

Final Report

NASA Grant NGR-06-004-068

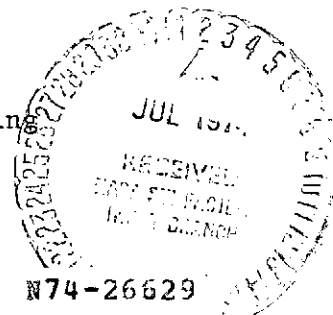
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DIRECT OXIDATION OF STRONG WASTE WATERS,  
SIMULATING COMBINED WASTES IN EXTENDED-MISSION SPACE CABINS

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## Introduction

The objective of this research was to explore applications of modern technology to the resolution of the problem of solid wastes in space cabin environments.

Originally, the research task consisted of an investigation of electrolytic degradation of human wastes. However, in view of the priority assigned by NASA to thermal methods for treating combined wastes, it was considered desirable to conduct exploratory studies toward the objective of identifying improved operating conditions for thermal methods.

Accordingly, with the sponsor's approval, the objective of NASA grant NGR-06-004-068 was shifted to exploration of operating conditions that would permit lowering of process temperatures in wet oxidation of combined human wastes.

## Background

The two principal methods that are currently being considered for elimination of solid wastes in spacecraft environments are both oxidation techniques, viz.,

- 1) wet oxidation
- 2) incineration.

At present, there are three major NASA contractors who are exploring these techniques with reference to wastes generated in spacecraft, namely,

Lockheed Missiles and Space Company

General American Research Division (GARD) of  
the General American Transportation Company

General Electric Corporation.

Lockheed is investigating wet oxidation, in which the oxidation occurs at about 550<sup>o</sup>F under conditions of continuous flow. GARD and GE, on the other hand, are investigating combustive systems that essentially involve dried wastes, with the result that temperatures are much higher (up to 1100<sup>o</sup>F). The drying and pyrolysis steps in the GARD and GE systems involve significant weight penalties, especially in transport of solids.

The first basic investigation of wet oxidation was reported by Fisher in 1971.<sup>1</sup> Fisher's principal conclusions including the following:

- a) the ultimate products of wet oxidation are the lower fatty acids;
- b) temperatures approaching the critical ( $\sim 350^{\circ}\text{C}$ ) are required to achieve essentially complete oxidation, even in pure oxygen atmosphere.

The Zimmerman (or Zimpro) process had been known for many years before Fisher's investigation, but there was little basic understanding of its limitations, and especially the nature of its products. Dr. Paul Schatzberg of the U.S. Navy Engineering Command has extended the understanding of the wet oxidation process in several investigations under his contractual supervision. In particular, research performed for Dr. Schatzberg has shown that wet oxidation of a strong sewage-type waste is achieved in two fundamental stages: (1) a rapid degradation to lower fatty acids (mainly acetic acid) followed by (2) a slow oxidation to the ultimate oxidation products, CO<sub>2</sub> and H<sub>2</sub>O.<sup>2</sup>

The studies of Bruce Jagow at Lockheed Missiles and Space Co.<sup>3</sup> have generally verified the Zimmerman results and Fisher's findings.

Jagow has employed oxidation catalysts, but only for the purpose of oxidizing ammonia-nitrogen to the nitrate state. Jagow's experiments are unique in that they are conducted under continuous-flow conditions.

Recently, interest in direct oxidation of sewage wastes has arisen within the chemical manufacturing industry. The prospect of converting sewage into chemical synthetic feedstocks is attractive where the waste volume is sufficiently large. The principle of such a conversion process is illustrated in the following sketch:

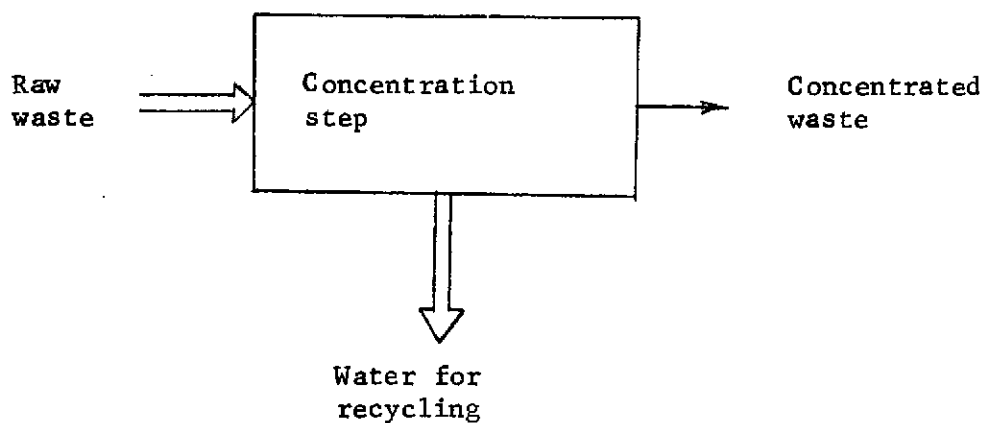


Fig. 1

The recycled water stream is capable of yielding potable water. Meanwhile, the concentrated waste stream provides a "strong" feedstock for potential chemical processing.

#### Research Program

The present investigation has been concerned with a systematic search for catalysts which would permit conversion of the "strong" waste water stream (Fig. 1) into a useful chemical feedstock at reasonable rates.

Initial emphasis, as in the case of Fisher's research<sup>1</sup> was directed to absolute degradation of the waste, expressed as reduction in COD.

A synthetic "strong waste" has been employed, consisting of a mixed-organic mash filtrate from the Adolph Coors brewery in Golden, Colorado, suitably diluted to yield an initial COD of about 15,000 mg/l for our tests.

Typical reaction conditions are summarized as follows:

Temperature	400°F
Pressure (O <sub>2</sub> )	300 psig
Reaction time	2 hours.

Heating to the reaction temperature level is performed under nitrogen atmosphere.

Oxidation is conducted in a Parr pressure reaction apparatus, constructed of 316 stainless steel, with a reaction chamber 1 liter in volume. A sample of 200 ml is used, under conditions of continuous stirring. COD measurements are performed according to standard procedures. Reaction temperature is controlled by an on-off controller

actuated by a chromel-alumel thermocouple.

Reaction conditions include the following parameters of interest to the investigation:

Temperature  
Catalyst  
pH.

In particular, the investigation has sought to identify a catalyst which permits maximum conversion at lowest temperature. However, the question of conversion products is still to be considered, i.e., whether the products of oxidation are useful as feedstocks for organic chemical synthesis.

The catalyst systems examined to date in the present investigation are summarized in Table 1. Catalysts employed fall into two categories:

- 1) free-radical generators
- 2) supported metals.

Parameters for investigation include pH and temperature. Although several metal compounds have been employed, the list is by no means exhaustive, because our objective was merely to determine the potential gains to be obtained from catalysis, in oxidation of strong organic wastes. Furthermore, the cost of the metals will be an economic factor in the process, even if the metals are recovered.

### Results

At the expiration date of the grant, only preliminary results had been obtained. However, these results were sufficiently promising to warrant continued investigation, and the study has been continued

under sponsorship of the University of Denver. The study will be concluded about June 1974.

The principal finding of the investigation to date is that the ultimate degree of degradation is not enhanced by use of a catalyst. This is evident in Fig. 2. In fact, the degradation may be suppressed (Table 1). However, several catalysts were found which increased the rate of degradation.

Some results seem to verify Dr. Paul Schatzberg's findings (see above) with respect to a two-stage mechanism.<sup>2</sup> That is, a drop in COD followed by an increase in COD has been observed in two cases. This can be explained by a fast degradation of organic materials to lower fatty acids followed by a slower degradation of these acids to CO<sub>2</sub> and H<sub>2</sub>O.

Another important finding is that most catalysts lead to a clear liquid product that possesses a faintly ethereal odor, while identical treatment in absence of catalyst produces a brown-colored liquid with a distinct odor of char. With catalyst, the suspended solids settle rapidly into a thin layer of light brown color after reaction; without catalyst, solids settle slowly, and possess a dark color. These findings are suggestive of different product compositions, but they have not yet been supported by quantitative chemical analysis.

#### Conclusions

The use of catalysts can alter the composition of products from oxidation of strong chemical waste waters, and can increase the

rate of oxidation. In addition, the temperature of oxidation can be reduced to 400°F, compared to a typical temperature of 550°F in conventional "wet oxidation" processes. It is possible that the optimum conversion to useful products, as opposed to complete degradation, may be achieved at much lower temperatures.

#### Future Work

No other catalyst combinations are planned for investigation. Future work will revolve around determination of optimum pH and minimum temperature. In addition, the nature of the products as a function of catalyst and temperature will be studied by chemical analysis.

#### References

1. W. J. Fisher, Water Research 5, 187-201 (1971).
2. Paul Schatzberg, personal communication.
3. R. B. Jagow, Paper presented to 1972 Environmental Control/Life Support Conference, San Francisco. ASME paper no. 72-ENAv-3.



Table 1  
 Organic Degradation Achieved by Various Catalyst  
 Systems in Two Hours of Oxidation

<u>Catalyst System</u>	<u>COD Reduction</u>
1. Ferrous Sulfate + Hydrogen Peroxide	65.8
2. Ferrous Sulfate + Benzoyl Peroxide	92.2
3. Cobalt Sulfate + Hydrogen Peroxide	85.8
4. Cobalt Sulfate + Benzoyl Peroxide	75.6
5. Ceric Sulfate + Hydrogen Peroxide	91.0
6. Ceric Sulfate + Benzoyl Peroxide	79.7
7. Silver Sulfate + Hydrogen Peroxide	84.7
8. Silver Sulfate + Benzoyl Peroxide	82.5
9. Chromic Sulfate + Hydrogen Peroxide	83.0
10. Chromic Sulfate + Benzoyl Peroxide	73.0
11. Nickel Sulfate + Copper Sulfate + Hydrogen Peroxide	88.8
12. Nickel Sulfate + Copper Sulfate + Benzoyl Peroxide	89.5
13. Mercuric Sulfate + Hydrogen Peroxide	79.4
14. Mercuric Acetate	67.3
15. Ferric Acetate	79.7
16. Ferrous Sulfate + Benzoyl Peroxide + 2-4 Dimethyl- aniline	61.5
17. Sodium Perborate	92.0
18. Raney nickel (W-2)	79.2 (90 minutes)
19. Platinum Black	67.8 (70 minutes)
20. No catalyst	90.2

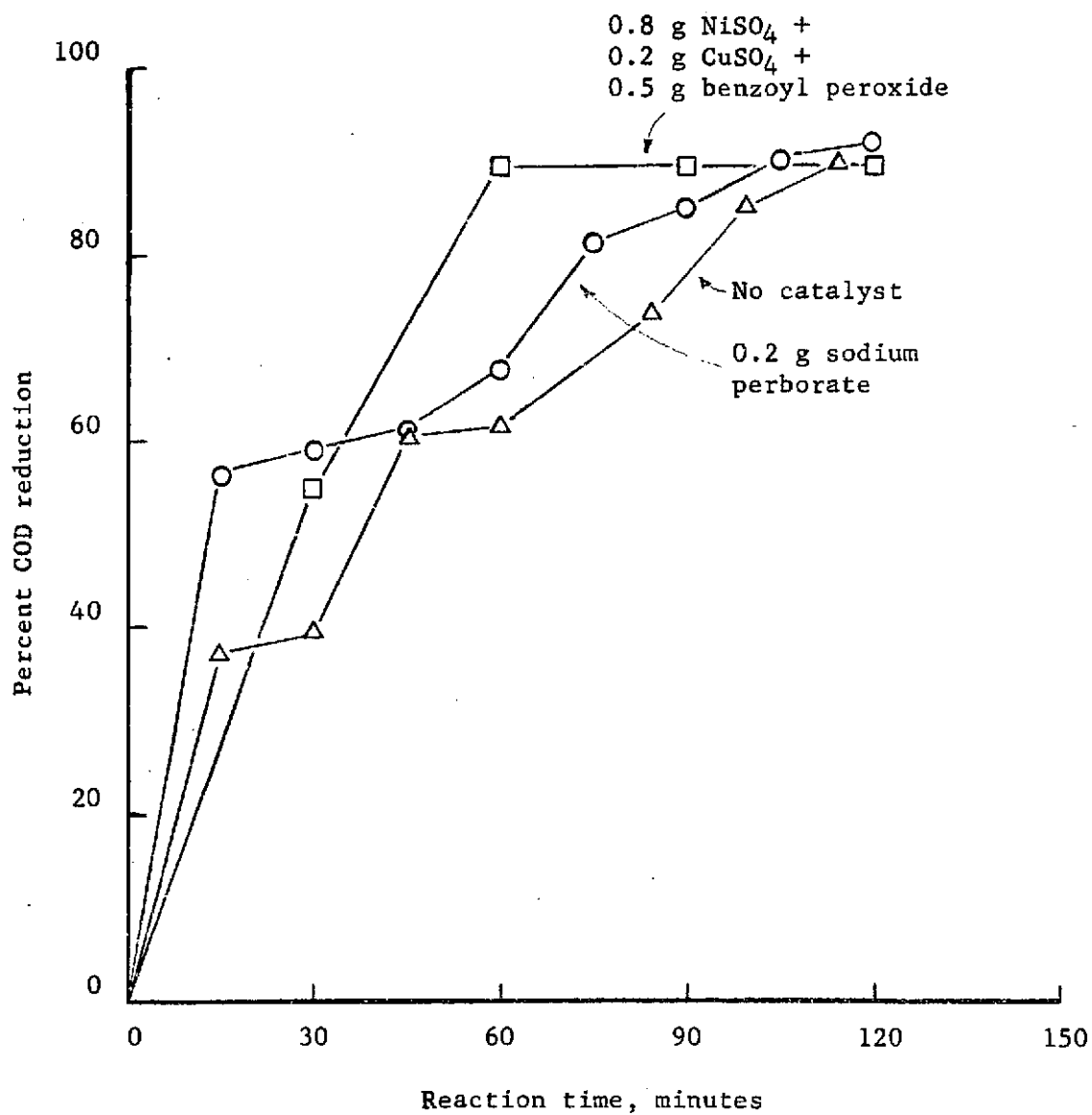


Fig. 2. Typical patterns of COD reduction, with and without addition of catalyst.