m > 3$ ) seen in Fig. 3 imply that diffusion effects and/or competitive reactions are adversely affecting the reaction rate of  $\text{CH}_2\text{Cl}_2$  oxidation. Slopes having values  $\leq 2$  suggest that the reaction rate is being dominated by favorable chemical kinetics, and not by the detrimental influences mentioned above.

Free chloride ( $\text{Cl}^-$ ) analysis was performed for samples from selected runs, using ion chromatography (IC). The trends in the chloride data indicate a mass balance closure of more than 80% for chloride, i.e. greater than 80% of the chlorine available from the oxidation of  $\text{CH}_2\text{Cl}_2$  appeared as free chloride. The remainder of the chlorine may be present in an intermediate oxidation product.

2. INEL 664-B: EDTA-laden MW. Mixed wastes containing EDTA pose a particular challenge in waste treatment due to the strong chelating action of EDTA towards heavy metals. EDTA can interfere with waste pretreatment involving chemical precipitation reactions, can promote the leaching of metals that have been solidified within concrete, and can be inimical to the curing of concrete.<sup>15</sup> Thus, EDTA must be destroyed or at least deactivated as a chelating agent before a final treatment scheme is used on an EDTA-laden MW. UV-Oxidation has shown usefulness in the oxidation of EDTA.<sup>16,17</sup>

INEL 664-B is a deep purple liquid MW that contains 19,250 mg/L EDTA together with approximately 4000 mg/L lead, 1600 mg/L chrome, and indicators. Samples of INEL

664-B underwent five UV-Ox runs at 30 °C using the photo-assisted Fenton system. All but the fifth run used MW material that had been diluted in half by water, so that any potential light-attenuating effects of the deeply colored solution would be lessened. For H<sub>2</sub>O<sub>2</sub>-based oxidation, it was assumed that the stoichiometry of H<sub>2</sub>O<sub>2</sub> to EDTA was 12:1 for the complete oxidation of the carbon and nitrogen present. Based on this ratio, the initial oxidizer concentrations for the five runs varied from 33% to 150% stoichiometric H<sub>2</sub>O<sub>2</sub>. The analytical results for measurable EDTA concentrations are given in Fig. 4. EDTA levels were determined by an offsite laboratory using the procedure defined by ASTM D 3113-87 (Method A), which is a titrative method that tests for total EDTA. Figure 4 shows that the total EDTA concentration decreases as more oxidizer is used, dropping from an initial untreated concentration of 9625 mg/L (at 50% volume dilution) to 355 mg/L at an oxidizer dose of 150% stoichiometric H<sub>2</sub>O<sub>2</sub>.

During each UV-Ox run of INEL 664-B it was noticed that a fine white precipitate formed soon after the beginning of each run. The final solutions from each run were analyzed for soluble Pb, using Atomic Absorption (AA); no analysis was done for Cr at this point, as it was suspected that all the Cr in solution was soluble in the form of Cr<sup>6+</sup> or CrO<sub>4</sub><sup>2-</sup>. Next, the final solutions from each run were subjected to a chemical pretreatment regime that consisted of chrome reduction (Cr<sup>6+</sup> → Cr<sup>3+</sup>) by the addition of ferrous chloride under acidic conditions, followed by pH adjustment and chemical precipitation by the addition of sodium hydroxide to achieve a final pH of about 9. After the chemical pretreatment steps, the clarified solutions were again analyzed with AA for soluble Pb and Cr. The results for the metals analyses are given in Fig. 5, wherein there is a significant difference seen between the soluble Pb data before and after the chemical precipitation steps. The soluble lead present after only the UV-Ox treatment (symbol=●) shows a sharp drop with increasing oxidizer concentrations, quickly decreasing over two orders of magnitude to levels near or below the RCRA treatment standard of 5 mg/L. However, the lead present after both UV-Ox and chemical pretreatments (symbol=■) shows a more gradual decrease, and is consistently *higher* than the data given for UV-Ox only. A possible explanation for these results is given as follows. It is postulated that the EDTA-Pb<sup>2+</sup> chelates were broken by the mildly acidic (pH≈3) oxidizing environment, thereby releasing the lead to drop out of solution as a white precipitate of PbSO<sub>4</sub> and possibly PbCl<sub>2</sub>. However, at this point the EDTA may have been only partially oxidized or disabled as a chelating agent. The disabled EDTA

appears to have been *re-activated* as a chelator when the solutions later underwent pH adjustment and chemical precipitation reactions, causing some of the EDTA-Pb<sup>2+</sup> chelates to be reformed, although the exact mechanisms by which this would occur are unclear. Thus, the Pb ■ data in Fig. 5 should give a clearer indication (than the Pb ● data) of the amount of EDTA that was oxidized to such an extent that it could not be reactivated to form EDTA-Pb<sup>2+</sup> chelates.

Finally, the soluble chrome data in Fig. 5 shows that the level of chrome in solution changed slightly, dropping from a value of about 810 mg/L (no oxidizer) to 650 mg/L (150% oxidizer), for a net decrease of 20%. The results for chrome indicate that EDTA-Cr<sup>3+</sup> complexes are very resilient and stable in an oxidizing environment. The stability of EDTA-Cr<sup>3+</sup> is confirmed by considering the stability constants (*K*) given in the literature for EDTA-metal complexes, where a higher value of *K* indicates that the complex is more stable. Comparing stability constants for EDTA with lead and chrome gives:  $\log K_{EDTA-Pb,2+} = 18.0$  and  $\log K_{EDTA-Cr,3+} = 24.0$ , where the values are reported for the conditions of medium ionic strength and 20 °C.<sup>18</sup> These *K* values help explain the results in Fig. 5, where the EDTA-Pb<sup>2+</sup> chelates appear to have been destroyed more readily than those of EDTA-Cr<sup>3+</sup>.

It will be necessary to adjust the oxidizing scheme to completely destroy the chelates formed between EDTA and Cr<sup>3+</sup>. Such an adjustment could entail a simple increase of the oxidizer concentration, or perhaps may involve multiple steps wherein UV-Ox is teamed with a traditional chemical oxidation method that has shown promise with EDTA oxidation, such as acidic permanganate oxidation,<sup>19</sup> and ion exchange (to remove CrO<sub>4</sub><sup>2-</sup>). In a parallel study with INEL 664-B we utilized KMnO<sub>4</sub> under acidic conditions to oxidize the EDTA such that the metals could precipitate out of solution, resulting in a final soluble lead concentration of 0.9 mg/L and a soluble chrome concentration of 89 mg/L. Drawbacks of using the permanganate-based oxidation scheme include heat evolution and the formation of a large amount of MnO<sub>2</sub> sludge.

3. TCA Still Bottoms. TCA Still Bottoms is an aqueous MW that is contaminated with organic constituents and chromium. Data from the waste generator indicated the untreated MW sample contained Cr at 3.3 mg/L (total metal basis), and 530 mg/L TCA, 4600 mg/L acetone, 2200 mg/L 2-propanol, and 140 mg/L DCA (although samples taken before UV-Ox runs showed markedly different levels of some of the organic components). Samples of this material underwent

three UV-oxidation runs using various amounts of oxidizer under the photo-assisted Fenton system. The oxidizer solution was incrementally injected into the mixture as near-equal doses every 30 minutes to provide a fairly constant oxidizer concentration for the duration of each run, and to avoid high oxidizer concentrations that promote the degradation of  $H_2O_2$  into byproduct gases (e.g.  $O_2$ ) via side reactions.

UV-Ox data (from GC-MS) is given in Figs. 6 and 7. Concentration-time data for TCA and DCA is given in Fig. 6, and Fig. 7 shows data for acetone and 2-propanol. Figure 6 shows a steady decrease of TCA throughout each run, where the net decrease of TCA for runs 1, 2, and 3 are 62.2, 73.8, and 85.2%, respectively. The DCA data given in Fig. 6 shows an initial rise of DCA concentrations in each run, followed by a sharp decrease. This behavior in the DCA data may be due to the fact that DCA is an oxidation intermediate of TCA that is formed during initial stages of TCA oxidation.

Figure 7 indicates that there is a significant decrease of 2-propanol during each run that is accompanied by an increase of acetone. It is postulated that acetone is the most immediate oxidation product from the oxidation of 2-propanol, following a 1:1 stoichiometric balance. The decrease of 2-propanol does not coincide closely with a stoichiometric increase of acetone, but the relative increases and decreases of these compounds are roughly within the same order of magnitude. The net decreases of 2-propanol in runs 1, 2, and 3 are 79.9, 694.5, and 124.5 mmol/L, respectively, while the net increases in acetone are 328.5, 147.7, and 299.5 mmol/L, respectively.

## VII. CONCLUSIONS AND RECOMMENDATIONS

The effectiveness of using an ultraviolet source to enhance the destruction of organic contaminants in water was investigated using a bench-scale UV-Ox system. The organic contaminants investigated include chlorinated compounds, 2-propanol, acetone, and EDTA. The oxidizers chosen for our studies included the UV/ $H_2O_2$  system, the dark Fenton system ( $H_2O_2/Fe^{2+}$ ), and the photo-assisted Fenton system (UV/ $H_2O_2/Fe^{3+}$ ).

Results show that the UV/ $H_2O_2/Fe^{3+}$  system provides the best performance for the oxidation of the above organic contaminants, where it can be concluded that this system holds good promise for the oxidation of  $CH_2Cl_2$ , EDTA, and TCA in aqueous wastes. For example, the methylene chloride-laden waste was treated such that the methylene chloride concentration was below or near the EPA treatment standard

of 30 mg/L. The EDTA-bearing waste was subjected to UV-Oxidation to destroy EDTA-metal complexes, and good results were obtained for the EDTA-Pb<sup>2+</sup> complex, but fair results were obtained for EDTA-Cr<sup>3+</sup>. INEL 664-B should be investigated further to determine the conditions under which the EDTA-Cr<sup>3+</sup> complex is satisfactorily destroyed. This may involve coupling UV-Ox with a traditional chemical oxidation method such as acidic permanganate oxidation, followed by ion exchange to remove the remaining chromate anions.

Analytical data for UV-Ox runs of the TCA Still Bottoms MW shows a steady decrease of TCA throughout each run, as the percentage decrease of TCA increases with increasing cumulative oxidizer dosages. The net decrease of TCA ranged from 62.2 to 85.2% where the experimental runs had cumulative oxidizer doses (stoichiometric) ranging from 50 to 200%, respectively. Further investigation is needed to determine what oxidizer doses will result in TCA levels below the UTS limit of 6 mg/L. UV-oxidation results for acetone and 2-propanol present in the TCA Still Bottoms MW show there is an increase of acetone corresponding to a decrease of 2-propanol during each run. Although the decrease of 2-propanol does not coincide closely with a stoichiometric increase of acetone, the relative increases and decreases of these compounds are within the same order of magnitude.

The following recommendations have arisen from this treatability study. First, it is crucial to maintain high oxidizer concentrations throughout the duration of a batch/semi-batch UV-Ox run. It is recommended that a fairly constant  $H_2O_2$  concentration be maintained through real-time monitoring of oxidizer levels in the reactant mixture, balancing kinetic considerations (reaction rates) with economic limitations (cost of oxidizer per unit of treated MW). Another recommendation is to investigate additional UV sources, intensities, and wavelengths, so that beneficial wavelengths can be pinpointed and detrimental wavelengths (those that promote side reactions) can be avoided.

## ACKNOWLEDGMENTS

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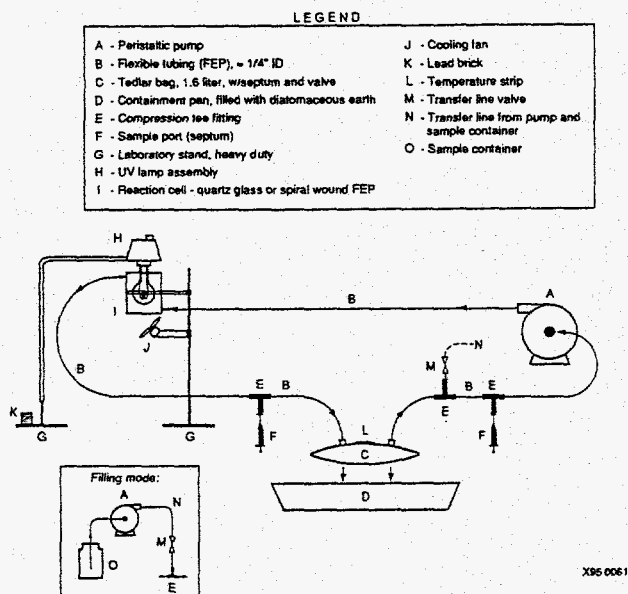
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Figure 1. UV-Oxidation system layout for treatability studies.



- Run 1: Initial Oxidizer = 200% Stoich. H<sub>2</sub>O<sub>2</sub>; Annular Quartz Reactor
- Run 2: Initial Oxidizer = 300% Stoich. H<sub>2</sub>O<sub>2</sub>; Annular Quartz Reactor
- ▲ Run 3: Initial Oxidizer = 300% Stoich. H<sub>2</sub>O<sub>2</sub>; FEP Tubular Reactor
- ▼ Run 4: Initial Oxidizer = 1000% Stoich. H<sub>2</sub>O<sub>2</sub>; FEP Tubular Reactor
- ◆ Run 5: Initial Oxidizer = 300% Stoich. Fenton Reagent; FEP Tubular Reactor
- Run 6: Initial Oxidizer = 300% Stoich. Fenton Reagent; FEP Tubular Reactor  
Second Oxidizer Dose = 150% Stoich. H<sub>2</sub>O<sub>2</sub> at 120 Min.
- ⊙ Run 7: Initial Oxidizer = 300% Stoich. Fenton Reagent; Dark (No UV)

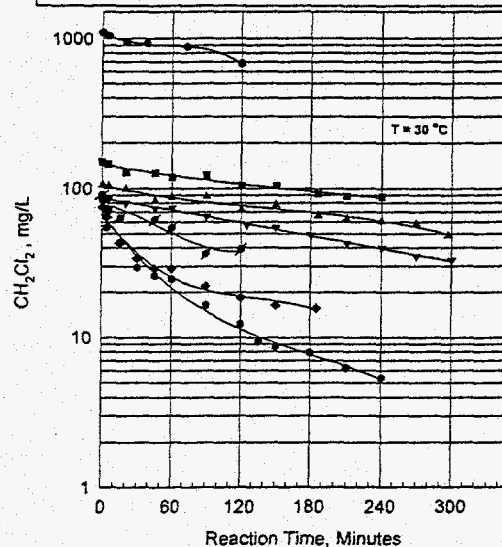


Figure 2. Summary of non-radioactive UV-Oxidation runs (using CH<sub>2</sub>Cl<sub>2</sub> in water as the surrogate waste). Linear plots imply first order reaction kinetics for the oxidation of CH<sub>2</sub>Cl<sub>2</sub>.

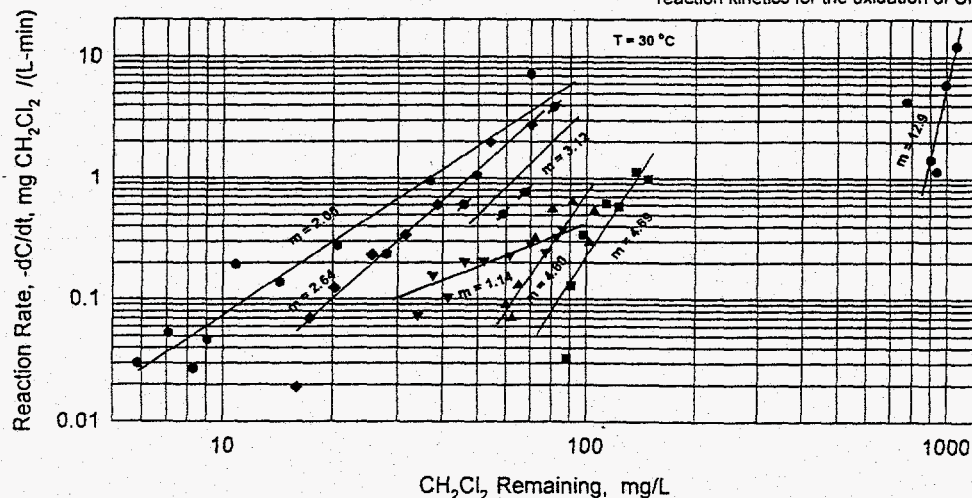


Figure 3. Differential analysis of non-radioactive UV-Ox runs (CH<sub>2</sub>Cl<sub>2</sub> in water).

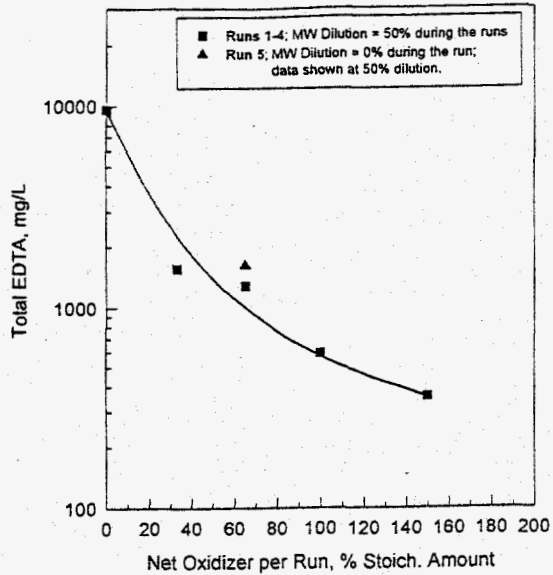


Figure 4. EDTA concentrations in INEL 664-B undergoing UV-enhanced oxidation, using Fenton's Reagent. Each data point represents a single experimental run. EDTA was measured by using ASTM D 3113-87, Method A ("Total EDTA").

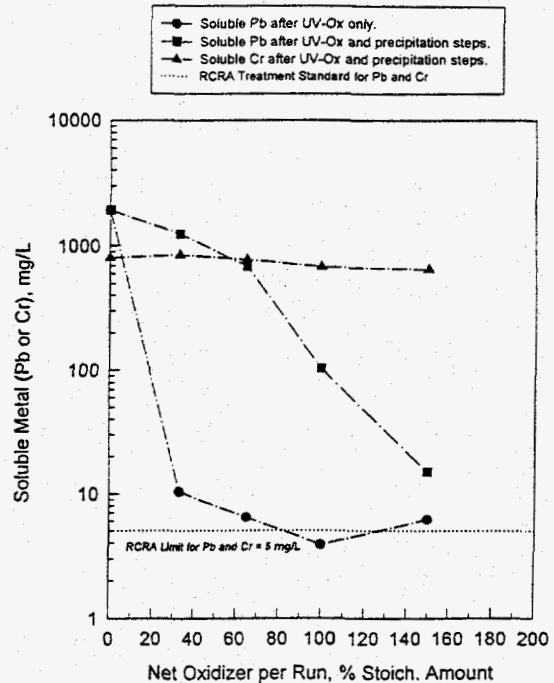


Figure 5. Soluble lead and chrome as a function of the net oxidizer dose, from the UV-Oxidation of INEL 664-B (EDTA-laden mixed waste). Oxidizer was Fenton's reagent, and 50% waste dilution was used for the shown runs.

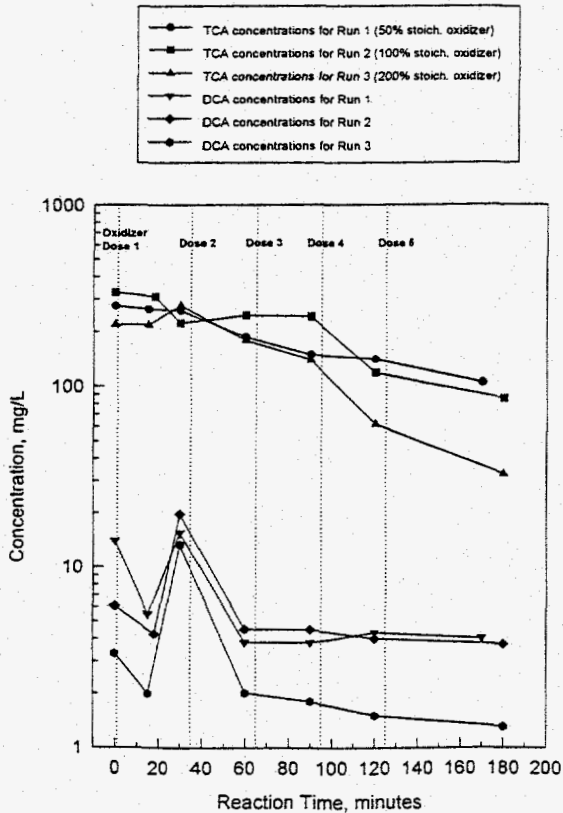


Figure 6. TCA and DCA concentrations for UV-Ox runs of TCA Still Bottoms MW. Oxidizer was photo-assisted Fenton reagent. Note: the MW was diluted by half in Run 3.

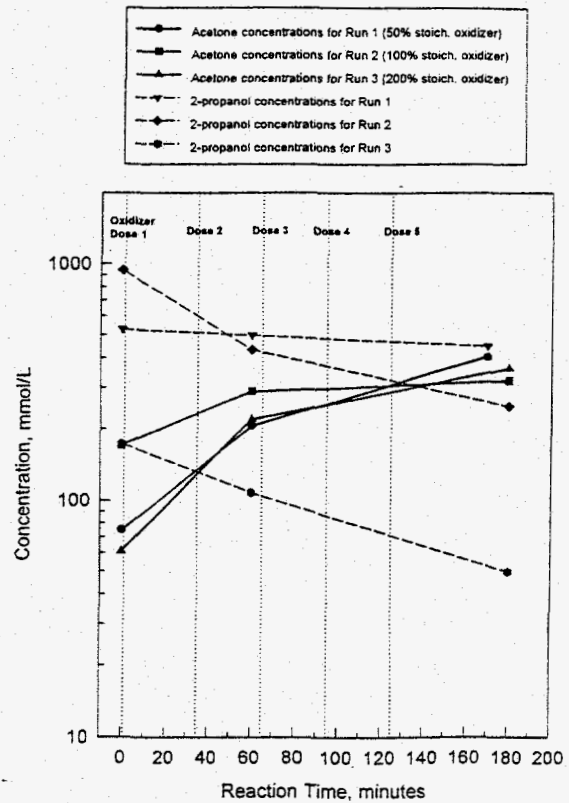


Figure 7. Acetone and 2-propanol concentrations for UV-Ox runs of TCA Still Bottoms MW. Oxidizer was photo-assisted Fenton reagent. Note: the MW was diluted by half in Run 3.