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Photolytic Destruction of Oxalate in Aqueous Mixed Waste

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Abstract

In aqueous plutonium processing, residual oxalic acid can be destroyed (oxalate kill) by UV light with hydrogen peroxide (H_2O_2) in 1 M HCl solutions. By controlling the amount of H_2O_2, the oxalate kill process will not affect the chloride concentration. In nitric acid solutions, UV light alone can destroy the oxalic acid. However, with H_2O_2, the rate of destruction is faster. After the destruction of oxalic acid, the acidic solutions may be reusable without further purification process.

I. Introduction

In aqueous processing associated with plutonium production, hydrochloric acid and nitric acid solutions have both been used. To separate plutonium species from the acidic solutions, excess oxalic acid is added to the solution to precipitate the plutonium as oxalates which are subsequently collected and calcined to form plutonium oxide. The excess oxalic acid in acidic solutions must be completely destroyed (called oxalate kill) before further processing for the following reasons: 1. in final waste forms such as grout, oxalic acid slowly decomposes into CO_2, generating gas, and 2. oxalic acid will interfere with the collection of residual ionic Pu species in acidic solutions by ion exchange. Several methods have been reported for destroying oxalate: 1. evaporation with 12 M HNO_3, (1); 2. oxidation with $KMnO_4$ at room temperature, (2); dichromate at 65 °C or less, or ozone at 80 °C (1). All the chemical oxidation methods are not suitable in HCl solutions because the chloride ion can also be oxidized.

We have previously studied the destruction of Trimsol (a mixture of organic compounds, containing 11% chlorine in the form of chlorinated organic compounds) using a ultraviolet/hydrogen peroxide (UV/H_2O_2) process (3). It has been found that all carbon atoms are oxidized to CO_2 and chlorine atoms are turned into chloride ions. The results have indicated that $OH\cdot$ radicals, generated from photochemical decomposition of H_2O_2, will oxidize organic carbons to CO_2 much more effectively than oxidize chloride ions. From this knowledge, it was anticipated that the UV/H_2O_2 process may be applicable to the destruction of oxalic acid in HCl solutions.

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II. Experiments

1. Apparatus

A UV/H_2O_2 system was built with a glass reactor. The lamp is a 450 W medium pressure mercury lamp (~25 cm long, Canrad-Hanovia). The total volume of the system is ~2 liters. A peristaltic pump was used to add H_2O_2 solution to the system and a magnetic bar was used to stir the solution. A diagram of the system is shown in Fig. 1.

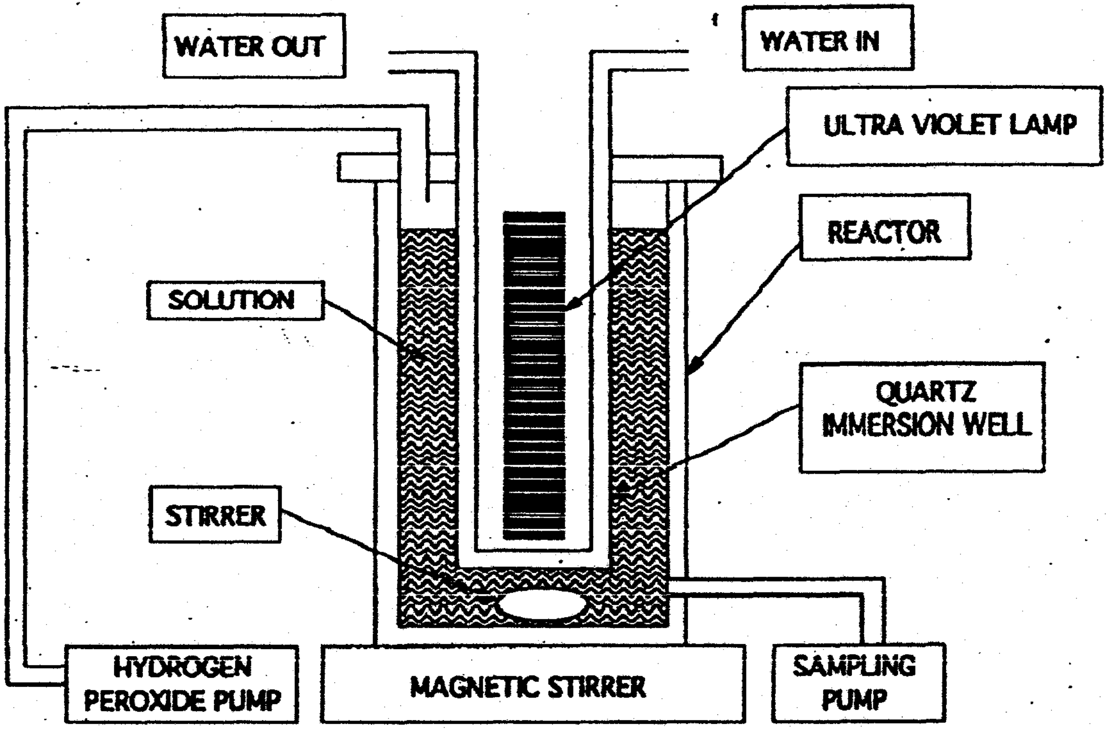

Fig.1 UV/H_2O_2 batch reactor

2. General Procedures

All solutions were prepared with deionized water in a large beaker. They were then poured into the reactor and stirred. After turning on the lamp, the H_2O_2 feed pump was started. Within a few minutes, the solution was heated to 40 °C and cooling was initiated to maintain the temperature. All runs described in this study were conducted at 40 °C. Samples for chemical analysis were collected through a plastic valve, and the volume of each sample was equal to the increment of solution in the reactor due to the addition of H_2O_2 so that the total volume of solution in the reactor was approximately constant. Analysis of total organic carbon (TOC) in solutions was done by using a TOC analyzer and the chloride ion analysis was done by ion selective electrode. The concentrations used in all plots were corrected from sampling and dilution by the H_2O_2 solution.

III. Results and Discussion

1. Reaction of ~1M HCl (no oxalic acid) with UV light with/without H_2O_2

The purpose of these experiments was to determine the effect of UV light on chloride ion in the presence and absence of H_2O_2. In one experiment a, solution of 30% H_2O_2 was added to the ~ 1M HCl at the rate of 1.0 mL/min; and for the other run, water was added at the same rate. The change of chloride concentrations for both runs are shown in Fig. 2. It is clear that chloride does not undergo photooxidation by UV light alone. However, with UV light and H_2O_2, OH· radicals are formed which can oxidize the chloride ions. We did not attempt to identify the oxidation products of chloride. A possible mechanism of the initial oxidation of Cl^- by OH· in acidic solutions is:

1 $HO\cdot + Cl^- \rightarrow HOCl^-$

2 $HOCl^- + H^+ \rightarrow H_2O + Cl\cdot$

3 $Cl\cdot + Cl^- \rightarrow Cl_2\cdot^-$

4 $Cl_2\cdot^- + OH\cdot \rightarrow HOCl + Cl^-$

The rate constants ($L\ mol^{-1}\ s^{-1}$) of eqs. 1 and 4 are 4.3×10^9 and 1×10^9 respectively (4). Hypochloric acid can be further oxidized by OH· radicals.

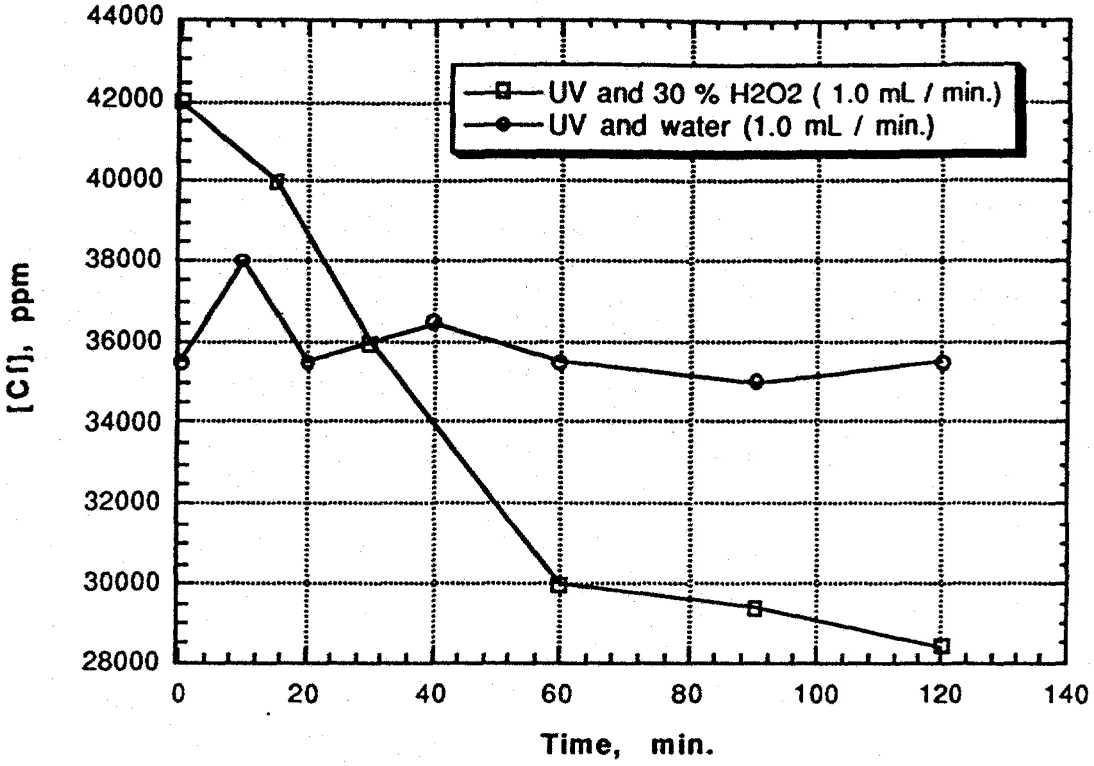

Fig.2 Reaction between UV light and HCl, with/without H_2O_2

2. Destruction of ~0.3 M oxalic acid in 1 M HCl by UV/H_2O_2

In all experiments, a ~0.3 M oxalic acid solution was used because it is representative of the concentration encountered in actual processing situations. The source of H_2O_2 was a 30% H_2O_2 solution. For the first two runs, the rate of H_2O_2 addition were 1.0 mL/min and 0.23 mL/min respectively. The results are shown in Figs. 3 and 4.

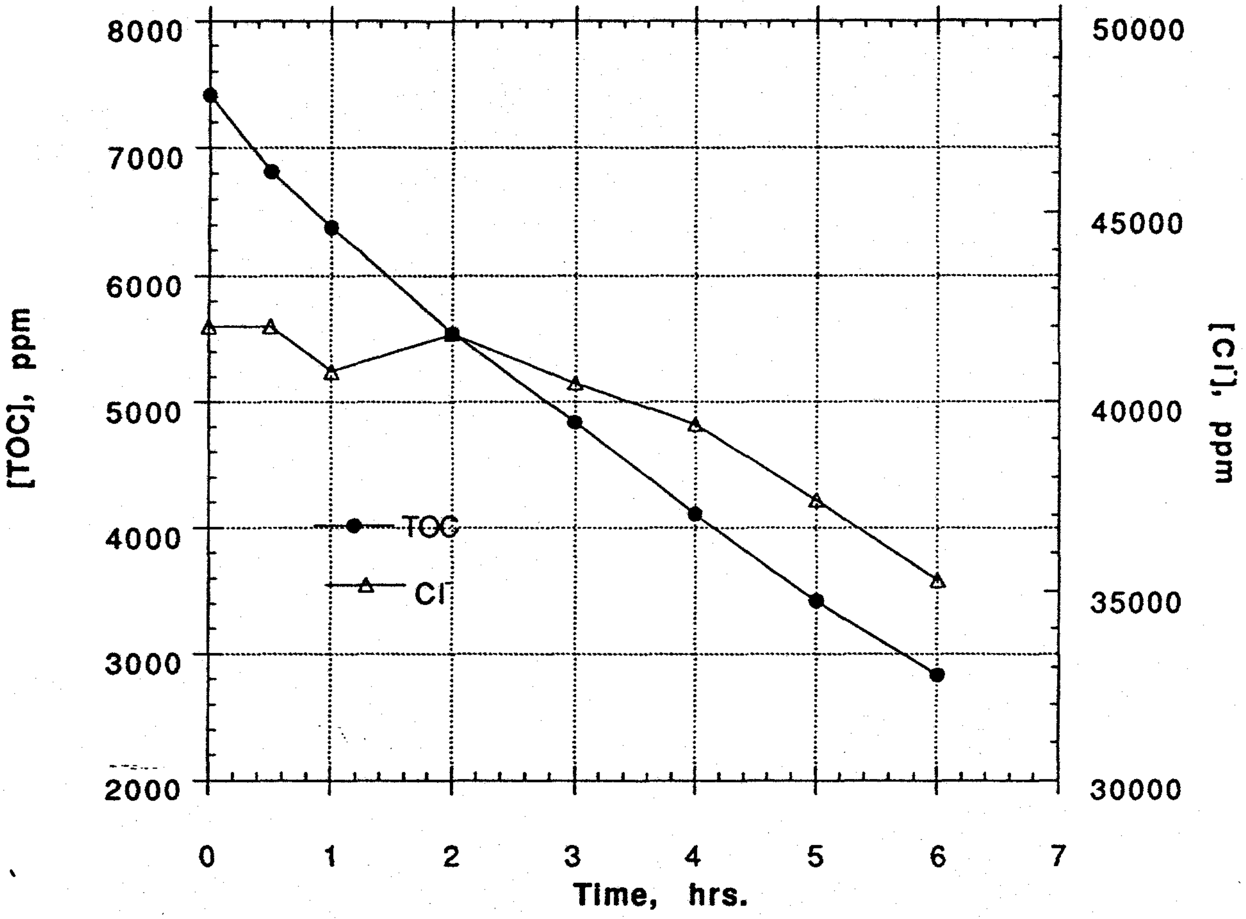

Fig.3 Oxalate destruction in HCl with 1.0 mL/min of H_2O_2

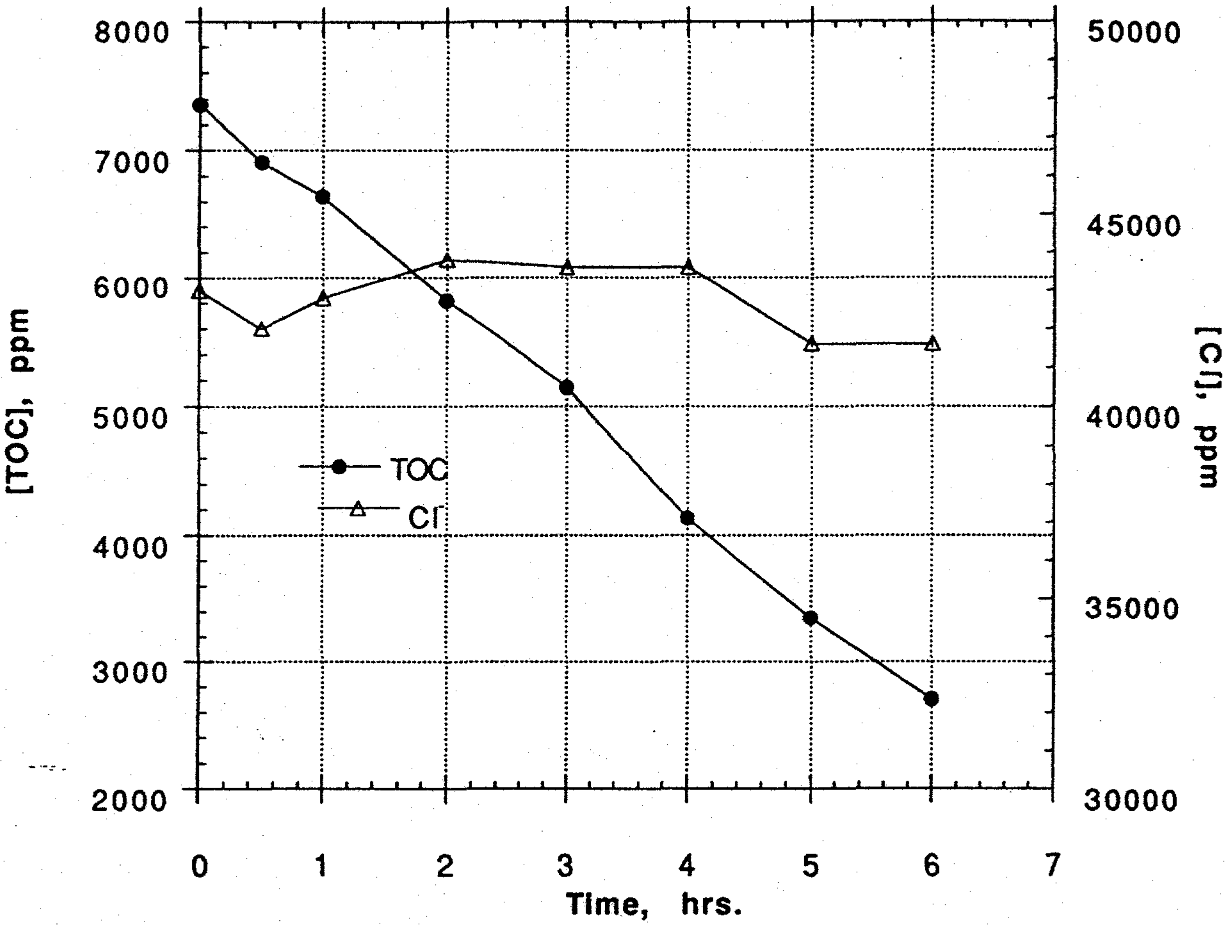

Fig. 4 Oxalate destruction in HCl with 0.23 mL/min of H_2O_2

With the ultraviolet light (200-300 nm), H_2O_2 will undergo photochemical decomposition to produce OH· radicals that are able to oxidize oxalic acid to CO_2. However in the presence of large excess of chloride ions in ~1 M HCl, the reaction rates between OH· and Cl^- (eqs. 1 and 2) are much faster than that of OH· and oxalic acid ($k = 1.4 \times 10^6$ L mol^{-1} s^{-1}) (4). It is likely that the oxalic acid is oxidized to CO_2 by Cl· radicals as shown in eq. 5:

5 $H_2C_2O_4 + 2Cl\cdot \rightarrow 2HCl + 2CO_2$

From Figs. 2 and 3, it seems clear that under the following two conditions, the oxidation of chloride ions can happen: 1) rate of OH· radicals generation is high due to higher rate of H_2O_2 addition, and 2) when the concentration of oxalic acid is low. Higher rate of OH· generation is likely to produce higher [Cl·] which can be either reduced by reacting with oxalic acid (eq. 5) or oxidized by reacting with chloride and OH· (eqs 3 and 4). This is illustrated in Fig. 3. When the concentration of oxalic acid is very low (Fig. 2 is the extreme case that has no oxalic acid), reduction of Cl· to chloride by oxalic acid will be diminished and the oxidation of Cl^- becomes the dominant reaction. To minimize the oxidation of chloride ions during the destruction of oxalic acid, the rate of H_2O_2 addition must be carefully controlled. As the concentration of oxalic acid decreases, the rate of H_2O_2 addition should also be decreased. Results of a demonstration run are shown in Fig. 5. For the first 2 hours, H_2O_2 was fed at a rate of 1.0 mL/min, followed by 0.5 mL/min for 5 more hours and 0.23 mL/min for the remaining 10 hours. In this run, the chloride concentration showed a slight decrease.

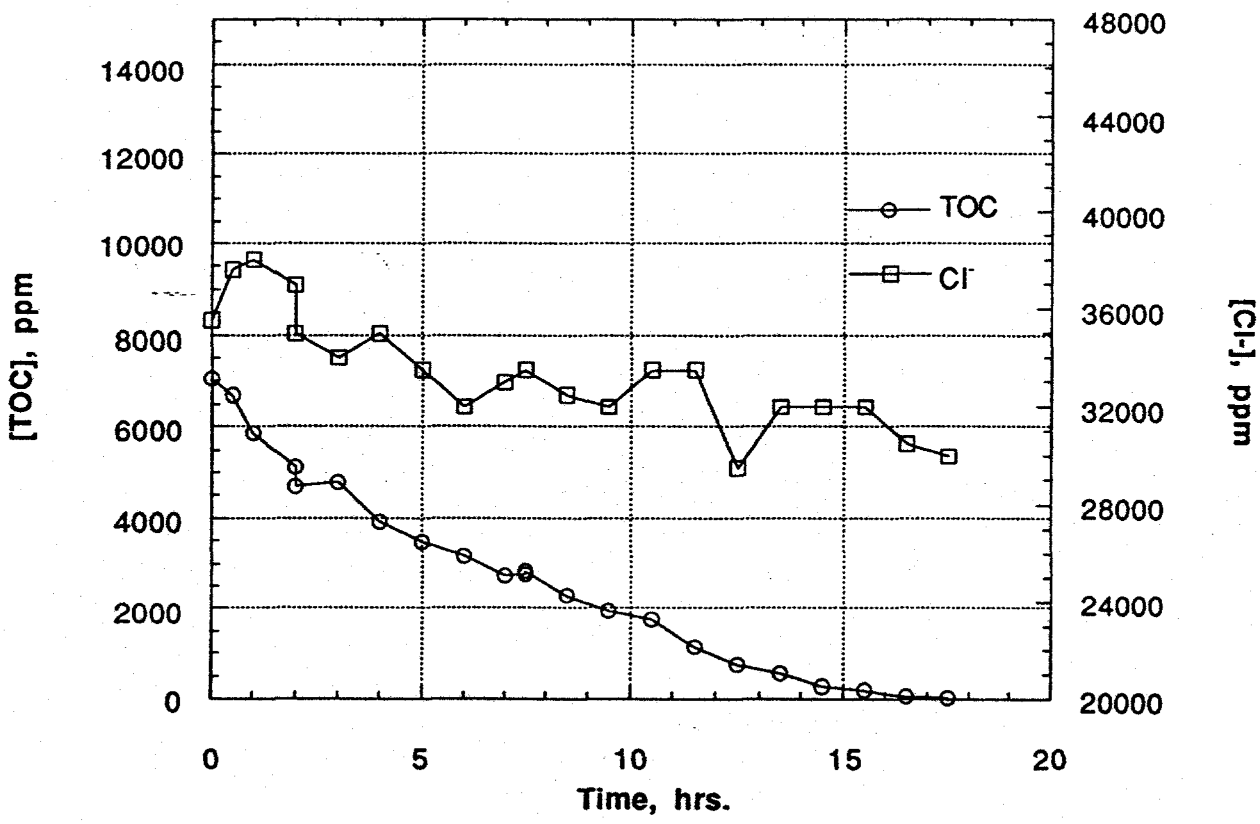

Fig. 5 Oxalate destruction in HCl with decreasing addition rate of H_2O_2

3.4. Photolytic destruction of oxalic acid in 1 M HNO_3 solutions

Three experiments were carried out: 1). ~0.3 M oxalic acid without H_2O_2, 2). ~0.3 M oxalic with H_2O_2 and 3). ~0.3 M oxalic acid with 30% H_2O_2 using a 2 kW mercury lamp and circulated reactor. The results of experiments 1 and 2 are shown in Figs. 6 and 7.

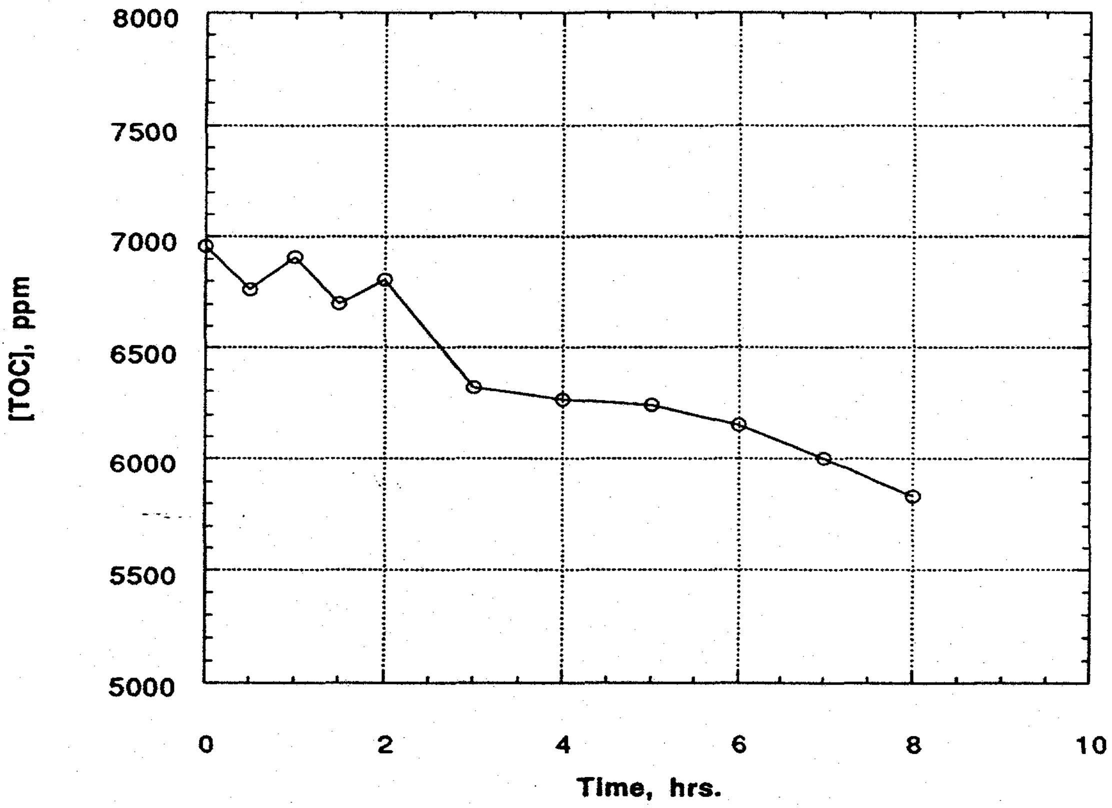

Fig. 6 Destruction of ~0.3 M oxalic acid in 1 M HNO_3 without H_2O_2

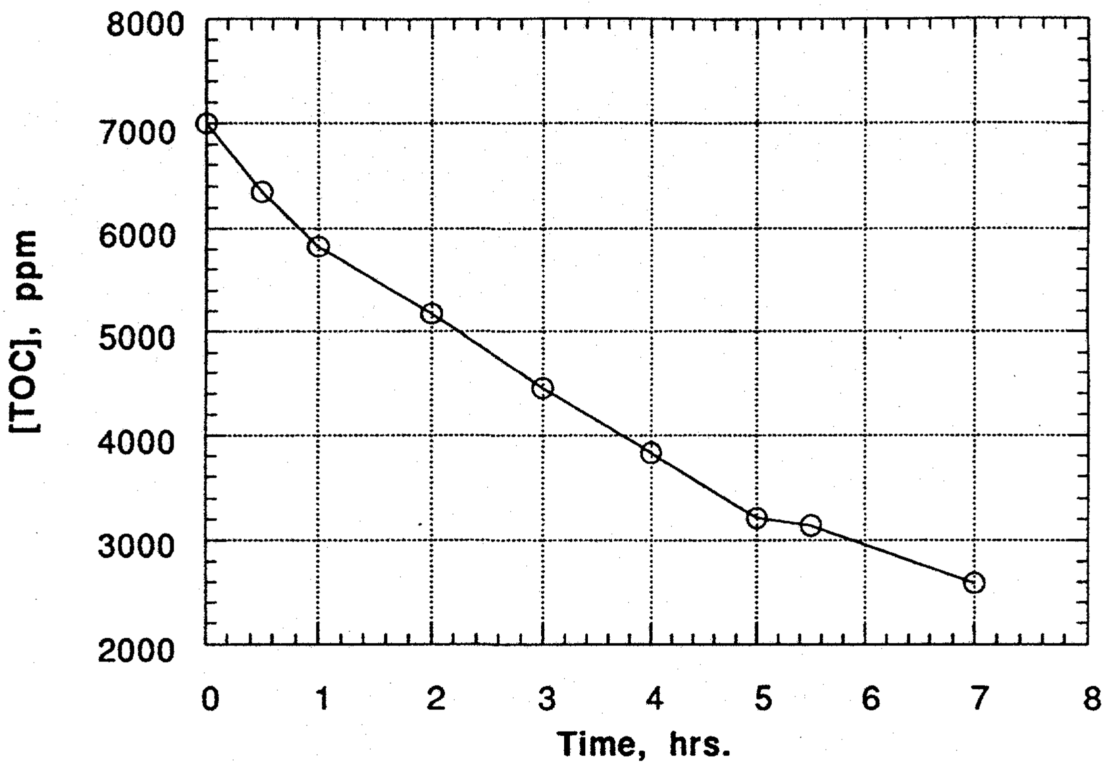

Fig. 7 Destruction of ~0.3 M oxalic acid in 1 M HNO_3 with H_2O_2

In Fig.6, it indicates that in dilute nitric acid solutions, the destruction of oxalic acid can be done with UV light only. This is because OH· radicals are generated by UV photolysis of NO_3^- (5). Nitrate absorbs UV light strongly in the region 200-250 nm (molar extinction coeficient = 49,000 cm^{-1} M^{-1} at 204 nm), (6) and little UV light will be absorbed by H_2O_2. Nevertheless adding H_2O_2 to the UV process does increase the rate of oxalate destruction, as shown in Fig. 7. The experiment using both UV light and H_2O_2 was repeated in a circulated reactor described in a previous report (3) with a ~2kW mercury lamp. The purpose of this run is to show that with a more powerful UV lamp, the rate of oxalate destruction can be increased significantly. The results are shown in Fig. 8.

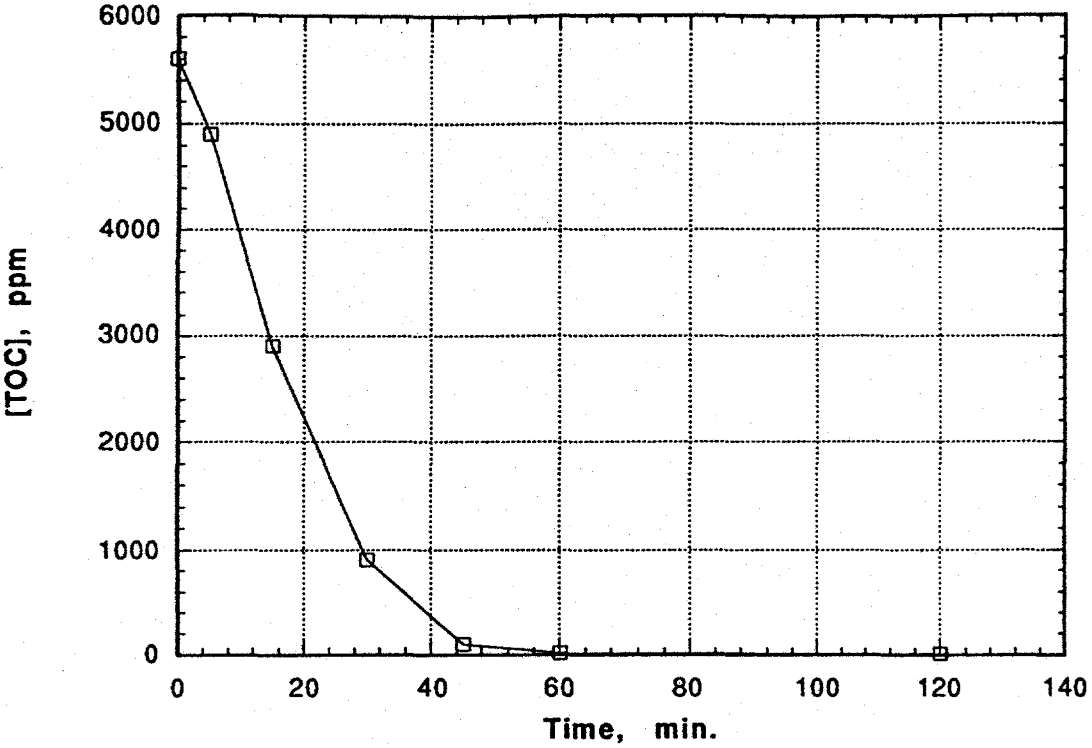

Fig. 8 Destruction of oxalic acid in HNO_3 with H_2O_2 and a ~2kW lamp

In real waste treatment, the oxalate kill process may have to be conducted inside a glove-box. We recommend that the UV light system be installed outside the box that has a quartz window, to avoid the corrosive atmosphere inside the box and to simplify the cooling of UV lamp.

IV. Conclusion

This study has demonstrated that destruction of oxalic acid by the UV/H_2O_2 process in both HCl and HNO_3 solutions is a valid method. It is clean and safe. The UV/H_2O_2 process is a mature technology and easy to operate. Since only benign chemical or no chemicals are used, after the destruction of oxalate, acid solutions may be reused. Waste minimization has become increasingly important for all industries, especially those producing mixed wastes.

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