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Catalyzed Wet Oxidation

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BENCH SCALE DEMONSTRATION AND CONCEPTUAL ENGINEERING FOR DETOXSM CATALYZED WET OXIDATION

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ABSTRACT

Laboratory and bench scale studies of the DETOXSM catalyzed wet oxidation process have been performed with the object of developing the process for treatment of hazardous and mixed wastes. Reaction orders, apparent rates, and activation energies have been determined for a range of organic waste surrogates. Reaction intermediates and products have been analyzed. Metals' fates have been determined. Bench scale units have been designed, fabricated, and tested with solid and liquid organic waste surrogates. Results from the laboratory and bench scale studies have been used to develop conceptual designs for application of the process to hazardous and mixed wastes. LA-UR-94-1618

I. INTRODUCTION

Incineration and similar thermal methods have encountered difficulties in obtaining permits for treatment of radioactive and mixed wastes.

DETOXSM, a patented process utilizing a novel catalytic wet oxidation by iron(III), can be used to destroy organic materials.^{1,2} The process is diagrammed in Figure 1. The composition of the catalyst solution is typically 60.% by weight iron(III) chloride and 3-4.% by weight hydrogen chloride. Catalyst A is typically platinum and/or ruthenium ions in solution. The process typically operates in the temperature range of 373. K to 473. K. Vapor pressure of the process solution over the typical operating temperature range is less than

atmospheric to approximately 1500. KPa (the process solution boiling point is approximately 408. K). Organic materials are oxidized to carbon dioxide and water. Halogens are converted to the hydrogen halides. Sulfur is oxidized to sulfate, phosphorous to phosphate, and nitrogen compounds in the presence of organics appear to be converted to nitrogen gas.^{3,4} No NO_x, SO_x dioxins, or furans have been seen in products from the oxidation reaction.

Figure 1: DETOXSM Process Chemistry

II. KINETIC AND MECHANISTIC STUDIES

A. Reaction Order and Activation Energy

The reaction of iron(III) with organic compounds has been shown to be pseudo-first order in iron(III).⁵

Reaction rate versus temperature studies in unstirred, TeflonTM-lined reaction bombs were used to calculate apparent activation energies for the oxidation of a variety of organic materials. In the activation energy studies, the organic material was added in great excess so that reaction rate was dependent on iron(III) concentration. Figure 2 shows a typical Arrhenius plot for oxidation of an organic with the process. Table I lists the apparent activation energies for oxidation of a variety of organics with DETOXSM.

Figure 2: Arrhenius Plot for DETOXSM Oxidation of Latex

Table I: Average Activation Energies for Iron(III) Oxidation of Organics with Platinum Cocatalyst

Organic	ΔE_A (Kcal/mole)
Benzene	7.5
Trichloroethene	6.0
Mineral Oil	6.6
Machining Oil	5.6
Cellulose	8.1
Nonylphenoethoxylates	6.5
Latex Rubber	6.6
Poly(vinyl chloride)	6.2
Polvethylene	9.4

The oxidation reaction also appears to be pseudo-first order in the organic compound. Early experiments in unstirred reaction bombs gave the results shown in Figure 3. At the experimental temperature the organic compound, o-xylene, is in the vapor phase. The reaction rate is dependent on the surface area of contact of the organic compound and the process solution, and is linear with organic compound concentration in the vapor up to about 0.03 mole/L. More recent experiments using a device where helium carrier gas containing organic vapor could be passed over a known area of

process solution at 423. K give results such as are shown in Figure 4. It is apparent that the reaction rate is linear with organic concentration over this concentration range. The estimated maximum rate of oxidation for organic compounds at the surface of the process solution is approximately 5×10^{-7} mole/cm²-sec at an organic vapor concentration of 0.03 mole/L or greater. An interesting corollary to these results is that a 0.6 m path length of thin film DETOXSM solution should be able to achieve six to seven "nines" destruction/removal efficiency for organic vapors in gases.

Figure 3: Reaction Rate versus Concentration

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Figure 4: Reaction Rate versus Concentration for o-xylene

B. Reaction Intermediates

Partial oxidation of organic compounds can be used to help identify the mechanism of the oxidation reaction. In a set of experiments trichloroethene, two scintillation fluids, and vacuum pump oil were partially oxidized and the resulting solutions analyzed for volatile and semivolatile organic components by EPA Methods 624 and 8270. Unfortunately, with the unstirred, Teflon-lined reaction bombs used, cooling required about 30. minutes, which was too long to isolate

more reactive intermediates. The intermediates seen are shown in Table II.

Table II: Organic Oxidation Reaction Intermediates

Organic Oxidized	Major Intermediates Detected
Trichloroethene	Tetrachloroethene Pentachloroethane
Scintillation Fluids (o-xylene, 1,2,4-trimethylbenzene, nonylphenolethoxylates)	1,2-dichloroethane benzoic acid 2,3,5-trichlorophenol
Mineral Oil	Benzoic acid Phthalate esters Paraffins and cycloparaffins

One of the first steps in oxidation of trichloroethene is apparently nucleophilic substitution of chloride for hydrogen, which involves abstraction of two electrons from one of the carbons. Tetrachloroethene is the principal intermediate seen in these experiments. At least part of the tetrachloroethene subsequently undergoes hydrochlorination with no oxidation to form pentachloroethane. After this step, the molecule apparently breaks apart quickly or is transformed into a compound which was not detected by the analytical methods used.

Oxidation of the scintillation fluids, which contained o-xylene, 1,2,4-trimethylbenzene, nonylphenolethoxylates (NPEs), and small amounts of fluorescing compounds, gave some more stable intermediates of 1,2-dichloroethane, benzoic acid, and 2,3,5-trichlorophenol. There were very small concentrations of other intermediates seen, including tetrachlorobutadiene, pentachlorobutadiene, benzyl alcohol, 1,3-benzene diol, methylbenzaldehyde, methylbenzoic acid, chlorobenzaldehyde, and chlorobenzoic acid. It appears that the ethoxylate groups from the NPEs are being broken off and oxidized through some pathways which at least partly involve formation of 1,2-dichloroethane, and that the methylated benzenes are being oxidized through formation of benzaldehydes and benzoic acids. Some hint of the fate of the aromatic rings may be seen in the presence of the butadienes, which are likely fragments of rings. All the chlorinated

compounds formed were present only in microgram quantities.

Partial oxidation of vacuum pump oil (a mineral oil) gave benzoic acid, some phthalate esters, and some paraffins and cycloparaffins. No partially oxidized straight chain hydrocarbons were seen, which would indicate that these materials react quickly once they have been formed, or that they were too heavy to be detected by the analytical methods used. The oil in general produced much less volatile and semivolatile organic intermediates than the other materials tested. LA-UR-94-1618

III. ORGANIC COMPOUNDS' DESTRUCTION STUDIES

A. Destruction Efficiencies for Neat Organic Materials

The results of destruction efficiency studies have previously been reported for a number of liquid organic materials, including bench scale, batch oxidation tests where >99.9999% destruction/removal efficiency (DRE) was obtained.⁶ Destruction efficiencies for solid organic materials in unstirred vessels have been determined, and are typical of other destruction efficiencies we have obtained in unstirred vessels, that is, from 99.% to 99.5%. It is apparent that a variety of organic materials can be completely destroyed by the process. The observed reaction rates indicate that from 5. to 50. Kg/hr of organic material (depending on its composition) can be destroyed in 200. L of process solution.

B. Destruction of Organics in Inert Matrices

The destruction efficiency for trichloroethene, o-xylene, and 1,2,4-trimethylbenzene absorbed into vermiculite have been reported previously as approximately 99.9%. In addition to these studies, 1.% by weight trichloroethene and 1.% by weight benzene in the six soil types given above have also been destroyed with great efficiency. Care was taken during these tests to mix the organic into the soil under sealed conditions and to maintain the soil under sealed conditions to keep the volatile organic in the soil matrix. For all soils less than 10. µg of either compound was detected in 5. g of soil after treatment, which represents greater than 99.98% reduction of these

organics in the soils and a final concentration of less than 2. µg/g. LA-UR-94-1618

IV. METALS' FATE STUDIES

A. "Soluble" Metals

A group of metals which were deemed to be soluble to some extent in the process solution were tested for extent of solubility over a range of acid concentration from approximately 1.8% to 7.2% by weight, and in the presence of 1.% to 2.% by weight sulfate or phosphate. Increased and decreased acid concentrations (as HCl) reduced solubilities for beryllium, cadmium, and chromium, and increased solubilities for neodymium, nickel, and vanadium. The presence of phosphate anions (added as phosphoric acid) reduced solubilities for beryllium, cadmium, and chromium, and increased solubility for nickel. Metals' solubilities in the presence of sulfate anion at room temperature are shown in Figure 5. Cadmium and neodymium solubilities were much less in the presence of 2.% sulfate. In the experiments with no phosphate or sulfate present, excess metal was precipitated as the chloride salt.

Figure 5: Metal Solubilities in DETOXSM with Sulfate at Room Temperature

B. "Non-soluble" Metals

Arsenic, barium, and lead should not be very soluble in the process solution, and this was found to be true.

Arsenic was found to be soluble in the standard process solution only to the extent of 3.0 g/L at room temperature. The oxidation state of arsenic in the process solution is +5, and excess arsenic precipitates as ferric arsenate. Excess arsenic

precipitated in clean sand could be rinsed from the sand using a 2.% by weight citric acid solution; the rinsed sand passed the RCRA Toxicity Characteristic Leach Procedure (TCLP) as a non-hazardous material.

Barium was found to be soluble in the process solution to the extent of 1.55 g/L at room temperature. Excess barium was precipitated as the chloride salt. The presence of sulfate anion in the process solution reduced barium solubility greatly, but it was found that maintaining 4.% to 8.% by weight calcium in the process solution would scavenge sulfate anion to allow barium solubility to be maintained at around 1. g/L. However, scavenging sulfate may not be necessary since the solids which resulted from barium in the presence of 1.% and 2.% by weight sulfate both were non-hazardous when tested by the TCLP.

Lead solubility in the standard process solution was found to be approximately 0.35 g/L at room temperature. Excess lead precipitated as lead chloride. Solubility increased to 0.57 g/L at 323. K and to 0.80 g/L at 348. K. Thus, it would be possible to selectively precipitate lead (and presumably other metals) from the process solution as the pure chloride salts as the solution was cooled.

C. Chromium(VI)

Chromium(VI) should be reduced to non-toxic chromium(III) in a process solution containing some organic material or iron(II). This was found to be true in process solutions containing 3.3% by weight iron(II), where no detectable amount of chromium(VI) remained after treatment of 1.% by weight chromium(VI) in the process solution.

D. Metals in Soils

The acidic process solution should be a highly effective medium for leaching metals from inert matrices, such as soils. To test the process solution's leaching ability, approximately 0.1% by weight arsenic, barium, beryllium, chromium(VI), and neodymium, and approximately 0.05% lead, were added to six soil types which were subsequently treated with the process solution at 473. K and rinsed with simulated process condensate (i.e., 1.% HCl). The metals were added to the soils as the oxides except chromium which was in the form of dichromate

salt. The soils were a sand, a sandy clay loam, a loam, a silty loam, a clay loam, and a clay. After treatment with process solution and rinsing with simulated process condensate, the metals were removed from the soils such that they were non-hazardous by the TCLP. An example of metal removal by rinsing is shown in Figure 6.

Figure 6: Removal of Arsenic from Soils by Rinsing

E. Separation of Metals from Process Solution

Studies have been conducted to determine whether toxic and radioactive metals could be separated from the process solution in order to isolate them in a more compact form for recovery or stabilization and ultimate disposal. It was surmised that adjusting the pH of the process solution by boiling off HCl would precipitate the iron in the process solution, while leaving many of the toxic and radioactive metals in solution. To determine the extent of separation which could be achieved, cerium, mercury, and neodymium were added to the process solution in concentrations from 0.1 g/L to 10. g/L. It was found that from 40. to 80.% of these metals could be separated in soluble form from the iron precipitate after pH adjustment to 3.0.

V. BENCH SCALE OXIDATIONS

Bench scale, stirred units for batch and continuous processing of liquid and solid waste surrogates have been fabricated and tested.

Table III lists the organic materials which have been oxidized in the units. Figure 7 shows an example of carbon dioxide levels over time in the recirculated gases during an oxidation run. The units have been operated for over 200. hours to date. HCl levels after the condenser have been

shown to be below 2. mg/m³. Tests with the bench scale systems are continuing with evaluation of long term performance and stirring efficiencies.

Table III: Organic Materials Oxidized in Bench-Scale Systems

n-Butyl Acetate
Scintillation Fluids
Mineral Oil
Texwipes™ (paper)
Cotton
Poly(vinyl chloride)
Latex Rubber
Polyethylene
Trim™ Sol (machining oil)
Granulated activated charcoal
Wood
Trichloroethene

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Figure 7: Carbon Dioxide Levels in Recirculated Gases, Bench Top Reactor

VI. PROTOTYPE CONCEPTUAL DESIGN

Figure 8 shows a generalized conceptual design for a mixed waste treatment prototype. Conceptual prototypes have been designed for application to polychlorinated biphenyls, tributyl phosphate, and solid combustible waste materials, at throughputs from 5. Kg/hr to 25. Kg/hr. Mass and energy balance calculations demonstrate that the reactor will have to be actively cooled for these waste applications. Flow, temperature, and pressure calculations have been made for these applications. Treatment of soils contaminated with hazardous organic compounds and toxic and/or radioactive metals is a more difficult application due to the solids handling equipment required. Treatment of water solutions containing radioactive and/or toxic metals, with or without the presence of hazardous organics, will require design of the treatment

system to handle removal of the excess water by evaporation. Component sizes, arrangement, and estimated costs have been determined. Estimates indicate that process systems for treatment of mixed wastes can be built as portable, skid-mounted units at a capital cost of \$500.K to \$2,000.K. LA-UR-94-1618

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Figure 8: Conceptual Prototype Design

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