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INVESTIGATION OF THE FEASIBILITY OF WET OXIDATION FOR SPACECRAFT WASTE TREATMENT

By Robert B. Wheaton, J.R. Calloway Brown, Ruben V. Ramirez and Norman G. Roth
Whirlpool Corporation, St. Joseph, Michigan

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ABSTRACT

Laboratory studies were made to determine the feasibility of adapting the principle of high temperature, high pressure, wet oxidation to the reclamation of water and the disposition of organic waste residues on board space vehicles. The process assures the balance of the water cycle and is a possible first step in the conversion of waste materials into reusable forms. The tests were conducted in a one liter oxidation chamber using pure oxygen. The effects of oxidation temperature, catalysts, influent concentration, stirring and similar variables were studied during the wet oxidation of a variety of waste materials.

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SUMMARY

Treatment of waste aboard spacecraft presents a variety of problems. Most terrestrial waste treatment methods are not suitable for spacecraft application. Wet oxidation, the combustion of water-entrained organic matter under oxygen pressure, provides rapid complete waste treatment without undesirable by-products.

This study was undertaken to investigate the feasibility of applying the wet oxidation principle to spacecraft conditions. Tests were conducted in a one liter oxidation chamber using pure oxygen. Influent waste material included raw urine and feces, residue resulting from urine distillation, cellulose and specific components of waste materials.

The effects of oxidation temperature, catalysts, influent concentration, salt concentration, stirring and similar variables were investigated under laboratory conditions that simulated spacecraft requirements. Detailed analyses were performed on the resulting liquid effluent to determine the extent of waste treatment and the suitability of the effluent for recovery as potable water. Analyses were performed on the headspace gases within the oxidation chamber to determine the characteristics and quantities of gases produced by the reaction and to determine, quantitatively, the utilization of oxygen.

Careful consideration was given to the engineering aspects of small scale wet oxidation and its application to spacecraft waste treatment systems.

INTRODUCTION

The problem of waste treatment aboard spacecraft is one of considerable importance. Satisfactory solution of this problem depends upon many factors. The type and duration of the intended mission are of great importance. Current short duration missions such as Gemini and Apollo are primarily concerned with efficient collection of body wastes under confined conditions. Treatment of the collected waste can be satisfactorily accomplished by chemical disinfection and storage. This arrangement will not be satisfactory for future missions of long duration. Storage space will be

at a premium and the body waste must be used as a resource for water recovery and, perhaps, food regeneration. Consequently, three general problems are presented by the collection of body waste aboard long duration spacecraft:

1) Waste materials must be treated and reduced to an inocuous and ultimately compact form;

2) Water contained in the waste material must be recovered for reuse, and

3) To satisfy some spacecraft system concepts, waste solids should be broken down to efficient building blocks, such as carbon dioxide and water, for the resynthesis of food.

Relatively few techniques will satisfy more than one of these three general problems. By far the most effort appears to be directed toward methods for the recovery of waste water from urine, and some of these methods appear quite satisfactory. However, their operation results in concentrating the urine solids into a disagreeable residue, which itself presents a waste treatment problem. Recovery of water from raw feces does not appear to be very promising by current techniques. The problems involved with handling raw feces do not seem justified in light of the yield of recoverable water. However, regardless of the justification or the technique, current methods used for recovery of water from body waste do not serve a waste treatment function. The solids, the disagreeable part of the waste, still remain a problem.

Satisfactory methods for treatment of these waste solids are few. Biological methods are relatively slow, bulky and usually provide incomplete treatment. Oxidation or combustion appears to be the most satisfactory method for treatment of waste solids from the standpoint of speed, efficiency and completeness of treatment.

Among the several methods used for combustion of waste material, the wet oxidation process appears to hold considerable potential. This method sometimes referred to as the "Zimmerman Process" named after the holder of the original patents, has been applied as an advanced method for the treatment of biologically digested municipal waste residue. Waste material, entrained in water, is placed in a pressure reaction chamber and air sufficient to oxidize the organic content of the waste is introduced under pressure. The mixture is heated to 500-600°F in the closed chamber where a pressure of about 2000 psi is developed. Holding time depends upon temperature and composition of the waste, but about one hour is generally sufficient to oxidize 80% of the organic material and yield a sterile inoffensive end product containing primarily the organic waste minerals.

Use of wet oxidation for treatment of spacecraft waste had not been considered seriously prior to this investigation. Some brief theoretical

considerations have been given to the method in comprehensive closed ecology system studies. However, there is a dearth of published information on small scale wet oxidation applications. Most municipal plants are at least 1000 times larger than any that might be contemplated for spacecraft use. Consequently, there has been some concern as to whether this process could be scaled down to spacecraft size. Further, there has been some concern over the pressures developed during the process even though these are not really high as reaction pressures are concerned. Other unknown factors prior to this investigation, were the effects of wet oxidation on raw body waste, operational parameters for small systems, effects of catalysts on the process and composition of the liquid and gas effluents obtained.

This investigation was undertaken to study these factors and to determine the feasibility of applying the wet oxidation principle to spacecraft waste treatment problems.

EQUIPMENT AND PROCEDURES

The investigation was a feasibility study carried out on a laboratory bench scale. Consequently, there was no significant equipment design or fabrication. Equipment used was typical of that available to chemistry laboratories. The only unique equipment was the oxidation chamber.

Oxidation Chamber

The oxidation chamber used for all of the wet oxidation studies was a chemical autoclave. This instrument was a one liter capacity unit made of AISI Type 316 stainless steel with provision for an internal stirring impeller. The chamber was heated by an external jacket-type heater rated at 2.1 KW at 110 volts. Glass wool insulation was added to the unit during operation. The chamber was supplied with several ports. One of these, used for the oxygen supply, was fitted with a high pressure valve and was connected by stainless steel tubing to an oxygen pressure tank. A modified Parr calorimeter bomb oxygen tank coupling was used to connect the stainless steel tubing to the oxygen tank. This allowed accurate filling of the chamber and provided a relief valve to depressurize the connecting tubing between uses.

Other ports were provided for sampling of the gas headspace within the chamber and the chamber liquid. A half inch diameter charging and cleaning port located in the chamber head was not used, since this did not allow easy access for the influent material and did not permit effective cleaning and inspection of the chamber between runs. The entire autoclave head was removed between runs for cleaning and inspection. The chamber was provided with a pressure gauge and a tachometer to determine the stirrer speed. Speed of the 1¼ inch diameter stirrer impeller was a constant 1500 rpm throughout the investigation.

The heater jacket contained two separate circuits, each of which were connected to rheostats for control of the chamber temperature. Temperature of the heater jacket was determined by an internal thermocouple. A thermocouple, located in a thermocouple well, recorded the internal chamber temperature. This temperature was recorded on a strip chart which became a permanent record of each run.

Oxidation Chamber Operating Procedures

Human body waste specimens for use as influent wet oxidation substrate samples were collected fresh prior to use and maintained under refrigeration. Urine and feces were collected separately and combined in known, measured proportions to prepare the mixed waste specimens. Pooled waste samples were used in some test series so that the results would be readily comparable from test to test. Other tests were run on individual samples of waste to evaluate the range of effects resulting from different waste samples.

Samples comprised of mixed urine and fecal material were prepared as a 10% suspension of fresh feces in urine. This ratio is proportional to the normal range in which these wastes are excreted or evacuated by humans. The ratio makes the assumption that about 150 grams of feces and 1350 grams of urine are excreted during a normal man-day. Where the test sample was comprised of urine residue and feces, the same ratio was used with the exception that an allowance was made for the removed water. Most of the waste samples oxidized during the investigation had a measured volume of 300 mls. This left 700 mls. of headspace in the one liter oxidation chamber. A volume of 700 mls. contains about one mole of oxygen at 500 psi which was sufficient to oxidize all of the sample with a slight excess to insure complete reaction.

Pure oxygen, obtained from pressure tanks, was used as the oxygen supply for all tests. Compressed air has been the universal oxygen supply for all of the municipal wet oxidation operations to date. We felt that pure oxygen should increase the efficiency of the wet oxidation reaction and certainly, pure oxygen would be the obvious oxygen source aboard spacecraft. The nitrogen present in air serves no useful function in the wet oxidation reaction and might affect the rate of reaction somewhat. Oxygen required for wet oxidation aboard a spacecraft could be produced by electrolysis of water. The water produced by combustion of the waste solids is sufficient to satisfy this requirement.

Heat was supplied to the reaction chamber by an external electric heating jacket as described above. This proved to be a rather inefficient method of heating as heat transfer through the heavy chamber wall was slow. However, this slow heating rate filled the requirements of this investigation very well, because it allowed continuous analysis, at progressively higher temperatures throughout each test run. The heating jacket input current was adjusted to hold the jacket at 1200°F. This resulted in heating the oxidation chamber gradually from ambient to 550°F in 4 hours.

Maximum attainable temperature within the oxidation chamber was 550°F.

All wet oxidation reactions were run on a batch basis. The waste substrate was placed in the chamber and the chamber was pressurized to 500 psi with pure oxygen. Heat was applied and the stirrer ran continuously during the reaction unless otherwise noted. At selected temperatures during the reaction, headspace gas samples were removed through a sampling valve and analyzed by the Orsat method. Reaction temperature was recorded continuously as described above. At the end of the reaction, the heaters were turned off and the chamber was allowed to cool before removing the effluent liquid. This effluent was subjected to analysis to determine the extent and nature of the reaction.

Analysis of Effluents and Headspace Gas

The wet oxidation effluents were analyzed for pH with a laboratory pH meter using standard technique. Total acidity was determined by titration of effluent samples with tenth normal acid or base depending upon the pH of the sample. Total effluent and raw waste solids were determined by drying measured samples to constant weight in an oven at 105°C. Ash was determined by ignition of dry samples in a muffle furnace to constant weight at 550°C. Total organic nitrogen content of the raw waste and effluent were determined by the standard Kjeldahl method as described in the twelfth edition of Standard Methods for the Examination of Water and Waste Water.(1) Ammonia nitrogen was determined by the distillation and titration method shown in the same "Standard Methods" manual. Chemical oxygen demand (COD) was determined by the acid-dichromate reflux method shown in the "Standard Methods" manual. Readout was accomplished by titration of the refluxed sample with standard tenth normal ferrous ammonium sulfate reagent.

Effluent samples were analyzed for volatile acids and related compounds by gas chromatography. A twin column chromatograph with a flame ionization detector was used. Column packing consisted of 10% diethylene glycol succinate on chromosorb. Helium was used as the carrier gas.

Headspace gas analyses were made during operation of the oxidation chamber by the customary Orsat method. Potassium hydroxide was used for carbon dioxide absorption, alkaline pyrogalol was used for oxygen absorption and a sulfuric acid solution was used for absorption of ammonia. Special analysis for headspace gas components was made by mass spectrometry at the Institute for Gas Technology in Chicago, Illinois.

RESULTS AND DISCUSSION

Wet Oxidation of Body Waste

Studies of wet oxidation of body wastes included normal urine and fecal material. Study was also directed toward wet oxidation of waste

components to achieve a better understanding of the mechanism involved, and to isolate specific oxidation problems peculiar to specific waste components.

Wet Oxidation of Waste Components

The waste components studied were separated into three general categories. These were: 1) Urine and urea, 2) Feces, and 3) Cellulose and carbohydrates.

The wet oxidation of urine depends very heavily upon the oxidation aspects of urea since this compound may constitute about 50% of the solid composition of urine solids. Solutions containing 2% of urea in distilled water were subjected to wet oxidation early in the program. Maximum oxidation temperature did not exceed 400°F and relatively little oxidation was achieved Most of the urea appeared to decompose to carbon dioxide and ammonia as a result of heat.

Effluent from the urea substrate was alkaline as a result of the dissolved ammonia. This effluent had a pH of 9.2 and a titratable alkalinity of 0.565 normal.

The problem with urea appears to be one of handling the ammonia produced by heat decomposition. There are several possible routes to solution of this problem. One of these is oxidation at higher temperature where some oxidation of ammonia to carbon dioxide and nitrogen does appear to occur. Another is oxidation in the presence of suitable catalyst which will be discussed in another section of this report.

One important fact regarding ammonia must be borne in mind. Except in the case of oxidizing pure urea in a distilled water solution, all ammonia produced during wet oxidation occurs in the ammonium ion form. Most wet oxidation effluents are either slightly acid or essentially neutral. The ammonia occurs as the acetate or carbonate.

The wet oxidation of urine is similar to urea, except that small amounts of a large variety of carbon compounds are also present. Normal urine samples were subjected to wet oxidation in pure oxygen. Reaction appeared to have begun at about 300°F with the ultimate production of about 11% carbon dioxide in the headspace gas.

The effluent from wet oxidation of urine was a clear solution with a trace of finely divided carbon. This effluent had a pH of 8.3 and a titratable alkalinity equal to a normality of 0.734. Total solids, determined by drying at 105°C were 2.26% and the ash content was 1.75%. Consequently, the effluent had about 0.51% residual organic material. This result was obtained with a maximum oxidation temperature of just over 400°F. At 500°F, this residual organic material was reduced to 0.17% or less.

The wet oxidation of feces differed considerably from urine. The wide variety of components in feces produced a different reaction and a different type of effluent. The primary effect on feces was oxidation whereas urine appeared to be most affected by heat degradation.

Feces was suspended in distilled water at several concentrations to study the effect of substrate density on oxidation These concentrations were 10%, 20%, and 40% whole wet feces by weight. They contained about 2.25, 5.00 and 10.00 grams of dry fecal solids per 100 mls. of suspension respectively.

Only 200 mls. of the 40% suspension was used instead of the usual 300 mls. This was necessary to provide enough oxygen in the autoclave vessel to ensure complete oxidation. Oxidation appeared to begin when the reaction temperature reached 300°F in all three concentrations. Initial oxidation proceeded quite rapidly, as evidenced by carbon dioxide production. This was followed by a slower rate of oxidation until complete reaction was obtained. Most of the oxidation appeared to be accomplished at temperatures below 500°F. However, complete oxidation does not occur until higher temperatures are reached. This will be discussed further in a later section of this report.

Table I shows the effect of wet oxidation on reduction of fecal solids. Three representative fecal suspensions are shown in this table. Several replications of these reactions have been run, but the data shown illustrate the mean information obtained. The effluent contained a bulky precipitate that separated very rapidly leaving a clear supernatant. This precipitate was primarily ash. The total fecal solids were reduced by 75% to 80% as a result of wet oxidation; however, the effluent solids contained a very high proportion of ash which could not be expected to oxidize. The total oxidizable organic solids in raw feces were reduced by about 95%. This occurred with all three concentrations of fecal suspension. This observation was an important one and appeared to agree with data published by Hurwitz and Dundas, 1960, [2] and earlier authors. Completeness of the wet oxidation reactions appeared to be relatively independent of substrate concentration provided sufficient oxygen is present and high enough temperatures were reached. Earlier work was based upon studies in large municipal plants using digested sewage sludge, but the phenomenon also appeared to hold true for raw feces in small oxidation chambers. This phenomenon greatly extends the potential flexibility of a spacecraft wet oxidation system, since uncontrollable variations in body waste production will not appreciably affect the system.

TABLE I

EFFECT OF WET OXIDATION ON REDUCTION OF FECAL SOLIDS

Percent Fecal Suspension	Raw Feces*			Effluent*			Percent Reduction	
	Total Solids	Ash	Organic Matter	Total Solids	Ash	Organic Matter	Total Solids	Organic Matter
10	2.27	.386	1.88	.446	.346	0.10	80.3%	94.7%
20	5.00	.776	4.32	1.14	.95	0.19	77.2%	95.6%
40	10.00	1.532	8.74	2.17	1.82	0.35	78.3%	96.0%

* Data are shown in grams of constituent per 100 mls. of suspension

Table II shows the effects of wet oxidation at 550°F on fecal nitrogen. Note that the ammonia content of the raw fecal suspensions was negligible. After wet oxidation, part of the nitrogen was converted to the ammonium ion. Some nitrogen was lost as a result of the wet oxidation as shown by the decrease in total nitrogen content of the effluent samples compared to the raw influent suspensions. This loss appeared to represent nitrogen converted to molecular nitrogen by the wet oxidation process. Calculation showed that about 0.03 grams of ammonia were produced for each gram of dry fecal solids oxidized. This is a small amount of ammonia, or ammonium ion, compared to that produced from urine solids.

TABLE II

EFFECT OF WET OXIDATION ON FECAL NITROGEN*

Percent Fecal Suspension	Raw Feces		Effluent			
	Total Nitrogen	Ammonia Nitrogen	Total Nitrogen	Ammonia Nitrogen	Non-Ammonia Nitrogen	Nitrogen Loss
10	0.154	0.000	0.106	0.053	0.053	0.048
20	0.305	0.002	0.246	0.171	0.075	0.056
40	0.610	0.004	0.521	0.350	0.171	0.089

* All data are shown in grams of constituent per 100 mls of suspension

Table III shows oxygen consumption and carbon dioxide production encountered during wet oxidation of the fecal waste suspensions. These calculations were based on gas analyses of samples taken from the autoclave headspace at temperatures above 500°F. About 1.0 to 1.2 grams of oxygen were required to oxidize each gram of dry fecal solids. This resulted in the production of about 1.4 to 1.6 grams of carbon dioxide.

The production of water of combustion resulting from wet oxidation was calculated by difference. Values obtained agreed closely among the several suspensions oxidized. About 0.35 grams of water of combustion were produced from each gram of dry fecal solids.

TABLE III

SUMMARY OF DATA OBTAINED FROM WET OXIDATION OF FECES*

Percent Fecal Suspension	Oxygen Consumed	Carbon Dioxide Produced	Water Produced	Ammonia Produced	Solid Residue	
					Total	Ash
10	1.02	1.38	0.36	0.04	0.20	0.15
20	1.17	1.60	0.34	0.05	0.23	0.19
40	1.19	1.64	0.35	0.04	0.22	0.18

* All data are shown in grams of constituents per gram of dry fecal solids.

The third general group of waste components studied were carbohydrate compounds. The carbohydrate compounds selected for study were sucrose, glucose and cellulose. These compounds represent oxidation of nitrogen-free substrates in which the end products could, under ideal conditions, be just carbon dioxide and water. Cellulose was important to the study in that it represented toilet paper, or its substitute, used packaging materials and undigested fruit and vegetable fiber in feces. Glucose was important in that it represents the primary hydrolysis product of cellulose and may be a route by which cellulose is ultimately oxidized, i.e., hydrolysis to glucose and oxidation of the glucose intermediate product. Sucrose, a disaccharide, represents a simple polysaccharide intermediate between glucose and cellulose. Samples of these substrates used for study consisted of 300 mls. of 5% solutions or suspensions.

Oxidation of glucose appeared to start at about 400°F and took place in about one-half hour. Carbon dioxide occupied about 29% of the headspace gas at the end of the apparent oxidation period.

Oxidation of sucrose appeared to start at about 350°F and the reaction proceeded very rapidly. About the same concentration of carbon dioxide appeared in the headspace gas as that observed for glucose.

Oxidation of cellulose appeared to start at about 410°F and proceeded somewhat more slowly than either glucose or sucrose. Carbon dioxide constituted about 50% of ultimate headspace gas. This represented nearly total theoretical conversion of cellulose to carbon dioxide and water.

The effluent resulting from oxidation of these substrates was a clear, rather acid, solution with a very slight black precipitate of what appeared to be finely divided carbon. All three solutions had a very faint, but noticeable, odor of acetic acid. Data obtained from analysis of the effluents are shown in Table IV.

TABLE IV.

ANALYSIS OF WET OXIDATION EFFLUENTS FROM CARBOHYDRATES

Substrate	Glucose	Sucrose	Cellulose
pH	3.6	2.0	3.5
Titratable Acidity (Normality)	0.045	0.400	0.117
Total Solids g./100 ml.	0.050	0.008	0.102
Ash g./100 ml.	0.000	0.006	0.012
Organic Solids g./100 ml.	0.050	0.002	0.090

These data show that the effluents were measurably acid, with sucrose showing more acid than either of the other two substrates.

The total solids determined by drying at 105°C are shown in Table IV together with ash as determined by ignition in the muffle furnace. The residue remaining after wet oxidation was quite low. Cellulose was reduced from 5 g./100 ml. to 0.09 g./100 ml. or a decrease of 98.2%. This was rather dramatic since the influent material was a rather heavy suspension of wet paper and the effluent was essentially a clear solution. The formation of small amounts of acid from carbohydrate compounds in mixed waste substrates is a definite adjunct in keeping ammonia in the ammonium ion form and this insures that it will remain in solution in the liquid effluent.

Effects of catalysts on wet oxidation of body wastes. -- The effect of oxidation catalysts on promotion of the wet oxidation reaction was one important facet of this study.

The effects of catalysts were first evaluated using pure sucrose solutions as the substrate. This provided a known reproducible substrate which facilitated comparison among the various tests. Wet oxidations were carried out using two general types of oxidation catalysts. One

catalyst consisted of silver oxide, the other was a mixture of base metal oxides prepared specifically for Whirlpool Corporation. Both catalysts were impregnated into alundum spheres. All wet oxidation reactions were carried out using 300 mls. of substrate and 700 mls. of oxygen at 500 psi.

The initial oxidation temperature was not appreciably affected by the silver catalyst, but the base metal oxides catalyst appeared to lower the initial oxidation temperature of 5% sucrose solutions from about 355°F to about 325°F. This effect is shown in Figures 1 and 2. Figure 1 shows the effect of the base metal oxides catalyst on the initial heat rise peak. This peak is caused by the rapid evolution of heat of combustion resulting from the beginning of oxidation. Therefore, the base of this peak marks the temperature required to initiate sustained combustion under any given set of experimental conditions; although the first stages of oxidation begin at a lower temperature. Figure 2 shows the effect of the various catalysts on carbon dioxide production at various temperatures. Results with 30 grams of silver catalyst were not significantly different from those obtained without catalyst. A ten-fold increase of silver catalyst to 300 grams did increase the amount of carbon dioxide produced and it appeared to lower the reaction temperature slightly. However, the initial oxidation temperature remained at about 355°F. The base metal oxides catalyst both increased the carbon dioxide production and significantly lowered the initial oxidation temperature.

It is obvious from Figures 1 and 2 that, although there was an initial abrupt reaction temperature rise corresponding to a rapid release of combustion heat, the production of carbon dioxide progressed at a slower and more gradual rate. This probably resulted from step-wise oxidation of the substrate to intermediate compounds.

Table V shows the effects of the catalysts on the oxygen consumption and the production of carbon dioxide and acid during wet oxidation of sucrose. Essentially, the consumption of oxygen and the production of carbon dioxide were not significantly affected by the presence or absence of the catalysts. However, the catalysts had a rather profound effect on the acid remaining in the effluent. The uncatalyzed reaction produced a significant amount of acetic acid in the effluent. The pH of this effluent was 4.1. The base metal oxides catalyst produced an effluent pH of 6.6. Titratable acidity was nil. Consequently, we can see that the value of a catalyst lies not only in its effect on reaction rate but in its effect on the final effluent.

FIGURE 1

EFFECT OF BASE METAL OXIDE CATALYST ON

TEMPERATURE RISE DURING WET OXIDATION.

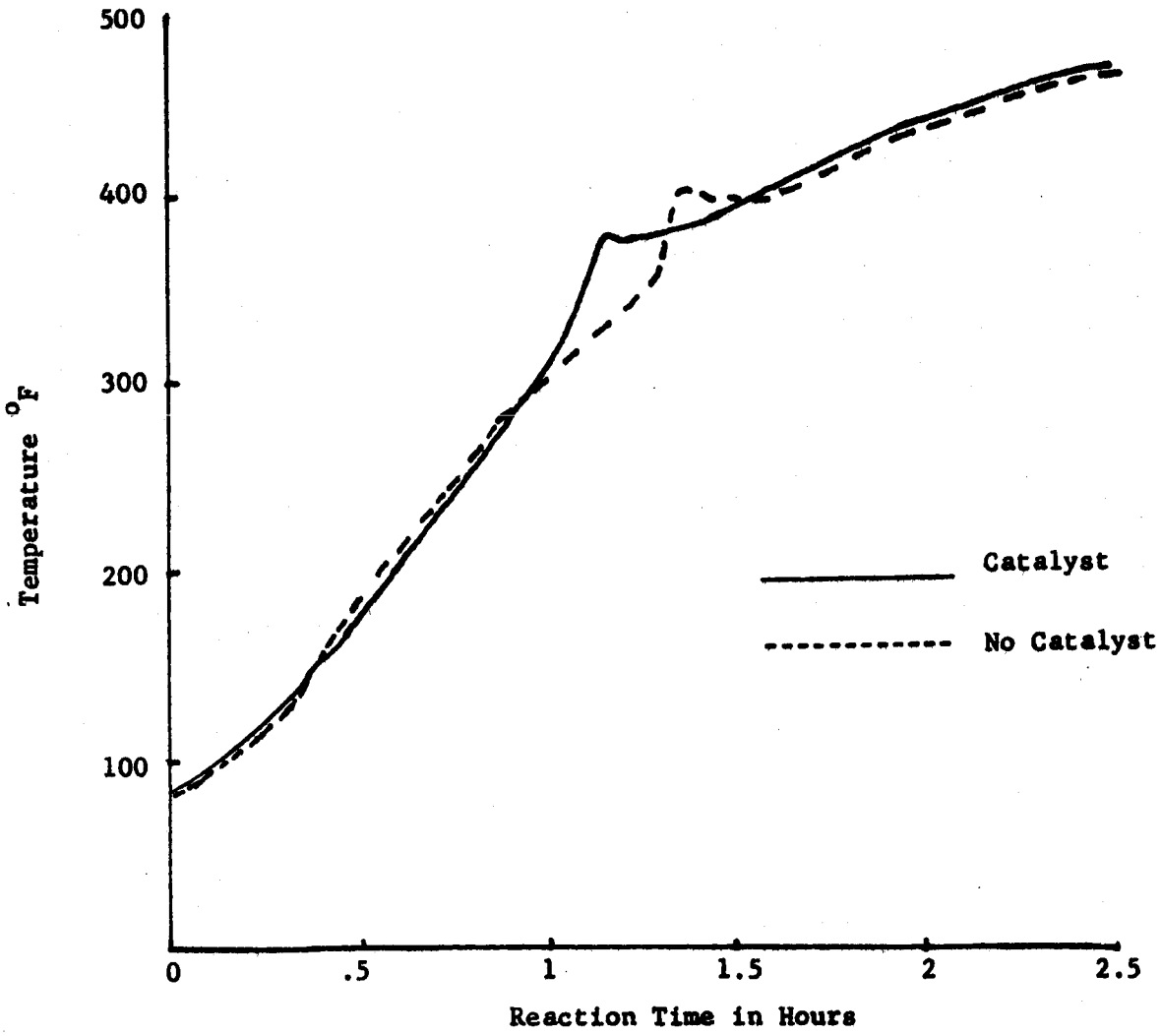


FIGURE 2

EFFECT OF VARIOUS CATALYSTS
ON WET OXIDATION OF SUCROSE

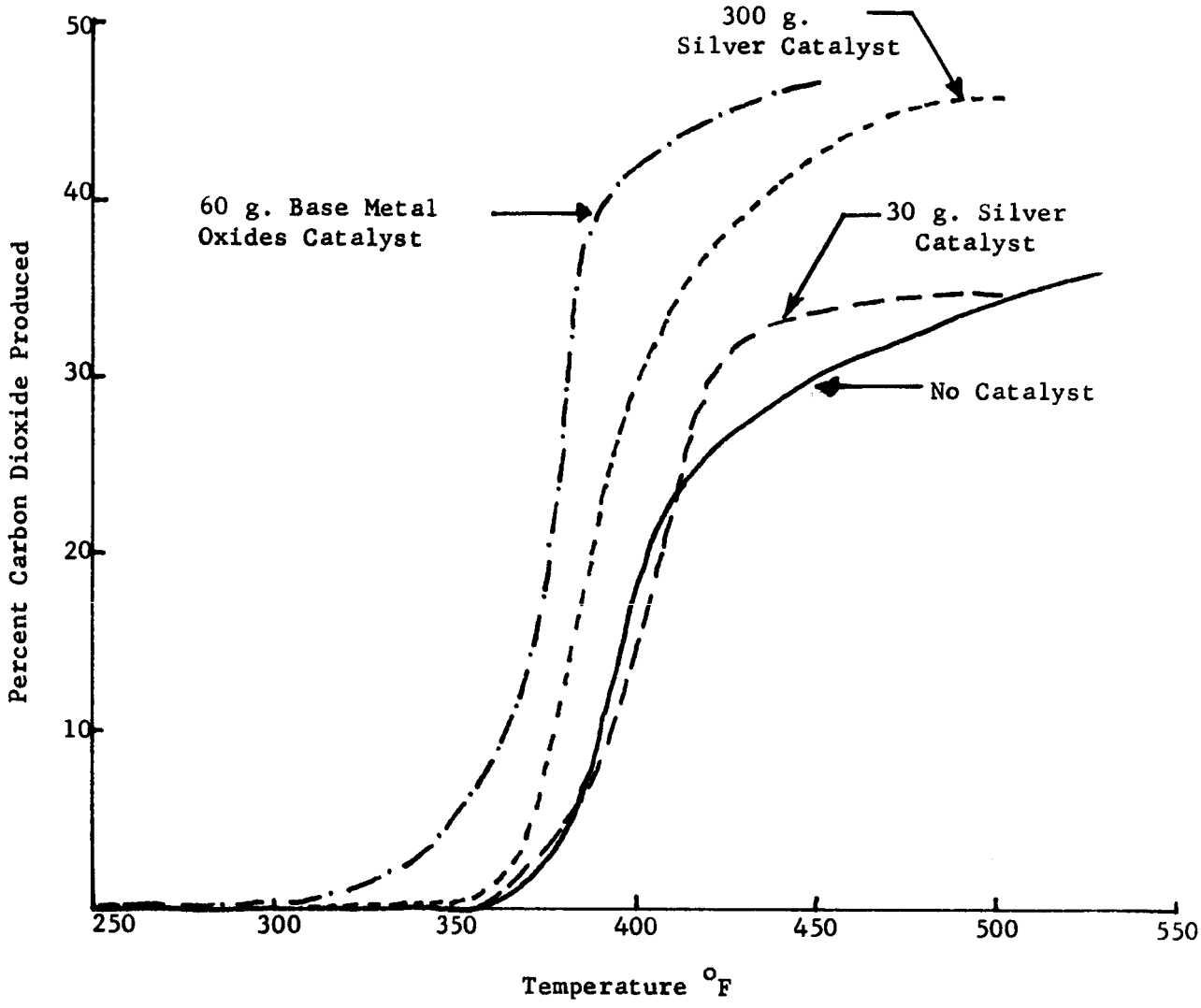


TABLE V

EFFECT OF CATALYSTS ON OXYGEN CONSUMPTION AND CARBON DIOXIDE AND ACID PRODUCTION FROM WET OXIDATION OF SUCROSE

Catalyst	Oxygen Consumed per Gram of Sucrose	Carbon Dioxide Produced Per Gram of Sucrose	pH of Effluent
30 g. Silver	0.86 g.	1.19 g.	4.2
300 g. Silver	0.91 g.	1.25 g.	6.1
60 g. Base Metal Oxides	1.01 g.	1.39 g.	6.6
None	0.92 g.	1.27 g.	4.1

Catalyzed and uncatalyzed reactions were also carried out using aliquots of 20% fecal suspensions. This provided a good comparison of the effect of the catalyst. There did not appear to be any significant differences in the temperature rise curves between catalyzed and uncatalyzed samples. Figure 3 shows curves of carbon dioxide production vs. temperature for one pair of samples. This method of evaluation did not show evidence of lower reaction temperature as a result of the catalyst. However, tests for evaluation of oxidized organic matter at various oxidation temperatures did show that the base metal oxides catalyst significantly increased the amount of organic matter oxidized at lower temperatures. The fact that fecal suspensions do not usually show a well defined temperature rise peak accounts for this discrepancy in observations.

Table VI shows the effect of base metal oxides catalyst on wet oxidation of fecal nitrogen. The catalyzed sample had an effluent ammonia content of 0.45 g. per 100 mls. of effluent, compared to 0.252 g. per 100 mls. for the uncatalyzed sample. This is more than a 5-fold decrease in effluent ammonia.

Further the non-ammonia effluent nitrogen was reduced more than 7-fold in the catalyzed sample compared to the uncatalyzed sample. This represented a very significant improvement in reducing the effluent ammonia problem.

FIGURE 3

EFFECT OF BASE METAL OXIDES CATALYSTS

ON WET OXIDATION OF FECES

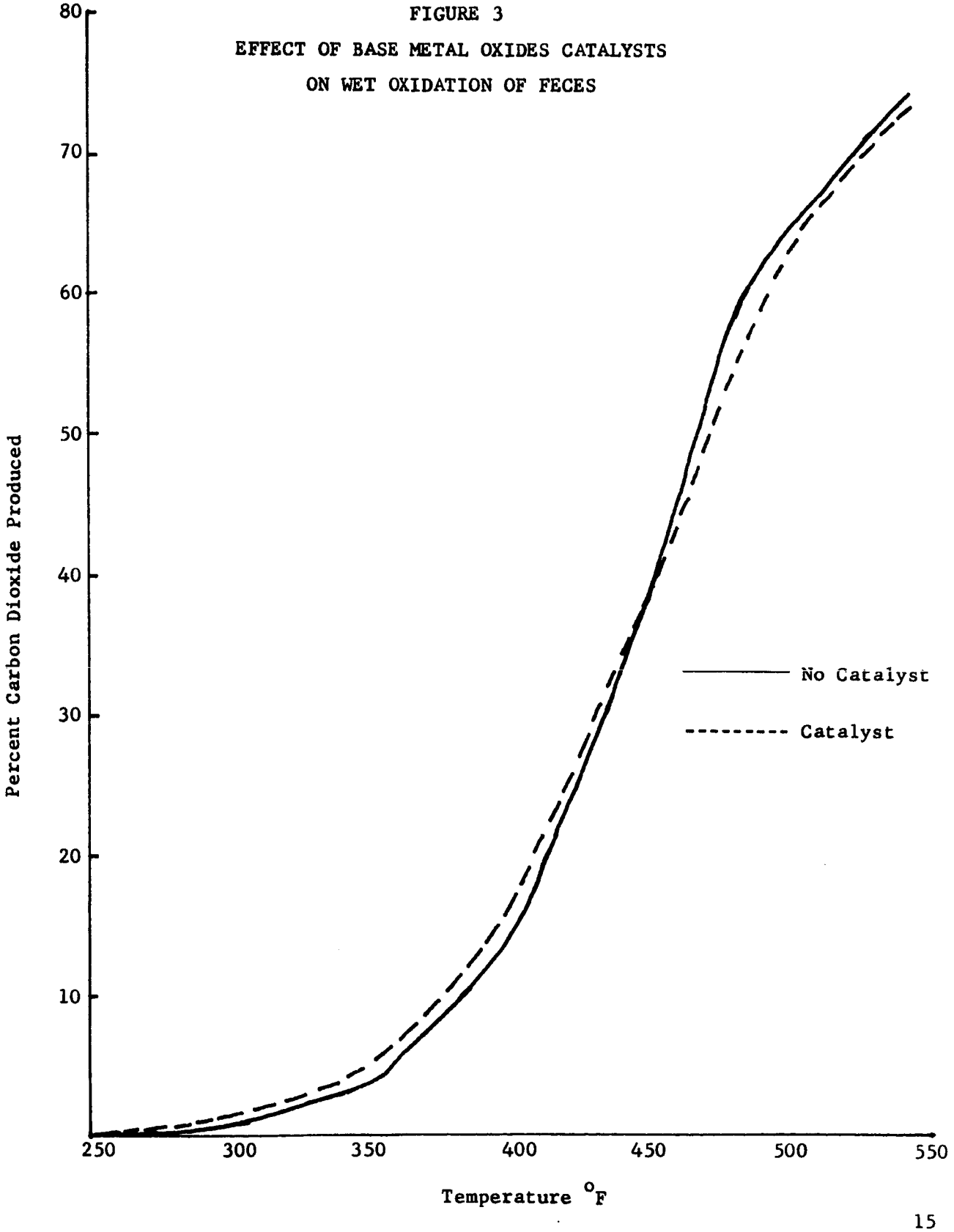


TABLE VI

EFFECT OF BASE METAL OXIDES CATALYST ON WET OXIDATION ON FECAL NITROGEN

CATA-LYST	RAW FECES		EFFLUENT			
	Total Nitrogen	Ammonia Nitrogen	Total Nitrogen	Ammonia Nitrogen	Non-Ammonia Nitrogen	Nitrogen Loss
60 g. Base Metal	.507	.006	.059	.045	.014	.448
None	.507	.006	.356	.252	.104	.151

Data are shown in grams of constituents per 100 mls. of suspension

Several experimental runs were made to determine the effect of the base metal oxides catalyst on wet oxidation of urine. The principal problem encountered with urine and urea, as described earlier in this report, was the tendency of urea to undergo heat decomposition to carbon dioxide and ammonia with little apparent oxidation of the resulting ammonia. The wet oxidation was carried out using 300 mls. of urine and 700 mls. of oxygen at 500 psi. Sixty grams of the base metal oxides catalyst were used. Maximum temperature was 550°F.

Table VII shows a very dramatic reduction in both total and ammonia nitrogen as a result of wet oxidation of urine in the presence of the base metal oxides catalyst. The uncatalyzed effluent contained over 0.4 grams of ammonia nitrogen per 100 mls. of effluent while the catalyzed effluent did not contain any detectable ammonia nitrogen. Some organic nitrogen was oxidized to nitrate by the process as indicated by analysis for nitrate. The remainder appeared to be converted to molecular gaseous nitrogen and this was detected in the headspace gas during the wet oxidation reaction. Consequently, use of the base metal oxides catalyst appeared to convert the waste organic nitrogen into inocuous forms that rendered the resulting effluent readily convertible to potable water.

The pH of the two urine effluents shown in Table VII illustrate the fate of ammonia rather well. The catalyzed effluent contained no ammonia and had a slightly acid pH which indicates oxidation of carbon compounds to acetic acid. The uncatalyzed sample had a rather alkaline pH from dissolved ammonia resulting from heat degradation of urea.

TABLE VII

EFFECT OF CATALYST ON WET OXIDATION OF URINE

Catalyst	RAW URINE		EFFLUENT		
	Total Nitrogen	Ammonia Nitrogen	pH	Total Nitrogen	Ammonia Nitrogen
Base Metal Oxides	812.0	8.4	6.2	0.0	0.0
None	812.0	8.4	8.1	588.0	431.0

All data except pH are shown as milligrams/100 mls.

The base metal oxides catalyst was subjected to repeated reuse in the wet oxidation of both sucrose and feces. No diminution of effect was detected as a result of reusing this catalyst. The catalyst beads did appear to undergo some mechanical destruction during the oxidation process, presumably as a result of the stirring. However, even this did not affect the catalytic effect. This appears to establish that the catalyst was not poisoned by waste components and that the catalyst was actually functioning as a catalyst and not as a simple oxidant.

Wet oxidation of mixed body waste. -- The mixed body wastes used extensively in this study were normal fresh urine and feces. Pooled substrate mixtures were prepared for use so that all runs in a given series would be comparable. This substrate mixture consisted of 10% raw feces in urine, by weight. This proportion of feces to urine is representative of the ratio produced normally by humans, as explained earlier in this report. Sufficient substrate mixture was prepared for a given test series and the mixture was thoroughly blended to insure homogeneity. The methods and equipment used for wet oxidation were the same as those already described. Substrate volume was 300 mls. in each case and the oxidation chamber was pressurized to 500 psi with pure oxygen. Maximum temperatures achieved during oxidation ranged from 400°F to 550°F in 50°F increments. Temperature was allowed to rise to the desired level and then the heater power was shut off and the chamber allowed to cool. Time at maximum temperature was about 15 minutes in each case.

Results of this series of wet oxidation reactions are shown in Table VIII.

TABLE VIII

EFFECT OF OXIDATION TEMPERATURE ON MIXED BODY WASTE EFFLUENT

	Raw Substrate	Wet Oxidation Effluent Samples			
Maximum Oxidation Temp.	--	400°F	450°F	500°F	550°F
Effluent pH	--	7.5	7.6	7.4	7.5
Total Solids/100 ml.	4.73g.	2.73g.	2.13g.	1.83g.	1.81g.
Ash/100 ml.	1.71g.	1.55g.	1.61g.	1.62g.	1.60g.
Organic Solids/100 ml.	3.02g.	1.18g.	0.52g.	0.21g.	0.21g.
Total Nitrogen/100ml.	982 mg.	932 mg.	862 mg.	767 mg.	590 mg.
Ammonia Nitrogen/100 ml.	369 mg.	638 mg.	605 mg.	571 mg.	487 mg.
COD mg./Liter	37 894	14 460	7615	3398	2150

The data in Table VIII illustrate the effects of temperature on the wet oxidation process. Except for ash and effluent pH, all values decreased with increased oxidation temperature. The observed increase in ammonia nitrogen at 400°F, over that shown for the unoxidized raw substrate sample, was the result of heat decomposition of urea. The ammonia was oxidized at higher temperatures, as indicated by the decreasing amounts shown at the higher oxidation temperatures.

The decrease in total nitrogen with increased temperature appears to result from oxidation of nitrogen compounds to nitrogen. The decrease in ammonia nitrogen is not great enough to account for the rather rapid decrease in total nitrogen observed.

The most dramatic effect of oxidation temperature appears to be the decrease in COD with increased temperature. However, the percent decrease in COD very nearly follows the percent decrease in organic solids. This effect is shown in Table IX.

TABLE IX.

EFFECT OF WET OXIDATION TEMPERATURE ON THE PERCENT DECREASE IN EFFLUENT ORGANIC SOLIDS AND COD

Maximum Oxidation Temp.	400°F	450°F	500°F	550°F
Percent Reduction of Organic Solids	61.0%	82.8%	93.1%	93.1%
Percent Reduction of COD	61.9%	79.9%	91.1%	94.4%

Two things appear obvious from these data: 1) Wet oxidation, at the higher temperatures, results in an appreciable reduction of both organic solids and COD. 2) The COD determination is a significant and direct measure of organic solids in wet oxidation effluents.

A study was made of the relative effects of oxidation temperature, and base metal oxides catalyst on mixed body waste. A large controlled batch of mixed body waste was prepared as the input substrate for all of these tests. Consequently, all test results were comparable. This mixed waste material consisted of 10% wet feces in urine as described above.

The wet oxidation method was the same as that described earlier in this report. Pure oxygen was used at a pressure of 500 psi. The effect of maximum oxidation temperature was determined by running a series of oxidation reactions in which the maximum temperature was gradually increased with each succeeding test. The temperatures selected were 300°F, 375°F, 400°F, 450°F, 500°F, and 550°F. When the material in the oxidation vessel reached the proper temperature, the vessel heaters were shut off and the material was allowed to cool. Because of the rapid combustion rate at about 400°F, temperature control was difficult and the vessel temperature was inclined to "override" the predetermined value.

Two separate series of tests were run. One of these used no catalyst. The other used 60 grams of the base metal oxides catalyst. Consequently, we are able to evaluate the effects of catalyst at the various oxidation temperatures selected.

Analyses were made on the cooled effluents obtained from the various test runs to determine the effects of wet oxidation at their respective maximum oxidation temperatures. Analyses performed were chemical oxygen demand (COD), total nitrogen, ammonia nitrogen, total solids, ash and pH. These analyses were made by methods already described.

The pH values obtained from the wet oxidation effluent samples did not reflect any significant differences at the various oxidation temperatures. However, there was a slight difference between samples resulting from the use of the catalyst. The mean pH of all the uncatalyzed samples was 7.8, while the mean pH of catalyzed samples was 8.1.

The chemical oxygen demand determinations showed the most conclusive effects of both catalysis and oxidation temperature. Figure 4 shows the COD results obtained from both catalyzed and uncatalyzed samples.

It is obvious from Figure 4 that oxidation was most rapid in the range of 350°F to 450°F. Oxidation began at a lower temperature in the catalyzed samples and more substrate was oxidized at lower temperature in the presence of the catalyst. However, at about 450°F, the extent of oxidation was about equal in both the catalyzed and uncatlyzed samples. At temperatures above 450°F, the catalyst appeared to increase the extent of oxidation as measured by COD. Oxidation at the highest temperature used, 550°F, resulted in a 92.5% reduction of COD without the use of catalyst and a 97.5% reduction of COD in the presence of catalyst.

Data shown in Figure 4 indicate that oxidation temperatures is the major key to determination of the completeness of the wet oxidation reaction. Presumably the highest feasible temperature would be the most advantageous. However, several considerations must be envisioned in light of the spacecraft environment. The higher the temperature, the more power is required by the system. Although efficient heat exchange can alter this requirement considerably. Another major consideration is operating pressure. Steam pressure in the oxidation chamber increases considerably at high temperatures. Table X shows the maximum pressures that might be expected at various temperatures within the wet oxidation range. These pressures were calculated on the basis of the experimental equipment described in this report, in which the chamber headspace contained a 500 psi oxygen pressure at ambient temperature prior to the wet oxidation run. Actual observed pressures were slightly lower than the calculated values. This was brought about by the solubility of part of the headspace gas in the liquid phase. This difference between calculated and observed values increased at higher temperatures as more carbon dioxide was produced in the headspace gas phase. The greater relative solubility of carbon dioxide than oxygen accounted for the greater difference at higher temperatures.

The wet oxidation of concentrated sludges and residues will be discussed later in this report. However, it is interesting to note here that the pressures produced during these test runs were nearly identical to the calculated values. This was probably a result of lower gas solubility in the concentrated substrates.

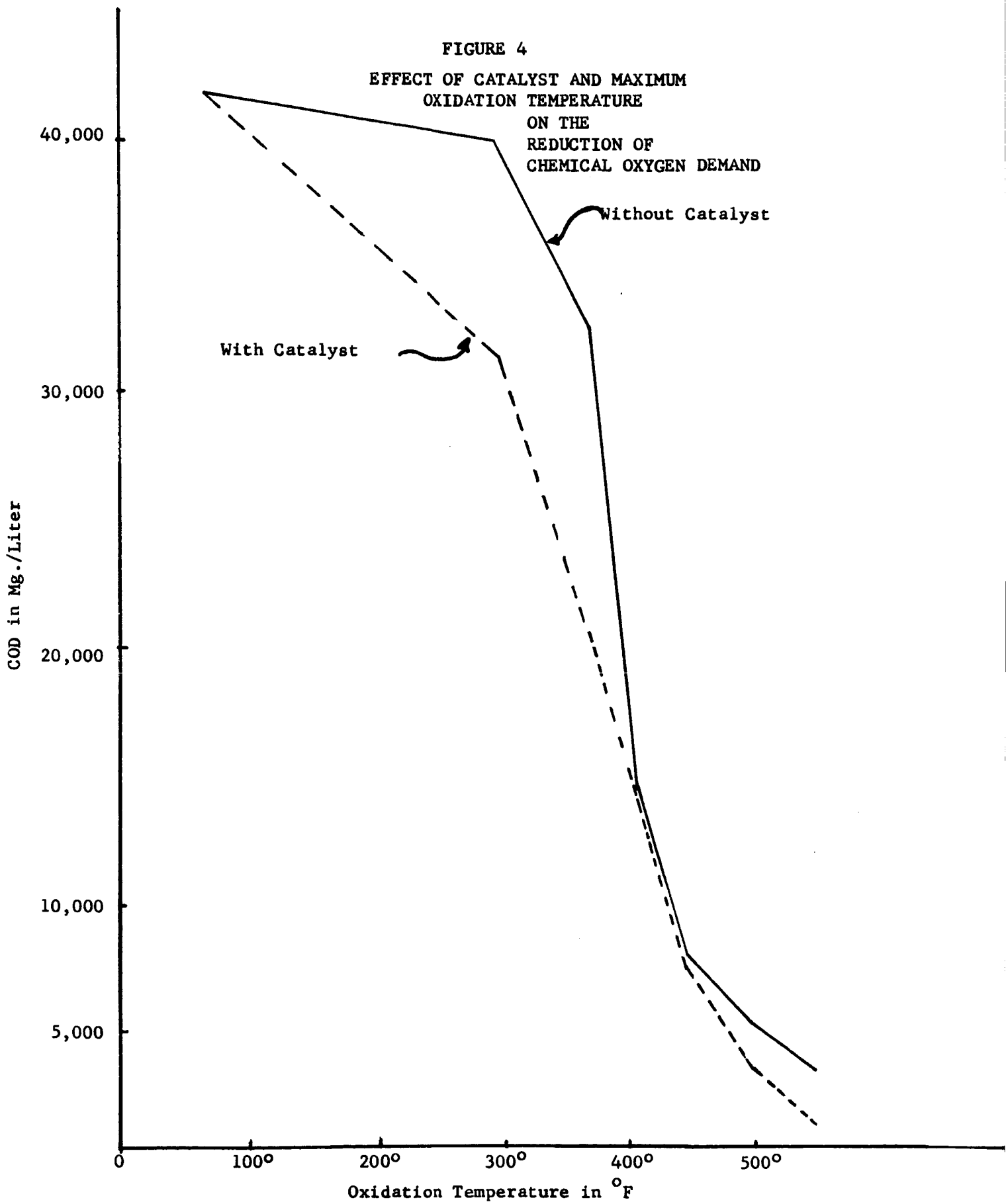


FIGURE 4
EFFECT OF CATALYST AND MAXIMUM OXIDATION TEMPERATURE ON THE REDUCTION OF CHEMICAL OXYGEN DEMAND
Without Catalyst
With Catalyst
40,000
30,000
20,000
10,000
5,000
COD in Mg./Liter
0
100°
200°
300°
400°
500°
Oxidation Temperature in °F

TABLE X

EFFECT OF OXIDATION TEMPERATURE ON WET OXIDATION CHAMBER PRESSURE

Temp. °F	Pressure in PSI	
	Calculated Values	Mean Observed Values
300	770	670
350	885	770
400	1043	915
450	1267	1110
500	1568	1380
550	1982	1750
600	2525	--

The maximum possible temperature for wet oxidation would be about 705°F, the critical temperature of water. However, it is unlikely that temperatures above 600°F would be practical for wet oxidation since any realized benefit would be very small and the problems of greater power requirement, increased pressure and heat loss would be multiplied. Oxidation temperatures in the range of 550°F to 600°F seem to be preferable for spacecraft use since pressures are not prohibitively high and oxidation of the waste material is readily complete within this temperature range.

A number of conditions bear directly or indirectly on the ultimate rate of the wet oxidation reaction. These include the nature of the substrate, oxidation temperature, rate of oxygen availability and rate of formation of oxidation-resistant intermediates. One factor of considerable importance is the rate of availability of oxygen. Since the actual oxidation process takes place in the liquid (water) phase of the system, the availability of oxygen at the site of oxidation is directly influenced by the solubility and rate of solution of oxygen into the water medium.

Himmelblau, 1960,[3] has reported rather completely on the oxygen-water system. Most interesting is a MINIMUM in oxygen solubility at about 212°F. At both lower and higher temperatures, the solubility is greater. This means that increasing the temperature above 212°F does not result in decreased solubility -- on the contrary, at higher temperatures oxygen is more soluble in water. The solubility of oxygen at 77°F is about 3% by volume, this decreases by 40% when the temperature is raised to 212°F, but increases steadily from the minimum value at higher temperatures.

The result is that oxygen solubility in the temperature range of most interest in wet oxidation, about 400°F to 550°F, is about the same as it is at room temperature. Solubility is affected somewhat by salt content and other contaminants but 3% by volume appears to be a good working figure. On this basis, 300 ml. of saturated solution would contain only enough oxygen to form 1.3% carbon dioxide in the 700 ml. headspace. Since much larger amounts of CO_2 appeared, evidently dissolved oxygen was readily replenished from the vapor phase under the described experimental conditions.

This can be illustrated using the rather simple example of oxidation of sucrose in the presence of base metal oxides catalyst. At the initiation of the wet oxidation reaction, the reaction proceeded rapidly as evidenced by the liberation of carbon dioxide and consumption of oxygen. Within 1.44 minutes, about 8.0 grams of oxygen had been consumed. After 9.96 minutes, an additional 6.8 grams of oxygen were consumed. Assuming equilibrium prior to the initiation of wet oxidation, the water suspending the sucrose should have contained only about 0.44 grams of oxygen. Consequently, an additional 7.56 grams of oxygen must have dissolved in the water within 1.44 minutes to furnish the total of 8.0 grams consumed during that period. This indicates that the rate of oxygen solution under the wet oxidation test conditions was appreciably high. Further, it is most unlikely that oxygen solubility rate or oxygen availability limits this reaction, since the vast majority of oxidation time occurred during the decreasing oxidation rate period that followed the initial oxidation phase. This is illustrated by the data shown above. During the initial 1.44 minutes, oxygen was consumed at a mean rate of 5.56 grams per minute. During the subsequent 8.52 minutes, oxygen was only consumed at a mean rate of 0.80 grams per minute. Presumably during the latter 8.52 minutes, considerably more oxygen was available in solution but the rate of consumption was limited by the actual rate of combustion or oxidation of the sucrose intermediates.

The wet oxidation reaction appeared to go to completion at varying oxygen concentrations so long as the oxygen supply was not depleted. Oxidations were run in which up to 93% of available oxygen was consumed in the reaction without any apparent effect on rate or completion of the reaction. This observation is in general agreement with the published literature dealing with large scale municipal wet oxidation systems. It appears that only a small excess of oxygen needs to be used in a spacecraft system to insure complete oxidation of raw mixed body wastes. This excess will be dependent more upon fluctuations in the oxygen demand of individual waste batches than in the basic requirements of the wet oxidation reaction.

Oxygen requirements for mixed body waste oxidation were determined both from headspace gas analyses and from COD reduction analyses. These data are shown in Table XI. Oxygen consumption values determined both by gas analysis and from calculation of COD reduction data agree very closely. Between 0.75 and 1.1 grams of oxygen were consumed per gram of dry waste solids. This was equivalent to a range of about 10 to 15 grams of oxygen

for 300 ml. batch of mixed body waste. As expected, the presence or absence of catalyst did not appear to affect the oxygen consumption values.

TABLE XI

OXYGEN CONSUMPTION OF MIXED BODY WASTE SUBJECTED TO WET OXIDATION AT 550°F.

Test	Catalyst	Grams of Oxygen Consumed per 300 mls. of Waste		Grams of Oxygen Consumed per Gram of Solids
		Gas Analysis Values	COD Reduction Values	
1	None	11.0	10.7	0.78
2	None	11.6	11.6	0.82
3	Base Metal Oxides	11.6	11.4	0.87
4	" " "	15.2	12.2	1.07
5	" " "	11.7	11.3	0.88

Data obtained from this study indicate that the use of about 1 gram of oxygen for 1 gram of mixed body waste solids should be satisfactory. This would be about equivalent to 50 grams of oxygen per liter of mixed body waste or 0.05 pounds of oxygen per pound of mixed body waste.

The headspace gas produced by wet oxidation of mixed body wastes consists primarily of carbon dioxide produced as a result of combustion plus the unused oxygen, and water vapor. Carbon dioxide content of the headspace gas was monitored during each wet oxidation run by the Orsat method. This provided a rapid method that was relatively insensitive to the large quantities of water vapor contained in the headspace gas. Headspace gas samples were also analyzed by difference for nitrogen. There was positive evidence that nitrogen increased in the headspace during wet oxidation. This tends to substantiate the probability that some of the waste nitrogen compounds are converted to nitrogen gas by the process.

The relatively low combustion temperatures employed in wet oxidation should not give rise to the oxides of nitrogen and sulfur that occur during dry incineration of waste materials. Concerted attempts were made to detect these and any other possible components of the headspace gas phase. Samples of the headspace gas produced during wet oxidation were sent to the Institute of Gas Technology, Chicago, Illinois, for detailed analysis by mass spectrometry. Samples were collected in evacuated gas sample tubes at the beginning and during the wet oxidation runs.

Table XII shows representative results of the mass spectrometer analysis. No oxides of nitrogen or sulfur were found, nor was ammonia vapor present. The substrate was identical for the catalyzed and uncatalyzed samples. The catalyst appeared to have an effect on the headspace gas composition. Acetone, carbon monoxide and hydrogen were present in the uncatalyzed sample, but not in the catalyzed sample. However, there was some evidence of carbon monoxide at intermediate temperatures in the catalyzed samples.

TABLE XII

MASS SPECTROMETER ANALYSIS OF WET OXIDATION HEADSPACE GAS

Gas	Without Catalyst		With Catalyst	
	Ambient Temp.	550°F	Ambient Temp.	550°F
Argon	*0.14	0.22	0.18	0.20
Acetone	0.0	<0.05	0.0	0.0
Carbon Dioxide	0.1	42.4	0.1	41.5
Carbon Monoxide	0.0	0.5	0.0	0.0
Hydrogen	0.0	0.3	0.0	0.0
Nitrogen	0.4	4.1	3.7	6.7
Oxygen	99.4	52.4	96.0	51.5
Unknown	0.0	0.1	0.0	0.1

*Note. All data expressed as mole percent concentration.

In general, the headspace gas produced by the wet oxidation process appears to be fully compatible with spacecraft application. This is an improvement over the flue gases produced by dry incineration.

The effluent derived from wet oxidation of mixed body waste consisted of a liquid portion and a dark grey to black, finely divided, precipitate. Upon standing, the precipitate settled rapidly leaving the clear, colorless to pale yellow supernatant liquid. Samples oxidized in the presence of the base metal oxides catalyst had a pale bluish to greenish cast, probably the result of trace amounts of dissolved copper from the catalyst. The effluent had a mild pyridine-like odor. A similar odor was apparently detected in the exhaust gas from the municipal wet oxidation systems by Hurwitz and Dundas, 1960.[2] This odor was not disagreeable as might be suggested by the reference to pyridine. Effluent pH was slightly alkaline, varying from about pH 7.5 in uncatalyzed samples to about 8.1 in the presence of base metal oxides catalyst.

The precipitate appeared to be primarily inorganic ash. Dry solids and ash determinations indicated that nearly all of the unoxidized organic residue was carried in the supernatant solution, while the precipitate contained only trace amounts. This was also determined by analyzing the COD of the effluent supernatant and precipitate fractions. Precipitate was sedimented in a high speed centrifuge and separated from the effluent supernatant solution. The precipitate was washed three times in distilled water and resuspended in an aliquot of distilled water equal to the original sample. COD determinations of the effluent supernatants and the precipitate suspensions are shown in Table XIII.

TABLE XIII

DISTRIBUTION OF COD IN WET OXIDATION EFFLUENTS

	Uncatalyzed Oxidation	Catalyzed Oxidation
Whole Effluent	2150 mg/L	992 mg/L
Effluent Supernatant	2220 mg/L	1547 mg/L
Precipitate Suspensions	79 mg/L	0 mg/L

These data show that the COD, and therefore the organic solids, were primarily located in the supernatant phase of the effluent. The values obtained for the supernatant solutions were somewhat higher than those of the whole effluent because of the enrichment effect that resulted from removal of the precipitate. The very small COD found in the precipitate from the uncatalyzed sample could have resulted from traces of organic materials in the precipitate phase. However, it is more likely to believe that the phenomenon resulted from traces of the supernatant that were not completely removed from the fine precipitate during the washing process.

Some inorganic material was also dissolved in the supernatant solution. Results indicated that the supernatant dry solids averaged about 2/3 inorganic matter and 1/3 organic matter. This varied somewhat with the electrolyte content of the urine included in the influent raw waste substrate.

Ammonia and organic nitrogen were found only in the supernatant solution. No evidence of these components was found in the precipitate.

The organic content of wet oxidation effluents appears to be dependent on the wet oxidation reaction mechanism. The actual mechanism of wet oxidation has not been precisely established; however, several plausible hypotheses have been advanced, as summarized by Koenig, 1963.[4] All of these assume some sort of sequential or step-wise oxidation of larger molecules to

increasingly smaller molecules and carbon dioxide. The smaller intermediates appear to be carboxylic acids. As the molecular size becomes smaller, the influence of the carboxyl group tends to strengthen the carbon-to-carbon bonds, thus making them more resistant to oxidation. Consequently, effluent organic material appears to be a mixture of low molecular weight acids derived from oxidation of carbon compounds, together with specific nitrogen compounds derived from heat degradation and oxidation of proteins, urea and similar nitrogen compounds.

Effluent samples were subject to gas chromatographic analysis as described earlier in this report. Acetic acid was the major component detected as one might infer from the oxidation mechanism. Propionic, butyric, and probably formic acid were also detected as shown in the reproduced chromatograph strip charts in Figure 5. Oxidation temperature had a significant effect on the effluent components.

Data in Table XIV show that the percent, by weight, of acetic acid in the wet oxidation effluent was slightly increased at higher temperatures while propionic acid was decreased. This followed the general trend of oxidation and degradation of larger molecules to smaller molecules at increased temperature. The average quantity of acetic acid appeared to be about 300 mg/100 mls. of effluent.

TABLE XIV

EFFECT OF OXIDATION TEMPERATURE ON ACETIC AND PROPIONIC ACID CONTENT OF WET OXIDATION EFFLUENT

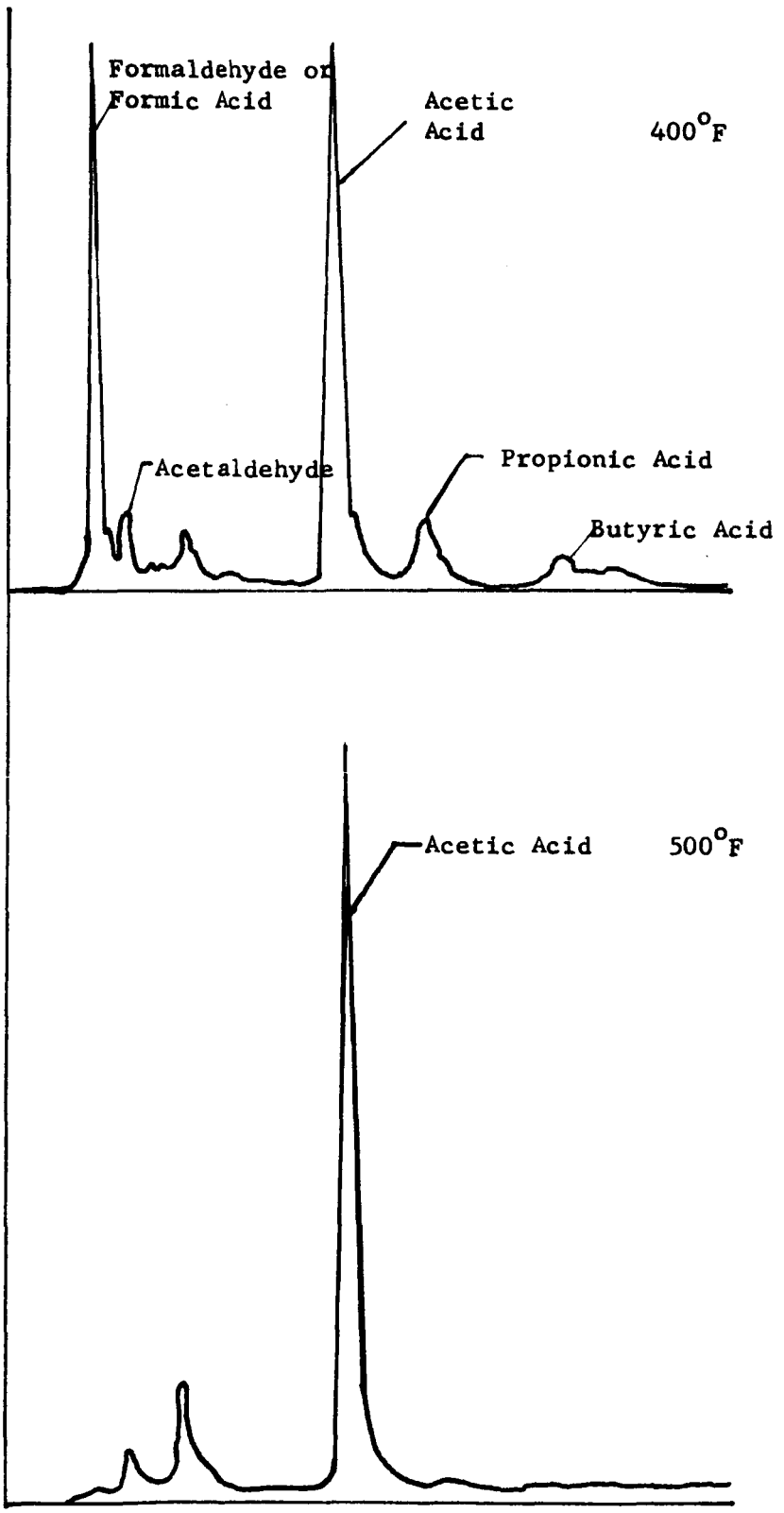
Oxidation Temperature	Acetic Acid	Propionic Acid
400°F	0.25%	0.02%
450°F	0.34%	0.01%
500°F	0.37%	0.01%
550°F	0.31%	0.01%

Gas chromatography also disclosed some additional effluent components that occurred in small quantities. The identities of some of these were not completely certain. The chromatography strip charts reproduced in Figure 5 indicate these components and the effects of oxidation temperature on their formation.

The 400°F effluent contained more components than the 550°F effluent, indicating that many of these were oxidized and removed at the higher temperature. Most notable of these was loss of the peak indicating either formaldehyde or formic acid and a sharp decrease in the propionic acid peak.

FIGURE 5

GAS CHROMATOGRAPHY RESULTS OF WET OXIDATION EFFLUENT AT TWO TEMPERATURES



Essentially, the effluent derived from wet oxidation of mixed body wastes consisted of a rather inert inorganic precipitate phase and a supernatant phase that contained inorganic salts and a small amount of simple low molecular weight organic compounds. This represented a considerable improvement over the input raw waste substrate.

This effluent appeared to be readily treatable for water recovery. Several possible approaches appear feasible. Filtration could be used to remove the precipitate. Ion exchange in one of its many forms could remove the dissolved solids, since these all appeared to be in some ionized form. Distillation could remove both precipitate and dissolved solids. Distillation could be accomplished by direct vaporization of the effluent from the oxidation chamber using excess combustion heat.

Effects of salt on wet oxidation of mixed body waste. -- Several systems approaches might be feasible for the application of wet oxidation to a spacecraft waste treatment system. Among these approaches are systems that might recover most of the water from the wet oxidation effluent and return the precipitate and dissolved solids to the raw waste influent substrate. Such a system would eventually saturate the influent waste with dissolved salts. Experience gained from municipal wet oxidation systems indicates that high dissolved solids concentrations of this type adversely affect the wet oxidation reaction. An experimental series of wet oxidation reactions were set up to determine the effect of sodium chloride saturation on the wet oxidation of raw waste in small systems.

The same 10% feces in urine mixture was used for the mixed body waste influent. Each test batch consisted of 300 mls. of the mixed body waste to which 120 grams of sodium chloride were added. This saturated salt influent was oxidized without catalyst at 500°F using 700 mls. oxygen at 500 psi. Results of representative reactions are shown in Table XV. Effluent COD determinations were not reliable because of the very large chloride interference. However, reduction of organic matter was determined by dry weight calculations. Results fell in the general range of 80% to 90% reduction of organic solids in the presence of sodium chloride saturation. This compared to a 95% or better reduction of organic solids in normal mixed body waste under the same wet oxidation conditions. Consequently, sodium chloride saturation did impair the wet oxidation reaction; however, a considerable reduction of organic solids was still accomplished. These data indicate that nominal dissolved salt buildup in the waste influent might be acceptable, but a significant impairment of oxidation will result if salts concentration are allowed to reach the point of saturation. In practice, residues might be allowed to accumulate for several runs, then they would be discarded and the process repeated.

TABLE XV

EFFECT OF CONCENTRATED SALT ON
WET OXIDATION OF MIXED BODY WASTE

Raw Influent	Effluent				Percent Reduction of Organic Matter
Organic Matter g./100 ml.	pH	Dry Solids g./100 ml.	Ash g./100 ml.	Organic Matter g./100 ml.	
3.00 g.	7.2	32.54 g.	31.92 g.	0.62 g.	79.4%
3.00 g.	7.1	32.23 g.	31.90 g.	0.33 g.	89.0%

WET OXIDATION OF WASTE SLUDGES AND RESIDUES

Wet oxidation could be applied to a spacecraft waste treatment system at one of two basic points. Either the whole mixed urine and feces could be oxidized and the effluent treated for water recovery, or the urine residue and feces could be combined for wet oxidation. The first situation would result in the wet oxidation of a large volume of dilute wastes while the second situation would result in wet oxidation of a small volume of concentrated waste. Effluent from the concentrated waste oxidation could be returned in total or in part to the urine water recovery system for secondary treatment.

There would be certain advantages to the wet oxidation of concentrated wastes. Less water would be heated to high temperatures and a smaller oxidation chamber could be utilized. The feasibility of wet oxidation of concentrated slurries of feces and urine residue were studied. These slurries were comprised of wet feces and the residue obtained by distilling 90% of the water from urine at ambient pressure. The feces and urine residue were combined in a ratio proportional to the quantities normally excreted. This resulted in 50 grams of feces combined with 45 grams of urine residue. This was quite a heavy slurry, but appeared to cause no problem in the oxidation chamber or stirring equipment. The 95 gram waste slurry samples were placed in the oxidation chamber and the chamber was pressurized to 500 psi with pure oxygen. Because of the 905 ml. available headspace resulting from the smaller waste sample, the chamber contained about 45.4 grams of oxygen.

Oxidation reactions were carried out at 550°F without catalyst. The resulting effluent appeared to be the same as that obtained from more dilute substrates except the dissolved salts were proportionally more concentrated, and a greater amount of precipitate was formed per volume of liquid effluent. The precipitate settled rapidly leaving a pale yellow supernatant solution.

Table XVI shows results obtained from analysis of representative effluents for COD, ash and solids. The raw slurry influent contained 13.18 grams of organic matter per 100 mls. and had a COD of 199 136.

TABLE XVI

ANALYSIS OF EFFLUENTS OBTAINED FROM WET OXIDATION OF FECES-URINE RESIDUE SLURRIES

Dry Solids g/100 mls.	Ash g/100 mls.	Organic Matter g/100 mls.	Percent Reduction Organic Matter	COD mg/L	Percent Reduction of COD
63.8 g.	5.97 g.	0.41 g.	96.1%	8 612	95.7%
7.14 g.	6.63 g.	0.51 g.	96.2%	10 360	94.8%
9.94 g.	9.32 g.	0.62 g.	95.3%	10 984	94.5%

The mean pH of slurry effluent was 8.2. Gas chromatographic analyses showed that the volatile acids in the slurry effluents were identical to those obtained from more dilute mixed body waste effluents.

Oxygen consumption ranged from 0.77 grams of oxygen per gram of dry slurry solids to 1.42 grams of oxygen per gram of dry slurry solids. This range is in general agreement with that obtained from the mixed body waste oxidation studies.

During the oxidation reaction, headspace gas samples were taken and analyzed by mass spectrometry as described earlier in this report. Samples were taken at ambient temperature before oxidation began, at 400°F and at the maximum oxidation temperature of 550°F. Results of these analyses are shown in Table XVII. These data are essentially the same as those obtained from wet oxidation of mixed body wastes, except some values are higher owing to the greater weight of oxidizable substrate in the slurry samples. Argon occurred as a contaminant in the oxygen supply. Most constituents increased at the higher oxidation temperature. Acetone, however, appeared to form at lower temperature and was itself oxidized as the temperature increased. Oxygen was used at a rate roughly corresponding to carbon dioxide formation. No simple explanation is available for the variability in nitrogen analysis. Oxides of sulfur and nitrogen were not detected.

TABLE XVII

MASS SPECTROMETER ANALYSIS OF HEADGAS
OBTAINED FROM WET OXIDATION OF FECES-URINE RESIDUE SLURRIES

Component	Oxidation Temperature		
	Ambient	440°F	550°F
Acetone	*0.0	0.3	0.03
Argon	0.18	0.20	0.23
Carbon Dioxide	0.3	21.7	53.3
Carbon Monoxide	0.0	0.4	0.6
Hydrogen	0.0	0.0	0.2
Nitrogen	3.4	2.6	4.2
Oxygen	96.1	74.7	41.3
Unidentified	0.0	0.08	0.11

* All results are expressed as mole percent concentration.

Based upon the data obtained in this study, wet oxidation of feces and concentrated urine residues appears to be well within the realm of feasibility. This should be given serious consideration in the design of possible spacecraft waste treatment systems using the wet oxidation principle.

Estimated Effect of Weightlessness on Wet Oxidation

Wet oxidation has never been carried out under weightless conditions; however, certain estimates of its effect can be made. Basically, there is no reason why weightlessness should affect the wet oxidation reaction *per se*. Wet oxidation will take place so long as the required heat, oxygen, water and oxidizable substrate are available. The behavior of liquids under weightlessness should not significantly hamper the effective entrainment of waste solids or the dissolution of oxygen into the system. The important facets are those associated with the engineering aspects of the wet oxidation equipment. These include heating liquids and liquid-gas separation under weightless conditions. These problems are common to nearly all spacecraft waste and water handling equipment. They will be neither better nor worse when applied to the wet oxidation principle.

Application and Engineering Aspects of Wet Oxidation

Several engineering aspects were studied in relation to the application of wet oxidation to spacecraft waste systems. One of these was the effect of stirring during the oxidation reaction. All of the data shown thus far in this report were obtained from continuously stirred wet oxidation reactions.

The wet oxidation reaction is believed to take place between the organic substrate and oxygen dissolved in the suspending water. Consequently, stirring should be an important adjunct to insuring adequate dissolved oxygen. Further, stirring should help release the accumulating carbon dioxide to the headspace gas phase of the system thus preventing possible interference or blanketing of the reaction. Aliquots of a single batch of mixed body waste (10% feces in urine) were used in this study to facilitate comparison of results. Each test aliquot consisted of 300 mls. of the waste mixture. The oxidation chamber was pressurized to 500 psi with pure oxygen and a maximum oxidation temperature of 550°F was used in each test run. Comparative test runs were made with and without the oxidation chamber stirring mechanism described earlier in this report and in the presence and absence of the base metal oxide catalyst.

Table XVIII shows that stirring had a significant effect on wet oxidation. However, even without stirring, the COD of the uncatalyzed sample was reduced from about 40 000 in the raw waste substrate to about 4700. Oxidation under the same conditions with stirring further reduced the COD to about 2100 or less than half of that obtained without stirring.

TABLE XVIII

EFFECT OF STIRRING ON WET OXIDATION

Test Condition	Stirred	Not Stirred
Without Catalyst:		
pH	7.5	7.7
Total Solids g/100 ml.	1.81	1.91
Ash g./100 ml.	1.60	1.63
COD mg./Liter	2150	4784
Catalyzed		
pH	7.4	7.5
Total Solids g/100 ml.	--	2.01
Ash g/100 ml.	--	1.88
COD mg./Liter	988	1456

Roughly, the same relationship between stirred and unstirred samples was shown in the presence of catalyst. However, lower COD values were obtained and the effect of stirring appeared to be less.

Based on the above data, it appears that if a choice must be made between stirring and the use of catalyst, the use of catalyst would produce the better result. Use of both stirring and catalyst would give the maximum result. Stirring within a sealed pressure vessel involves some engineering problems. Generally, it appeared that a spacecraft wet oxidation system should be designed to employ stirring. However, if this proves to be infeasible, the use of an effective catalyst appears to compensate for the lack of stirring.

Another engineering aspect is that of effluent recovery from the wet oxidation chamber. Effluent may be pumped from the chamber, forced out by the chamber pressure, or the water can be evaporated using chamber heat. The latter method would require some method for removal of the solid or concentrated residue, but has the advantage of a simple distillation to separate most of the dissolved salts from the effluent water. A test was run to determine the effectiveness of separating effluent water and dissolved solids by this method. Waste influent composed of 300 mls. of mixed body waste was oxidized in pure oxygen at 500 psia and a maximum temperature of 550°F as described earlier in this report. No catalyst was used. After the oxidation temperature reached 550°F, steam was bled from the chamber through a stainless steel tube condenser cooled with ice water. The first 200 mls. of water were collected. The chamber was cooled and the remaining 100 mls. of residue were removed. Analyses of both the distillate and residue were performed.

Table XIX shows results of the analyses and two individual samples. The pH varied quite widely between distillate and residue. Ammonia or ammonium ion appeared to distill while organic acids appeared to concentrate in the residue. This is shown in the analyses for ammonia. Solids, ash and COD were greatly reduced in the distillate. The second sample showed a dramatic reduction in solids from 5.66 gram/100 ml. to 0.004 gram/100 mls. This is not an amazing accomplishment for normal distillation; however, it must be borne in mind the process shown took place at 550°F and at a pressure over 1700 psi.

This appears to be a possible method for recovery of wet oxidation effluent water from the oxidation chamber. More complete recovery would be possible; however, some liquid would probably have to be left with the solid residue to insure its complete removal from the chamber by pumping or pressure expulsion. This distillate was not potable water but most of the dissolved solids were removed and conversion to potable water should be rather simple.

TABLE XIX

EFFECT OF DISTILLATION RECOVERY OF WET OXIDATION EFFLUENTS

Test		pH	Ammonia Nitrogen mg./100 ml.	Total Solids g./100 ml.	Ash g./100 ml.	COD mg./L
1#	Distillate	8.9	240	0.27	0.16	408
	Residue	5.6	106	7.43	6.57	7956
2#	Distillate	9.1	403	0.004	0.00	607
	Residue	5.3	59	5.66	5.03	7691

A third engineering aspect is that of heat. Heat was supplied to the oxidation chamber described in this report by an external electric resistance heater. This provided slow and inefficient heat transfer through the heavy stainless steel walls of the chamber. An internal electric heater would be considerably more efficient and provide a more rapid temperature rise within the chamber.

The amount of heat required for the process depends to a very large part upon the actual equipment that will be used for oxidation and the specific heat losses that will be associated with this equipment. The heat required to raise the temperature of the oxidation substrate and oxygen from ambient to the oxidation temperature can be calculated from the enthalpys of the system at the temperatures involved. This would require about 511 BTU to raise one pound of waste influent from an ambient 70°F to a maximum oxidation temperature of 550°F. This assumes no heat loss or heat input to the equipment.

Part of the required heat may be derived from combustion of the waste material. A waste influent such as the mixed body waste described in this report has an average COD of about 40 g. of oxygen per liter. This roughly corresponds to 240 BTU of combustion heat per pound of waste material. Rapid combustion and heat evolution was shown to begin at about 400°F. Consequently, if the required 337 BTU were supplied to raise one pound of mixed body wastes to 400°F, the heat of combustion would be more than adequate to supply the additional 174 BTU required to raise the oxidation mixture to 550°F. Again, however, this assumes no heat losses or heating of the oxidation chamber, etc. Obviously, considerably more heat would be required to heat the equipment and to compensate for losses. The exact amount of this additional heat would depend entirely upon the specific equipment and system involved. The large municipal wet oxidation

units employ a continuous process system. These are generally self-sustaining as to heat if the sludge contains about 6% total solids and a COD of about 90 g/L.

A spacecraft wet oxidation system would most likely be a batch operation to effect simplicity and reliability of operation. Such a system could employ tandem oxidation chambers and an efficient heat transfer arrangement so that heat evolved from cooling one chamber could be used to heat the second chamber. Such a system could be very economical to operate from the heat and power standpoint. In fact, by combining efficient heat transfer and insulation with oxidation of heavy waste residue slurries, a self-sustaining system may possibly be achieved even with a small spacecraft-sized batch operation. A prototype unit should be constructed and the feasibility of this goal should be determined. It appears to be within the realm of possibility if the proper equipment design is achieved.

CONCLUSIONS

Several conclusions can be drawn from this study in regard to the feasibility of very small scale wet oxidation systems and their possible application to spacecraft waste treatment systems.

1. Wet oxidation was feasible and efficient in very small systems. A 95% or greater removal of organic body waste matter and COD was achieved by the process. This study indicates that a properly designed wet oxidation system should be applicable to spacecraft waste treatment.

2. The use of pure oxygen proved to be very satisfactory and resulted in a five-fold reduction in the required headspace gas volume when compared to the use of air. About 1 g. of oxygen was required for each gram of dry waste solids.

3. Tests using a base metal oxides catalyst showed that a suitable catalyst was capable of promoting wet oxidation at lower temperatures and ultimately promoted more complete oxidation at higher temperatures.

4. The effluent obtained from wet oxidation of mixed urine and fecal waste was comprised of a dark, rapidly settling, precipitate, and a clear colorless to pale yellow supernatant. The precipitate was entirely composed of inorganic ash. The supernatant contained small amounts of dissolved organic matter and inorganic salts. The dissolved organic matter included ammonium salts, and low molecular weight carboxylic acids and aldehydes. Acetic acid appeared to be the dominant organic constituent. Based on its constituent analysis, this effluent should be easily converted to potable water by a variety of currently available methods.

5. The gases and vapors produced by wet oxidation of urine and fecal waste are primarily water vapor and carbon dioxide. Small amounts of acetone vapor, carbon monoxide, hydrogen and nitrogen have been detected. Oxides of nitrogen and sulfur were not detected.

6. Heavy slurries prepared from mixtures of feces and the residues obtained from urine distillation were readily oxidized by the wet oxidation process. Effluents obtained were very similar to those from the more dilute normal wastes.

7. The wet oxidation reaction was enhanced by continuous stirring during oxidation, and retarded by saturation of the influent waste with salt.

8. Based on observations and data taken during this study, it is believed that weightlessness should not adversely affect the wet oxidation reaction. However, typical engineering problems associated with the handling of liquids and gases under weightlessness would be encountered.

9. The temperature required to oxidize 95% or more of urine and fecal wastes was about 550°F; although, oxidation began at temperatures below 300°F. Heat input required to reach proper oxidation temperature depends upon the specific equipment employed. A properly designed spacecraft wet oxidation system, using efficient heat exchange and conservation, together with full use of the available heat of combustion, could operate on relatively small power input.

10. Further effort should be devoted to the application of wet oxidation to spacecraft waste treatment.

Whirlpool Corporation
Life Support Department
St. Joseph, Michigan, August 30, 1967

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