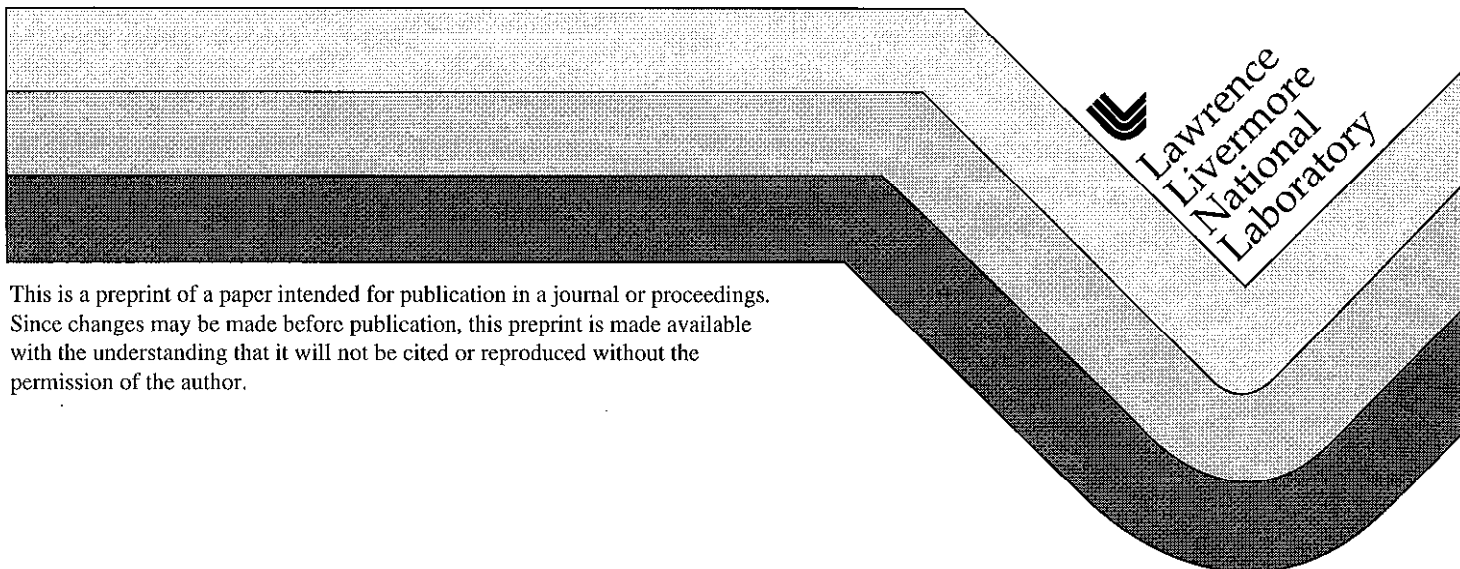


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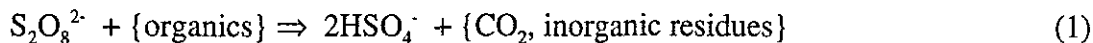
Transition Metal Catalysts for the Ambient Temperature Destruction of Organic Wastes using Peroxydisulfate

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I. INTRODUCTION

Direct Chemical Oxidation (DCO) is a non-thermal, ambient pressure, aqueous-based technology for the oxidative destruction of the organic components of hazardous or mixed waste streams. The process has been developed for applications in waste treatment and chemical demilitarization and decontamination at LLNL since 1992, and is applicable to the destruction of virtually all solid or liquid organics, including: chlorosolvents, oils and greases, detergents, organic-contaminated soils or sludges, explosives, chemical and biological warfare agents, and PCB's. [1-15]

DCO uses solutions of the peroxydisulfate ion (typically sodium or ammonium salts) to completely mineralize the organics to carbon dioxide and water. The net waste treatment reaction is (Eq. 1):



Peroxydisulfate is one of the strongest chemical oxidants known (oxidation potential is +2.05V), and is exceeded in oxidative power only by fluorine, ozone, and oxyfluorides. The oxidation potential of peroxydisulfate is high enough to oxidize nearly any organic substance. [16-17]

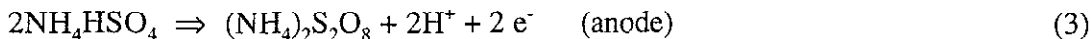
While many oxidants exhibit a redox potential capable of broad-spectrum organic oxidation, peroxydisulfate uniquely combines a high oxidation potential with a rapid, nucleophilic charge-transfer capability. Oxidation occurs principally through the formation of the sulfate radical anion $\text{SO}_4^{\bullet-}$, following mild thermal (70-100 °C) or UV activation of peroxydisulfate solutions [18-24]:



The subsequent reaction of the sulfate free radical with the organic and with water results in a cascade of active oxidants including organic free radical fragments and hydroxyl free radicals. The decomposition of peroxydisulfate produces a number of intermediate oxidizers including peroxymonosulfate (a strong industrial bleach), hydrogen peroxide, and nascent oxygen.

The oxidant ammonium or sodium peroxydisulfate is sufficiently stable at or slightly below room temperature to be stored almost indefinitely as a solid or a wet slurry for months. This being the case, the process of waste destruction can be decoupled in time and place from the generation of the peroxydisulfate oxidant. The oxidant becomes reactive only at elevated temperatures or through contact with the catalysts described above. This allows the oxidant to be slowly produced and stockpiled for use in intermittent waste treatment campaigns of short duration.

The expended oxidant may be electrolytically regenerated to minimize secondary waste. The ammonium (or sodium) hydrogen sulfate produced as a byproduct of the organic waste oxidation process is relatively non-hazardous, and may be encapsulated in a subsequent inorganic treatment step, or recycled in a flowing electrolyte cell. If recycled, an industrial cell is used which employs a platinum or glassy carbon anode, an inert graphite cathode, and a porous ceramic separator to prevent cathodic reduction of the product. The anodic reaction is (Eq. 3):



while the cathodic half reaction is the reduction of water to form hydrogen gas. [26-28] For such cells, this gas is best immediately oxidized to water (in a catalyzed bed), and the water internally recycled. Commercial catalysts are available and used for this purpose. In specialized applications where the production of hydrogen gas is not desirable (such as in a confined space), the cathodic reaction can be replaced with oxygen reduction using a porous gas diffusion electrode. This modification also reduces the cell voltage by 1 volt (about 20%).

The DCO process normally operates at 80-100 °C, a heating requirement which increases the difficulty of surface decontamination of large objects or, for example, treatment of a wide area contaminated soil site. Alternatively, the radical-generation process shown in Eq. 2 may be accelerated at near ambient temperatures (20-50 °C) through the use of a catalyst such as metallic platinum, or with dissolved silver, iron, or copper ion catalysts.

Available literature data includes the catalysis of peroxydisulfate oxidation of organics by a number of transition metal catalysts. [18-20,29-34] These catalysts include the ions of Cu [29-31,34], Ag [18-20,32-34] and Fe [34]. In addition, a number of organic substrates were studied, including alcohols, aldehydes, and ethers. In general, the catalysts act to accelerate the decomposition of peroxydisulfate into the sulfate free radical anion (Eq. 2 above) which leads to a higher rate of organic oxidation by this aggressive oxidant.

A generalized rate equation applicable to all combinations of catalyst, organic substrate, and oxidant concentrations is not easily formulated. In addition, the actual mechanism is often dependent on the particular catalyst, making a universal statement about transition metal catalysis impossible. For example, Fe(III) appears to accelerate some reactions while inhibiting others. However, the general rate equation for the reduction of peroxydisulfate (Eq. 1 above) follows the form (Eq. 4):

$$d[S_2O_8^{2-}]/dt = -k [S_2O_8^{2-}]^x [\text{catalyst}]^y \quad (4)$$

where x is some value between 1/2 and 3/2 and y is some value between 0 and 3/2, with negative values possible in some cases. Note that this rate equation is independent of the organic concentration, i.e., the rate of organic oxidation is limited only by the rate of the formation of the sulfate free radical anion (assuming no mass transport limitations).

II. EXPERIMENTAL

Experiments were conducted at a laboratory scale (1.0 liter reactor), using acidified (0.1 M H₂SO₄) solutions of 1.0 M (NH₄)₂S₂O₈. Catalyst ions were added in the form of the sulfate salts of the appropriate transition metal, except in the case of Ag which was by addition of the nitrate salt. Solutions were put into lightly stoppered 250 ml glass flasks immersed in a circulating water bath at the appropriate temperature. Four organic substrates were tested: ethylene glycol, 1,3-dichloro-2-propanol, tributyl phosphate, and the hydrolysis product of 1,1,1-trichloroethane. [35] Initial organic loading was between 500 and 6000 ppm total carbon, and the catalyst concentrations were varied between 1 and 1000 ppm (with the exception of additional Fe tests at 5900 ppm). Destruction and Removal Efficiencies (DRE's) were determined by Total Organic Carbon (TOC) analysis of the resultant solutions at the end of the experiment. Determination of peroxydisulfate concentrations was done by quenching the reaction in an ice bath, followed immediately by an iodometric titration (peroxydisulfate reacts with iodide to form iodine).

III. RESULTS

In order to assess the effect of several transition metal ions on the DCO system at normal operating temperatures, the reduction of peroxydisulfate and the mineralization of the organic were studied at 80 °C. Measurements were made of both the instantaneous concentration of peroxydisulfate (by titration) and the conversion of organic to carbon dioxide (by on-line IR gas analysis). Ethylene glycol and the hydrolysis output of chlorosolvent hydrolysis were used as substrates; several typical transition metals were tested with each.

Figure 1 shows the decrease in peroxydisulfate concentration as a function of time during the oxidation of ethylene glycol. Each of the catalysts systems, except for 100 ppm Fe(II),

showed some catalytic activity for the decomposition of peroxydisulfate, with the silver system being the most pronounced.

Figure 2 shows the output of carbon dioxide obtained during each of seven runs, with and without the catalysts as noted, during the oxidation of ethylene glycol at 80 °C. The expected output based on the amount of ethylene glycol initially added was 420 ml CO₂ with a system measurement precision of ±10%. All of the results fall within this range, but the silver system is noticeably different, both in terms of a higher CO₂ output as well as a much steeper rise. Although the latter result is expected due to the catalytic activity, a reason for the former observation is not known.

Previous work on the effect of transition metal catalysts on the rate of oxidation of organic substrates by peroxydisulfate [18-20,29-34] focused primarily on the decomposition of the peroxydisulfate, and not on the mineralization of the organic. For the current work, it was felt that a more realistic approach with regard to waste treatment by DCO was to measure the overall Destruction and Removal Efficiencies (DRE's) on a matrix of catalysts, temperatures, and organic substrates. In addition, most of this current work is focused on 20-50 °C as this regime is closer to temperatures likely to be encountered when using DCO to treat waste under close to ambient conditions. No additional oxidant was added in most cases, except as noted, in order to more closely simulate a "one-pass" treatment approach.

Results for ethylene glycol are shown in Figures 3-5, while those for 1,3-dichloro-2-propanol are shown in Figures 6 and 7. Tributyl phosphate is only partially soluble in water, and results with this organic substrate gave inconsistent results. The initial conditions of the TBP experiments were such that the added level of organic was 1700 ppm as carbon, but TOC results on this initial solution gave results of 200-300 ppm as carbon. Indeed, a second phase was observed on the walls of the reaction flasks and thus the data are judged to be invalid.

IV. CONCLUSIONS

As shown in Figures 1 and 2, the concentration of peroxydisulfate decreases rapidly at 80 °C due to its reduction by organic and, to a lesser extent, water. All of the added transition metals tested had some effect (with the exception of low concentrations of iron), and this effect was towards an acceleration of the peroxydisulfate decomposition rate. In the case of ethylene glycol as the added organic substrate (Figure 1), silver ion showed the highest perturbation, which is expected based on the fact that silver showed the highest catalytic effect in the destruction tests. The effect of silver was not nearly as pronounced in tests where chloride ion was present. However, based on results obtained with and without catalysts at 80 °C, peroxydisulfate does not appear to be a very aggressive oxidant at concentrations of less than about 0.3M. Catalysts did not change this cutoff value appreciably. Thus, any DCO waste treatment system would have to keep the oxidant concentration greater than 0.5M for optimal efficiency.

During the experiments, it was noted that additional heat outputs were obtained at 80 °C with the catalysts, and the amount of extra heat correlated well with the acceleration in peroxydisulfate decomposition/organic destruction. As noted in the organic destruction tests detailed in the following section, silver exhibited the most pronounced effect. As the oxidative destruction of organics is exothermic, any organic waste treatment system using peroxydisulfate *must* take into account the extra heat output encountered when transition metal ions (especially silver) are present.

It was noted that, when treating chlorinated organics, catalysts also affected the production of chlorine gas. However, this effect followed no logical pattern; in some cases the chlorine production (observed by watching the reactor offgas trap color) was immediate and quantitative and in other cases it was minimal.

For the organic destruction tests on surrogate waste materials shown in Figures 3-7, all of the transition metals studied exhibited some effect on the rate of oxidation of the organic substrates by peroxydisulfate, although the magnitudes varied greatly. This is not surprising, as peroxydisulfate has a sufficient oxidation potential to oxidize all of the transition metals to their highest valent state, and the participation of these higher valence states in organic oxidations is

well-known. [36-39] It was generally the case that the transition metals which exhibited the most facile organic oxidation capability (Ag(II), Co(III), Fe(III)) also exhibited the most pronounced catalytic effect in these studies. Note that this order of catalytic effectiveness is surprisingly similar to the results obtained on Mediated Electrochemical Systems as described in references [36-39]. Although an all-encompassing maxim for the rate enhancements obtained with a specific catalyst is not possible, a general rule of thumb is that the effectiveness of the catalysts followed the general order $Ag \gg Co > Cu, Fe > Pt$. Individual results varied depending on the temperature regime, the organic substrate, and the matrix. This has been noted before in the literature. [18-20,29-34] The above results lead to the conclusion that catalysis of organic destruction by peroxydisulfate is merely due to the formation of another, favorably solvated transition metal cation with a high oxidation potential.

Complete destruction of the organics tested was achievable with silver as a catalyst, even at 20 °C in a relatively short time, and cobalt, iron or copper showed some enhancement although a much longer time was required. This result is backed by previous literature studies as discussed above. However, it was also noted in this current study that different organic substrates exhibited different behavior with respect to catalysis.

In all the cases studied, the enhancement of the organic destruction rate was a function of the catalyst concentration, and this is reflected in the literature as well (Eq. 4). Thus, higher rates of organic destruction can be achieved with higher catalyst concentrations. Due to the copious data available in the literature, a systematic reinvestigation of the order of the catalyst concentration on the rate equation was not attempted.

Although rate equations such as that shown in Eq. 4 would predict that destruction of organics might be faster with higher oxidant concentrations, the present work was not sufficiently detailed to either bolster or refute this statement. Additional oxidant made only a slight difference in DRE's, at least at close to ambient conditions. However, with higher organic loadings it may be necessary to periodically replenish the oxidant in waste treatment systems. See also the following section regarding oxidant concentration.

During catalyzed oxidations, there is an incubation period during which the carbon content of the solutions is unchanged from the initial value. This is presumably reflective of the fact that oxidation is occurring, but has not proceeded to the stage of evolving carbon dioxide from the solution and thus the carbon content of the solution remains unchanged from the original value. This incubation period was not noticed with silver, as oxidations with this catalyst proceeded much faster than the sampling timescales at the temperatures tested.

In waste systems containing chloride ion, or containing organic chlorine, silver ion is ineffective as a catalyst. AgCl, being highly insoluble, immediately precipitates thus removing the active catalyst. Along these same lines, silver will be ineffective as a catalyst in systems where the pH is sufficiently high to result in the precipitation of silver hydroxide. In fact, this latter characteristic would presumably be extendable to all potential transition metal catalysts in systems at high pH.

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Figure 1. (1400 ppm C loading. Initial $[S_2O_8^{2-}]$ is 1.0 M, in 0.1 M H_2SO_4 , 80 °C)

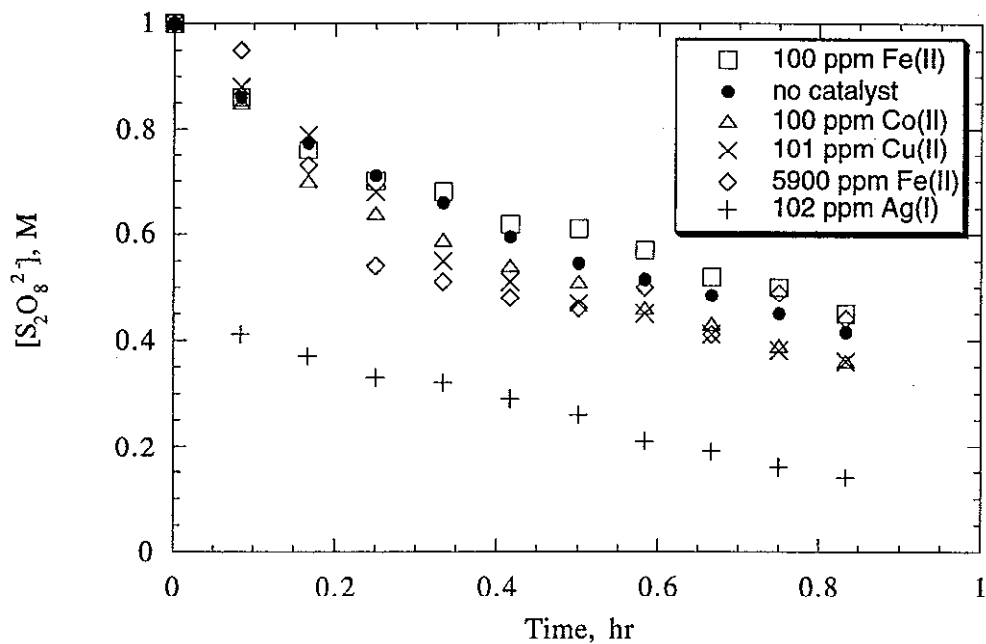


Figure 2. (1400 ppm C loading. Initial $[S_2O_8^{2-}]$ is 1.0 M, in 0.1 M H_2SO_4 , 80 °C)

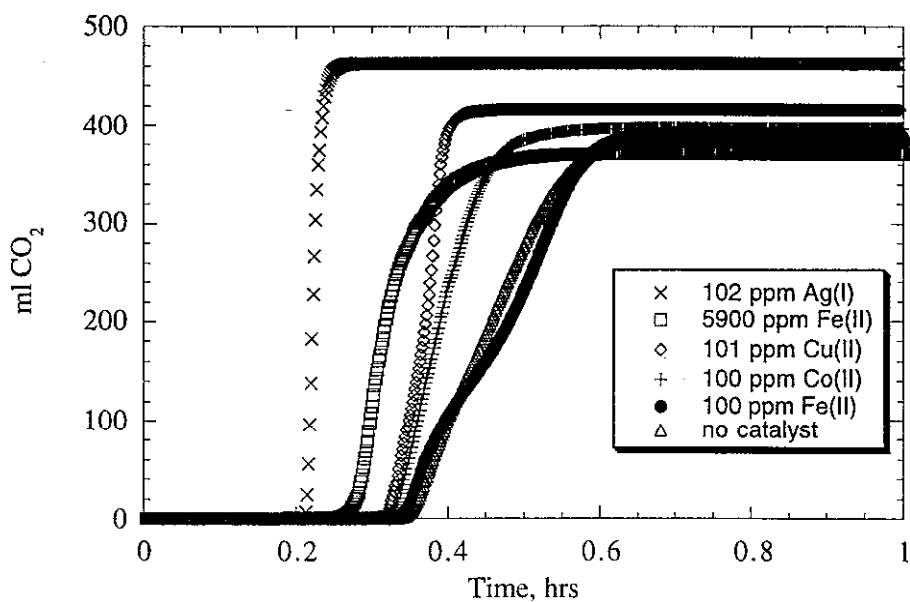


Figure 3. (EG, 1800 ppm carbon loading, 50 °C)

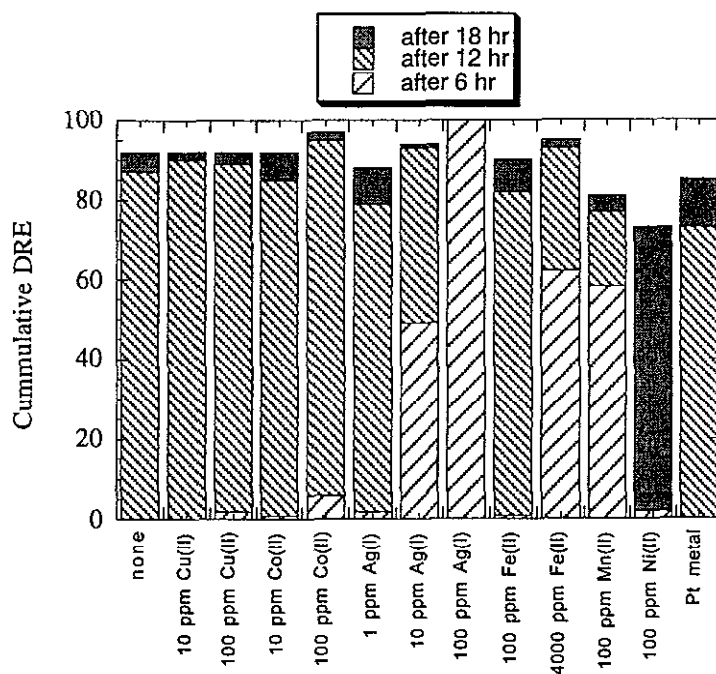


Figure 4. (EG, 1800 ppm carbon loading, 35 °C)

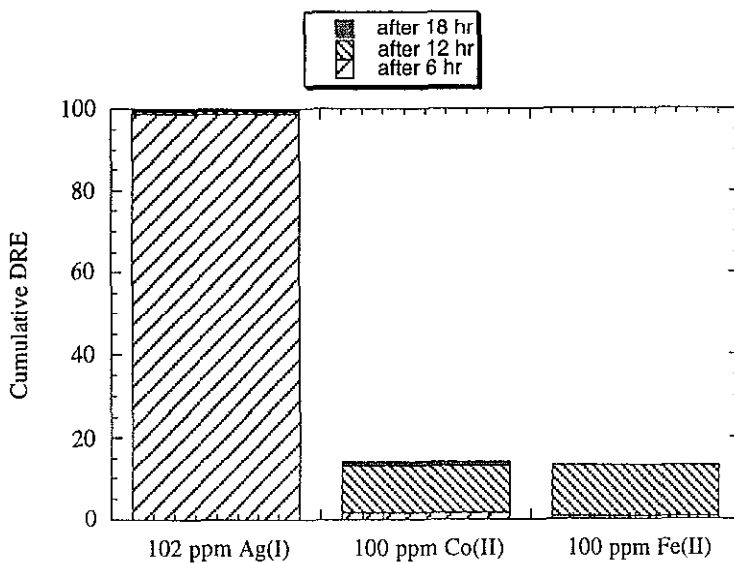


Figure 5. (EG, 1800 ppm carbon loading, 20 °C)

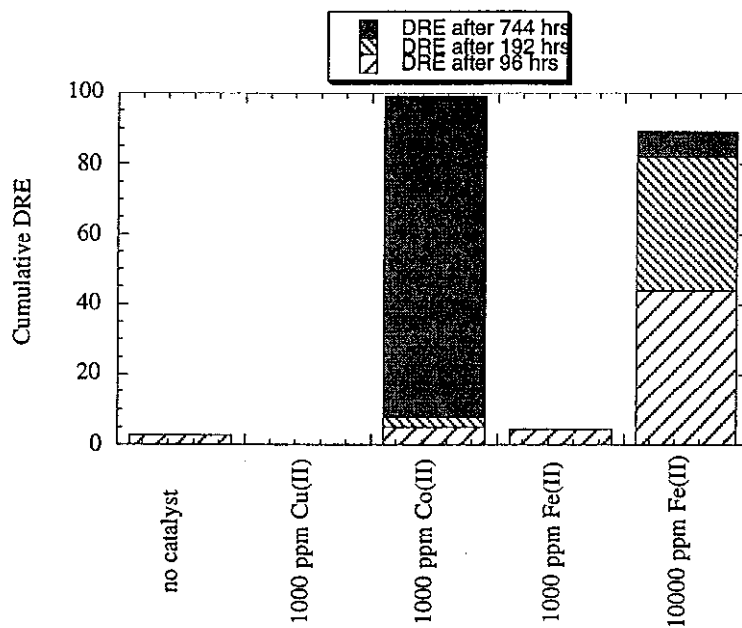


Figure 6. (DCP, 1700 ppm organic loading, 50 °C).

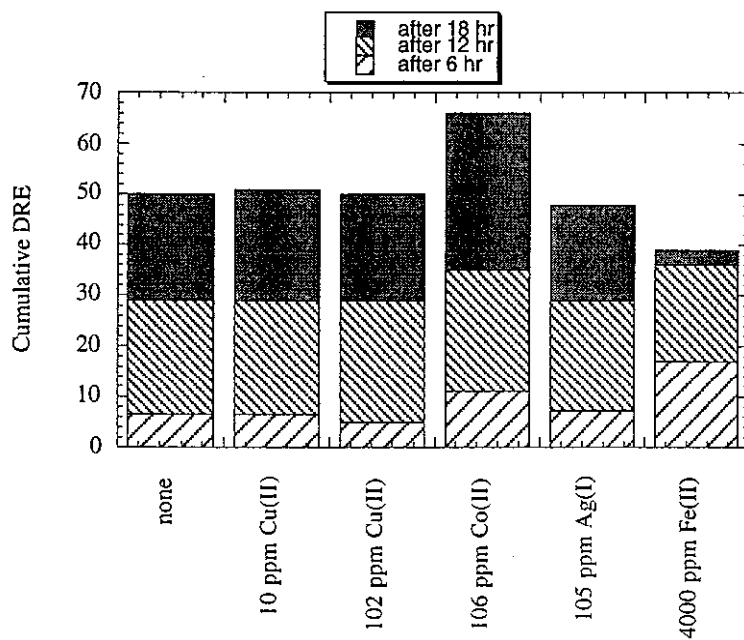


Figure 7. (DCP, 1800 ppm organic loading, 20 °C)

