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Direct Chemical Oxidation of Hazardous and Mixed Wastes

by

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Abstract

Direct Chemical Oxidation (DCO) refers to the use of continuously-regenerated peroxydisulfate (with possible hydrogen peroxide supplements) to effect total destruction of organic wastes in aqueous media. The process does not involve toxic catalysts or the cogeneration of secondary wastes. Peroxydisulfate ($S_2O_8^{-2}$) is one the strongest known chemical oxidants. It is routinely used in laboratory total carbon analyzers--uncatalyzed at 100 °C, or catalyzed by UV, platinum or dissolved transition metal ions--and detects by oxidative destruction to 0.01 ppm levels. We report: (1) development of a waste treatment approach grounded in industrial electrolysis practice and in reaction rate data for Pt-initiated $S_2O_8^{-2}$ oxidation at 100 °C; (2) tests of an electrochemical cell generating 1.5 N peroxydisulfate solutions; (3) lower-limit rate data for destruction of surrogates for chemical warfare agents and compounds with functional groups resisting oxidation; and (4) destruction of a Dowex® ion exchange resin, such as used in nuclear processing. This technique is particularly suited for applications in analytical laboratories or in manufacturing industries where the waste generation is low in volume, highly toxic or fugitive, or changing. The process may be tailored for destruction of very small to bulk quantities of chemical warfare agents.

INTRODUCTION

Direct Chemical Oxidation. We are developing a process we call "direct chemical oxidation" (or "DCO") for destruction of the organic fraction of radioactive, mixed and hazardous wastes [1]. It may also provide a combustion-free route to the destruction of broad classes of chemical warfare agents [2], either in bulk or weaponized form. The process operates in the aqueous phase at ambient pressure and at temperatures below 100 °C, and uses acidified peroxydisulfate ion (one of the strongest chemical oxidants known) to convert organic materials to water, carbon dioxide and inorganic minerals. During this oxidation, the peroxydisulfate is reduced to sulfate ion:

$$(NH_4)_2S_2O_8 + (\text{organics}) \Rightarrow 2NH_4HSO_4 + (CO_2, H_2O, \text{inorganics}) \qquad (1)$$

The sulfate is then recycled by electrolysis to produce peroxydisulfate. The anodic and cathode reactions occur in parallel flow channels separated by a porous ceramic block:

$$2NH_4HSO_4 = (NH_4)_2S_2O_8 + 2H^+ + 2e^- \text{ (anode compartment)} \qquad (2)$$
$$2H^+ + 2e^- = H_2 \quad \text{(cathode compartment)} \qquad (3)$$

(The hydrogen may be recombined with oxygen using a catalyst or discharged, or avoided altogether by using an oxygen-reducing cathode.) Because of the electrical cost of regenerating the peroxydisulfate ion, it may be attractive in some cases to supplement

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treatments of waste with inexpensive, purchased hydrogen peroxide, so that the peroxydisufate is predominately used in difficult steps such as reaction initiation, oxidation of recalcitrant intermediate species, or polishing of the final product.

The standard electrode potential of acidified peroxydisulfate ($E^\circ = 2.05$ V) is exceeded by ozone (2.07 V) and fluorine (2.87 V), but these have no practical application in treatment of bulk, concentrated wastes. Ozone gas is unstable above 5% concentration, and contacting is difficult; fluoride secondary wastes are toxic. Strong transition metal couples ($E^\circ < 2.0$ V) are used in mediated electrochemical oxidation (e.g., Ag(I)/Ag(II) or Co(II)/Co(III)); such catalysts are toxic and must be removed from secondary waste products [3].

In contrast, acidified ammonium peroxydisulfate is stable at room temperatures in 1-5 N solutions, but becomes a rapid oxidant at moderate temperatures (80-100 °C), or at lower temperatures when activated by UV radiation, platinum, or certain transition metal catalysts (Cu(II), Ag(I)) [4-6]. We expect the following benefits from the DCO process: (1) recycling the oxidant avoids the accumulation of secondary wastes; (2) no toxic catalysts are required; (3) fugitive losses are minimized by confining the reaction within a liquid medium; (4) the thermal inertia of the reaction medium stabilizes the process against thermal runaway. The overall process of waste oxidation and sulfate recycle is shown in Figure 1.

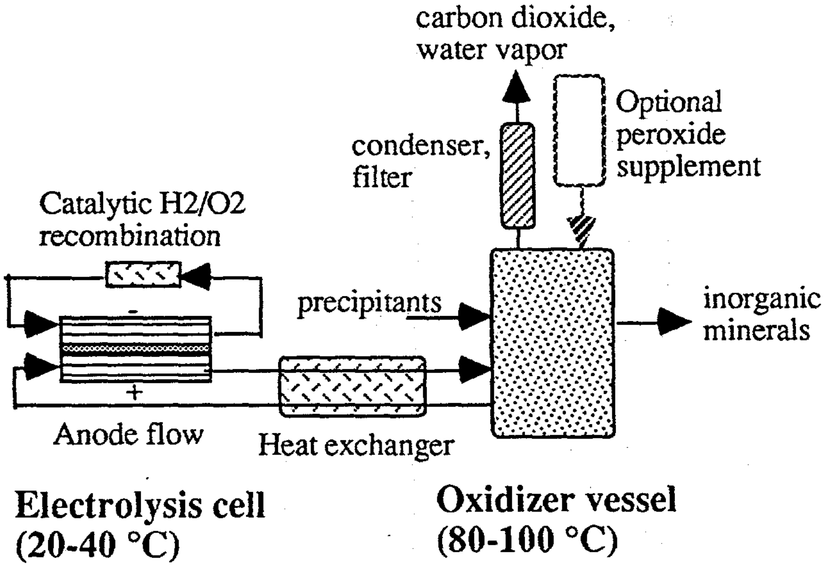

Figure 1. Direct chemical oxidation refers to the use of regenerated peroxydisulfate solutions to destroy organic wastes, with possible assistance of bulk hydrogen peroxide supplements. The sulfate is recycled to peroxydisulfate in the electrolysis cell and therefore does not constitute a secondary waste.

Industrial Basis of the Process. Because of its properties, peroxydisulfate has found widespread use in total organic carbon (TOC) analyzers: following oxidative destruction of organic substances to concentrations of ~0.02 ppm, the evolved CO_2 is concentrated and detected by spectroscopy [7]. Peroxydisulfate is used for cleaning and etching in electronics fabrication, industrial bleaching, paper pulp treatments, etc. [8] and in some actinide recovery techniques [16]. Several thousand tons are used annually to oxidize *in situ* the liquid polymers which are used in the hydraulic fracture of petroleum-containing rock during recovery operations [9].

Electrolysis cells with flowing electrolyte have long been used to produce peroxydisulfate from sulfate as an intermediate step in the production of hydrogen peroxide[10]. Until the 1960's, the world's supply of hydrogen peroxide was produced by oxidizing water with peroxydisulfate in steam-jacketed vessels, from which the peroxide was continuously distilled under reduced pressure. The resultant sulfate liquors were then returned to electrolysis cells for regeneration of the peroxydisulfate at 5-6 V and 75-85% efficiency. The electrolysis cells used platinum anodes, inert separators (e.g., porous ceramics) and inert graphite or lead cathodes. Three variants used by the industry were defined by the composition of the working liquors: the Weissenstein process (based on 5 M H_2SO_4), the Pietzsch & Adolph process (using concentrated ammonium sulfate, from which potassium peroxydisulfate is precipitated), and the Loewenstein process (using continuously-circulated ammonium sulfate). The latter process produces peroxydisufate at high coulomb efficiencies (>80%) in concentrations (Table 1) which are useful directly as the oxidant in a platinum-catalyzed waste destruction process.

Advanced electrolysis cells of increased voltage and coulombic efficiency are commercially available, and are generally based on parallel-plate geometry with provisions for rapid electrolyte flow[11,12].

Table 1. Operating compositions of the Loewenstein process

Composition	Entering cells	Leaving Cells
Ammonium sulfate	1.59M	0.58 M
Ammonium peroxydisulfate	0	1 M (2 N)
Sulfuric acid	2.65 M	1.63 M

Purposes of this work. The goal of our work is to develop a generalized ambient temperature, water-based process for treatment of undifferentiated organic liquid and solid wastes. Specific objectives of the work reported here are:

1. Construct a bench-scale electrolysis cell and verify operational voltages and efficiencies for production of peroxydisulfate sufficiently concentrated for bulk waste treatment.
2. Measure rates of destruction of organic materials characteristic of certain mixed waste streams, difficult-to-oxidize compounds, and compounds having functional groups similar to those found in chemical warfare agents.
3. Apply the technique to the destruction of surrogate ion exchange resins used in nuclear processing.
4. Assess the scale-up and scale-down potential, and applications to chemical demilitarization and waste treatment.

EXPERIMENTAL APPROACH

Electrolysis cell. The electrolysis cell shown in the schematic in Figure 2 was designed to produce peroxydisulfate under any of the conditions used in the peroxide industry, for bench top evaluation in either batch or continuous mode. The anodes were 1 mm Pt wires of length up to 75 cm coiled around a glass tube to make active areas of up to 24 cm^2 surface area. The anode wires are cross-coiled to allow parallel paths to prevent overheating at high currents. The 360 cm^2 cathodes are three graphite rods of diameter 1.27 cm and (wetted) length of 30 cm. A porous ceramic separator of diameter 8.8 cm and 2 mm thickness separates a 1.67 L anode chamber from a cathode chamber of the same volume. A water jacket allows flow of refrigerated cooling water, which was maintained at 7-15 °C and controlled to maintain an anolyte temperature below about 20 °C. This cell was left vented to prevent accumulation of hydrogen gas.

Cell voltage and electrode potentials (measured against a platinum reference electrode immersed in the H_2-saturated acid catholyte) are shown in Figure 3.

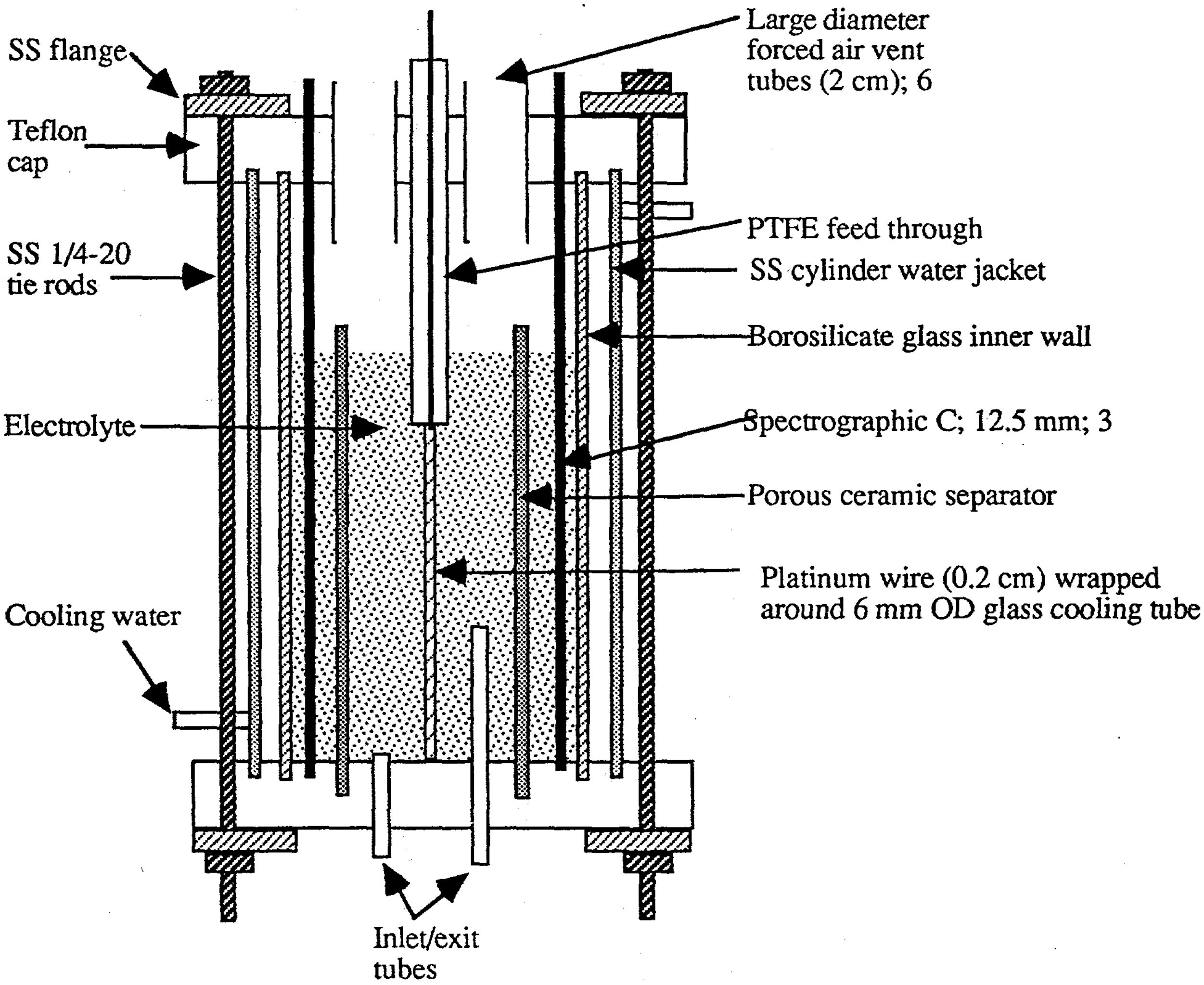

Figure 2. A bench scale electrolysis cell of cylindrical was constructed to produce peroxydisulfate under conditions similar to those used industrially.

The accumulation of peroxydisulfate is plotted against time for a fixed current of 10 A (10 kA/m^2) in Figure 4. The efficiency of the cell is determined to be 82% by comparison of the experiment curve for peroxydisulfate against the theoretical line derived from Faradays law:

$$[Ox] = It/FV_a \tag{4}$$

where [Ox] is the oxidant concentration in equivalents per liter (2 equivalents per mole of peroxy species), I is current, F is the Faraday constant (96500 coul/equiv.), and V_a is the anolyte volume. Total oxidant concentrations are determined by reduction with an excess of Fe(II) ion followed by back titration with standardized permanganate solution. The electrolyte produced by this cell will contain peroxydisulfate, peroxymonosulfate and a small amount of hydrogen peroxide from the slow hydrolysis reaction.

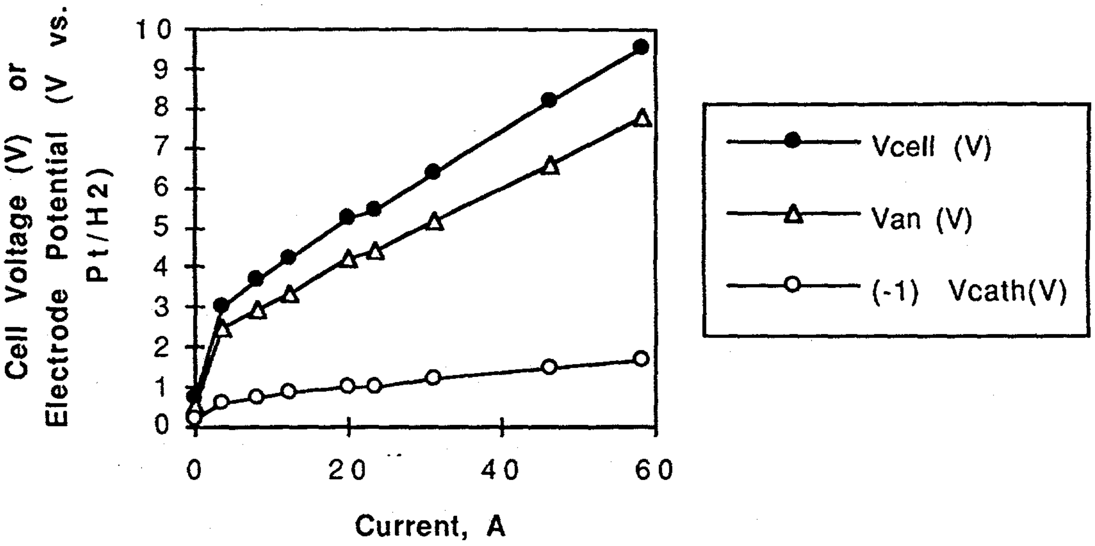

Figure 3. Polarization curves for the electrolytic production of $(NH_4)_2S_2O_8$ at 16 °C from the electrolyte, 2.65 M H_2SO_4 and 1.59M $(NH_4)_2SO_4$. Anode area is 24 cm^2.

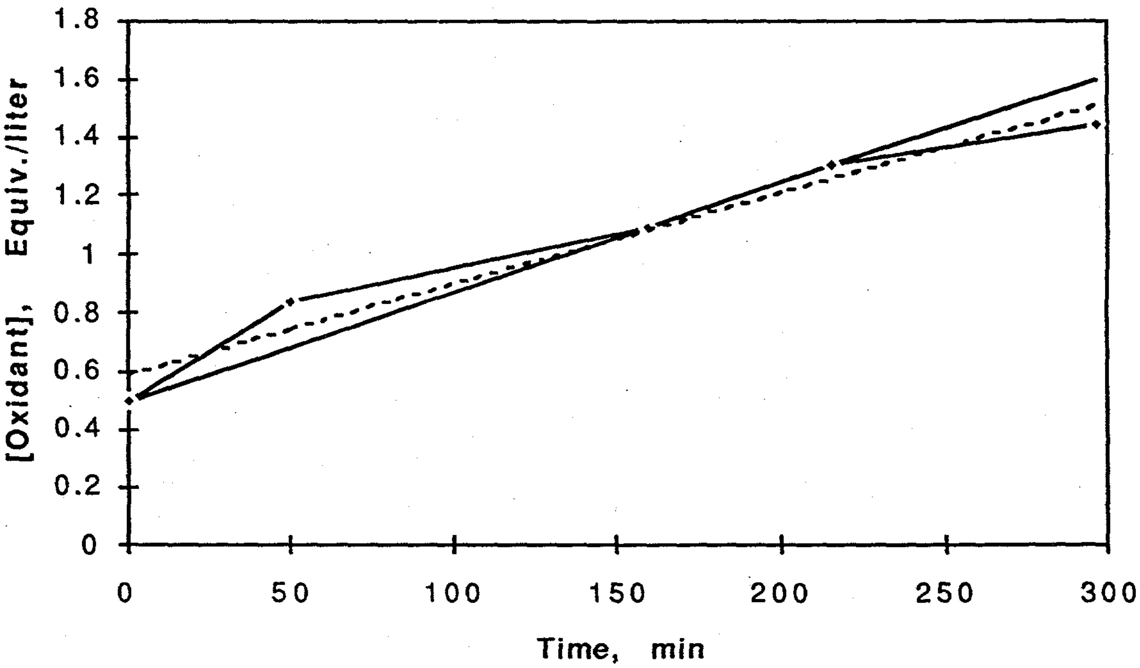

Figure 4. The accumulation of peroxydisulfate (data) for fixed electrolysis at 10 A and 16 °C is plotted against electrolysis time. The solid line is the theoretical concentration (It/FV_a); the broken line is a least square curve fit, indicating a coulomb efficiency of 82%.

Oxidation of Representative Compounds Our choice of organic materials for destruction efficiency and rate determinations was based on the similarity with the composition of the products of the first stage of detoxification of chemical warfare agents (which were not available to us). Taken together, the compounds methyl phosphonic acid (MPA), $(CH_3)P(OH)_2O$; 2,2'-thiodiethanol (TDE), $S(CH_2CH_2OH)_2$; and Di-isopropyl-methane-phosphonate (DIMP), $(C_3H_7O)_2P(CH_3)O$, have some bonds and functional groups similar to those of hydrolyzed GB, HD (Mustard), and oxone-detoxified VX, respectively, and are commonly used as relatively benign chemical surrogates for these materials. The test on tri-ethyl amine (TEA) was intended to test an alkyl amine which is known to be resistant to oxidation by hydrogen peroxide in wet oxidation technology [13,14], and might constitute the slowest step in the oxidation of VX detox fragments containing a tri-substituted amino group. In acid solutions ammonium ions are not oxidized by peroxydisulfate.

To conduct these tests, a conventional total carbon analyzer (Model 700 TOC , O.I. Analytical, Inc.; ref. [7]) using sodium peroxydisulfate acidified with phosphoric acid was used to provide rough destruction efficiency and empirical rate data for certain surrogate wastes by fixing the reaction time and temperature. Weighted quantities of organic materials were dissolved in water and diluted; aliquots were taken for analysis in the total carbon analyzer for reaction times fixed at 3 minutes (rather than the 6 minutes normal procedure). The carbon concentrations (ppm as C) determined from the weights of the compounds and dilution factors were compared with those determined from the CO_2 which was collected and passed through the integrating IR spectrometer tuned a CO_2 absorption frequency. A platinum wire was provided to activate the peroxydisulfate. The results appear in Table 2. The destruction extent after 3 minutes may be used to estimate the first order rate constant, assuming a rate equation of the form:

$$\Delta[X]/\Delta t = k_a\,[S_2O_8{}^{2}] \qquad (5)$$

Here $\Delta[X]$ is the reduction in concentration of the substance (equiv/L in the reaction vessel of the TOC, equal to the product of destruction efficiency and the initial concentration); $[S_2O_8{}^{2}]$ is the nearly constant concentration of peroxydisulfate in the vessel (equiv./L); and Δt is the reaction time.

Table 2. Destruction efficiencies and estimated destruction rates of surrogates for chemical warfare agents.

Compound	Equiv. wt.	[C], by wt.	[C], TOC*	Destruction	$10^2 \times k_a$
	g/equiv.	ppm	ppm	%	min^{-1}
MPA	12.003	22.53	22.5	99.8	2.1
DIMP	4.095	23.39	23.2	99.1	0.43
TDE	4.364	28.51	28.3	99.4	0.82
TEA	2.881	15.80	14.7	93.0	0.10

Analytical conditions: T= 100°C ; Fixed reaction time = 3 min.; $[H_3PO_4]$= 0.0574 M (pH~1.24); $[S_2O_8{}^{-2}]$ = 0.287 N; Pt wire catalysis.

Destruction of ion exchange resin For the very large amount of underground storage tank wastes located at Hanford WA, ion exchange resins will be used to separate the highly radioactive elements, such as Cs^{137}. Eventually the spent resins must be destroyed, and thermal combustion processes may not be acceptable. Accordingly, we sought to evaluate the DCO technique using surrogates for this waste.

Solids cannot be analyzed with the TOC apparatus. Therefore an electrically heated, 500 ml three-neck round-bottom flask was used as a reaction vessel. The center neck was connected to a water-cooled condenser. A mixture of 5 mL (~3.4 g dry) Dowex® I-x4 anion exchange resin and 100 mL of dilute sulfuric acid (pH~2) was added to the reactor, and the mixture was stirred and heated to the boiling point (100-101°C). A 4.5 N $Na_2S_2O_8$ solution was continuously added into the reactor, using a peristaltic pump. The rates of peroxydisulfate addition were 1.0, 2.0 and 4.0 mL/min. The reaction between the peroxydisulfate and the resin was vigorous and exothermic. The resin is porous, and the pore volume can change during the destruction reaction. We measured the total apparent volume of resin with a graduated cylinder at various points during oxidation, as a rough measure of destruction extent. Liquid samples were also taken at the time of volume measurement, and the total organic carbon was measured (TOC analyzer).

The change of total volume of resin with reaction time is shown in Figure 5. The increase in volume at the beginning may reflect the swelling of the resin particles when heated in acid. Toward the end of each run, the resin particles became powdery. The destruction of the solid was accompanied by a build up of a fully dissolved organic materials (i.e., having no separate oil phase), which reached a maximum concentration of 3500-4000 ppm (determined by TOC) just as the solids vanished. The ion exchange resin is an organic polymer containing amino functional groups. These dissolved materials may well contain tri-substituted amines which are difficult to oxidize--such as were found following treatment in boiling Fe(II)-catalyzed hydrogen peroxide ("wet oxidation") [13]. The rather high dissolved concentration might indicate the mineralization of some dissolved organic reaction intermediates is slower than the heterogeneous oxidation of the solids containing ionic groups.

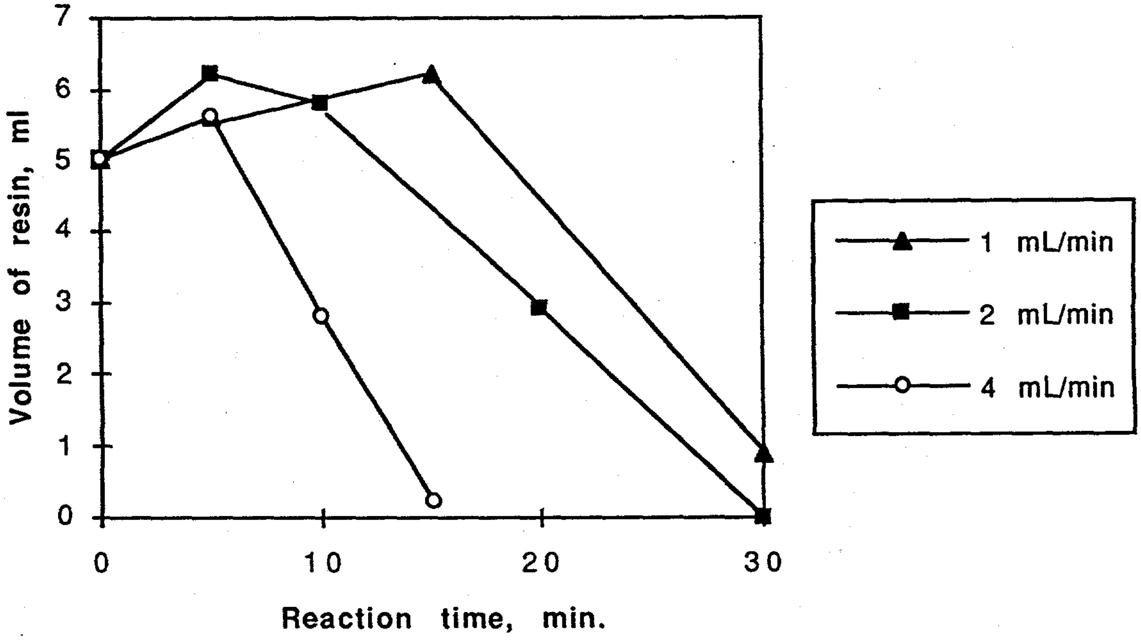

Figure 5. Destruction of Dowex® I-x4 anion exchange resin by acidified $Na_2S_2O_8$ at 100 °C, as monitored by decrease in apparent volume of the wetted particles.

DISCUSSION

Cell results. We produced ammonium peroxydisulfate under conditions similar to those of the Loewenstein process (Table 1.) We achieved a coulomb efficiency of 82% from operation at 16°C at a current of 10 A and a current density of 10 kA/m^2, under batch conditions. In contrast, the industrial process makes use of a cascade of cells, achieving a net efficiency of 82-84% at a higher temperature (28-33 °C), with a flow-through of 110 L/h. The production of peroxydisulfate at the platinum electrode is self-limiting because of the concurrent formation of peroxymonosulfate from Pt-catalyzed decomposition of peroxydisulfate [10]:

$$H_2S_2O_8 + H_2O = H_2SO_5 + H_2SO_4. \qquad (6)$$

Although peroxymonosulfate is a strong oxidant, it can depolarize the anode reaction leading to increased oxygen evolution and a corresponding decrease in coulomb efficiency [10]. Consequently, industrial cells are designed for cascaded flow through with minimum volume and residence times. A significant difference is the "current concentration" in the electrolysis cells of 17 A/L (Loewenstein) vs. 6 A/L (this work).

Destruction tests. The chemistry of peroxydisulfate reactions is reviewed by House[6]. In the presence of transition metal catalysts (such as Ag^+ or Cu^{++}), reduction of peroxydisulfate is bimolecular and depends on the concentrations of catalyst and peroxydisulfate:

$$-d[S_2O_8^{-2}]/dt = k_2\,[S_2O_8^{-2}][Ag+] \qquad (7)$$

In the absence of catalysis, reactions are often first-order unimolecular and the initial step is the slow decomposition of peroxydisulfate into sulfate free radicals,

$$S_2O_8^{-2} \dashrightarrow 2SO_4^{-\circ}\,, \qquad (8)$$

followed by a rapid attack on reducing agents. In general the oxidation rate shows a first order dependence on peroxydisulfate concentration

$$-d[S_2O_8^{-2}]/dt = k_o\,[S_2O_8^{-2}],\ \text{or} \qquad (9)$$
$$-d[R]/dt = k_o'[S_2O_8^{-2}] \qquad (10)$$

if reducing agents R are present. The rate constants in the presence of reducing agent k_o' are generally much larger than that for aqueous oxidation k_o, and vary from reductant to reductant. This might be explained by formation of free-radical fragments of the reducing agent by reaction with the sulfate free radical; these fragments then speed the decomposition reaction (8) and result in a higher steady-state reduction rate (10). First order dependencies are found with, for example, water, hydrogen peroxide, thiosulfate, formate, formic acid, and 2-propanol; for example, at 40 °C, the rates are 0.33×10^{-4} min^{-1}, 123.0×10^{-4} min^{-1} and 81.3×10^{-4} min^{-1} for water, formate and formic acid respectively [6]. The platinum wire (recommended in total carbon analysis of water-insoluble saturated hydrocarbons) accelerates the formation of sulfate free radicals or OH° free radicals through reactions of a peroxymonosulfate intermediate.

In interpreting our total carbon analysis experiments, we were able to measure total carbon dioxide emissions after 3, 6 or 12 minutes of treatment with 0.287 N peroxydisulfate. (Six minute reaction time is recommended for TOC under these conditions). We were able to set a lower bound to a hypothetical first-order apparent rate constant k_a from the concentrations of initial concentrations of MPA, TDE, and DIMP according to an empirical law of the form (10). These data appear in Table 2. The apparent rate constants of 0.004- to 0.02 min^{-1} for these compounds are probably underestimated, because the reactions were essentially complete at 3 minutes. The relatively slow rate for tri-alkylamine (which was only 93% oxidized after 3 minutes) is consistent with its appearance in the products of wet oxidation of ion exchange resins.

Resin destruction. The destruction of ion exchange resin by DCO is effective. Even a 100-fold scale-up (to a 50 L reactor) should destroy resins at a rate of 1 kg/hr. Under roughly similar conditions of temperature and oxidant concentration, wet oxidation of the same resins required over 5 hours of treatment in hot boiling media fed continuously with hydrogen peroxide.

APPLICATIONS

An ambient pressure and temperature waste treatment system using regenerated peroxydisulfate ion might find value in waste treatment where more conventional approaches (such as combustion or bleaching) are unacceptable for reasons of scale, secondary waste generation, public acceptance, economics or compliance. Direct Chemical Oxidation uniquely confers the following combination of benefits: (1) general applicability to organic solids and liquids, including chlorinated, saturated-hydrocarbon, or graphite-containing wastes; (2) no toxic catalysts are required; (3) primary waste containment is in a dust-free condensed phase; (4) thermal stability follows from electrolytic control and the high thermal inertia of medium; (5) the technique is based on mature technologies practiced by large industries; (6) potential scale-up (ton/day) or scale-down (g/h), using commercially available electrolysis cells and available unit process equipment.

A chemical warfare demilitarization application would involve (1) detoxification of the agent by water or base hydrolysis or by minimal application of a oxidant; followed by (2) total mineralization of the *detoxified* products by DCO. For example, VX would be detoxified using peroxymonosulfate (produced *in situ* by platinum-catalyzed decomposition of peroxydisulfate), then the non-lethal phosphonic and sulfonic acid fragments would be mineralized. The detoxification step is the same found with Oxone, a commercial bleach containing peroxymonosulfate, where the reaction has a half life of 27 minutes at ambient temperatures [15].

The scale-up and scale-down flexibility is achieved by replication of industrial electrolysis cells of optimized size. This flexibility suggests transportable units scaled appropriately for temporary duty in treaty verification and enforcement, site remediation, or on-site destruction of highly specialized, very toxic or fugitive materials. A bench-scale unit might be valued by small analytical or manufacturing industries wherein waste production is small, unpredictable, or intermittent. Radioactive or mixed wastes may be safely destroyed in dust-free conditions within a liquid phase at ambient temperatures, which strengthens the first level of confinement over that achieved by a open combustion process.

CONCLUSIONS

A low temperature and ambient pressure waste treatment process may be developed by combining aspects of a mature electrolysis technology with the effectiveness of peroxydisufate oxidation, as demonstrated by total carbon analysis and by bulk oxidation applications. We have replicated the operating conditions and efficiencies of the Loewenstein process for sulfate/peroxydisulfate production, to produce a reagent of useful (1.5 N) concentration. Using a modified total carbon analyzer using ~0.3 N peroxydisufate at 100 °C, we have shown destruction of surrogates for chemical warfare agents with apparent first order rate constants of 0.004- to 0.02 min^{-1}, as required for practical scaleup. The destruction of ion exchange resins is sufficiently fast to suggest kilogram per hour rates in small vessels.

The appropriate next stage of engineering is the integration of a peroxydisulfate electrolysis cell with a digester vessel for continuous operation in a closed loop, with the objective of developing the data base for scaleup, optimization and eventual permitting.

Acknowledgments

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