AD-771 745

MATERIALS FOR WET OXIDATION PROCESSING EQUIPMENT (SHIPBOARD)

NATIONAL MATERIALS ADVISORY BOARD (NAS-NAE)

PREPARED FOR

DEPARTMENT OF DEFENSE

NOVEMBER 1973

DISTRIBUTED BY:

NTIS

National Technical Information Service
U. S. DEPARTMENT OF COMMERCE

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER: NMAB-312

2. GOVT ACCESSION NO.:

3. RECIPIENT'S CATALOG NUMBER:

4. TITLE (and Subtitle): "Materials for Wet Oxidation Processing Equipment (Shipboard)"

5. TYPE OF REPORT & PERIOD COVERED: FINAL

6. PERFORMING ORG. REPORT NUMBER:

7. AUTHOR(s): NMAB ad hoc Committee on Materials for Wet Oxidation Processing Equipment (Shipboard)

8. CONTRACT OR GRANT NUMBER(s): DA-49-083-OSA-3131

9. PERFORMING ORGANIZATION NAME AND ADDRESS:
National Materials Advisory Board
Division of Engineering-National Research Council
National Academy of Sciences-National Academy of Engineering
2101 Constitution Avenue, N.W., Washington, D. C. 20418

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS:

11. CONTROLLING OFFICE NAME AND ADDRESS:
ODDR&E, Department of Defense
The Pentagon, Washington, D. C.

12. REPORT DATE: November 1973

13. NUMBER OF PAGES: 87

14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office):

15. SECURITY CLASS. (of this report): Unclassified

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE:

16. DISTRIBUTION STATEMENT (of this Report):
This document has been approved for publication release and sale; its distribution is unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report):

18. SUPPLEMENTARY NOTES:

19. KEY WORDS (Continue on reverse side if necessary and identify by block number):

Wet Oxidation Process
Materials of construction
Titanium, Tantalum, Ceramics
Design
Continuous piping array
Batch

20. ABSTRACT (Continue on reverse side if necessary and identify by block number):

This report is intended to provide an overview of the wet oxidation process and the potential materials of construction for the reaction vessel (for shipboard applications).

Since the wet oxidation process requires the concainment of corrosive products (the material being processed can range from

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

Continuation of Block No. 20 (Abstract):

very acidic to slightly basic and over a broad spectrum of wastes), at elevated temperatures and pressures, these conditions lead to difficult but solvable materials-of-construction problems.

Based on the current state of the art, wet oxidation systems can be constructed from commercially pure titanium as well as from titanium alloyed with palladium (.12-.25%). This type of system, it is felt, can be operated safely at approximately 500°F with reasonable assurance of moderate life (approximately 10 years). However, should a longer life system be desired and one which is virtually indestructible from a chemical point of view, a tantalum-lined and coated titanium system would provide the best choice of materials.

For higher temperature operation up to 600°F and a projected equipment life of 15 years, a ceramic-lined and coated carbon steel or titanium system would have to be developed. Here, an added advantage to ceramic lining is improved heat insulation. This allows for a reduction of external insulation. In addition, a penetration monitoring system (of the electrical resistance type) can be incorporated in the ceramic lining.

From an overall design consideration point of view, it appears that the wet oxidation process can be operated in a continuous manner in shipboard installations and the reaction vessel can consist of a piping array configuration. Several distinct operating advantages (viz space-saving) are expected from this configuration, and thus it is recommended that further development of the process and equipment be based on this particular design approach.

MATERIALS FOR WET OXIDATION PROCESSING EQUIPMENT (SHIPBOARD)

Report of

The Ad Hoc Committee on

Materials for Wet Oxidation Processing

Equipment (Shipboard)

National Materials Advisory Board

Division of Engineering - National Research Council

Publication NMAB-312

National Academy of Sciences - National Academy of Engineering

2101 Constitution Ave., N.W.,

Washington, D. C. 20418

DECEMBER 1973

ib

NOTICE

The project which is the subject of this report was approved by the Governing Board of the National Research Council, acting in behalf of the National Academy of Sciences. Such approval reflects the Board's judgment that the project is of national importance and appropriate with respect to both the purposes and resources of the National Research Council.

The members of the committee selected to undertake this project and prepare this report were chosen for recognized scholarly competence and with due consideration for the balance of disciplines appropriate to the project. Responsibility for the detailed aspects of this report rests with that committee.

Each report issuing from a study committee of the National Research Council is reviewed by an independent group of qualified individuals according to procedures established and monitored by the Report Review Committee of the National Academy of Sciences. Distribution of the report is approved, by the President of the Academy, upon satisfactory completion of the review process.

This study by the National Materials Advisory Board was conducted under Contract No. DA-49-083 OSA-3131 with the Department of Defense.

Members of the National Materials Advisory Board study groups serve as individuals contributing their personal knowledge and judgments and not as representatives of any organization in which they are employed or with which they may be associated.

The quantitative data published in this report are intended only to illustrate the scope and substance of information considered in the study and should not be used for any other purpose, such as in specifications or in design, unless so stated.

For sale by the National Technical Information Service, Springfield, Virginia 22151

AD HOC COMMITTEE ON MATERIALS FOR WET OXIDATION PROCESSING EQUIPMENT (SHIPBOARD)

Chairman: Louis R. McCreight
Manager, Materials Research and Development Section
General Electric Company
P.O. Box 8555
Philadelphia, Pa. 19101

Elton J. Cairns
General Motors Research Laboratory
Electrochemistry Dept.
12 Mile and Mound Road
Warren, Michigan 48090

William H. Hartt
Associate Professor Ocean Engineering
Florida Atlantic University
Boca Raton, Florida 33432

William B. Crandall
Senior Scientific Advisor
IIT Research Institute
10 W. 35th Street
Chicago, Illinois 60616

Robert J. McGrattan
Chief, Ocean Systems Engineering
Electric Boat Division
General Dynamics Corporation
Groton, Connecticut 06340

NAS-NMAB Staff

Donald G. Groves
Staff Engineer
National Academy of Sciences
National Materials Advisory Board
2101 Constitution Ave., N.W.
Washington, D. C. 20418

Liaison Representatives

Paul Schatzberg
Senior Research Chemist
Pollution Abatement Division
U. S. Naval Ship Research and
Development Center
Annapolis, Maryland 2140.

Don Vreeland
Metallurgist
U. S. Naval Ship Research and
Development Center
Annapolis, Maryland 21402

ABSTRACT

This report provides an overview of the wet oxidation process and the potential materials of construction for the reaction vessel (for shipboard applications).

Since the wet oxidation process requires the containment of corrosive products (the material being processed can range from very acidic to slightly basic and over a broad spectrum of wastes), at elevated temperatures and pressures, these conditions lead to difficult but solvable materials-of-construction problems.

Based on the current state of the art, wet oxidation systems can be constructed from commercially pure titanium as well as from titanium alloyed with palladium (.12-.25%). This type of system, it is felt, can be operated safely at approximately 500°F with reasonable assurance of moderate life (approximately 10 years). However, should a longer life system be desired and one which is virtually indestructible from a chemical point of view, a tantalum-lined and coated titanium system would provide the best choice of materials.

For higher temperature operation up to 600°F and a projected equipment life of 15 years, a ceramic-lined and coated carbon steel or titanium system would have to be developed. Here, an added advantage to ceramic lining is improved heat insulation. This allows for a reduction of external insulation. In addition, a penetration monitoring system (of the electrical resistance type) can be incorporated in the ceramic lining.

From an overall design point of view, it appears that

the wet oxidation process can be operated in a continuous manner in shipboard installations and the reaction vessel can consist of a piping array configuration. Several distinct operating advantages (viz, space-saving) are expected from this configuration, and thus it is recommended that further development of the process and equipment be based on this design approach.

PREFACE

As a result of increased concern for the quality of the environment, and the consequent need for abatement of water pollution, the Office of the Director, Research and Engineering, of the Department of Defense requested in early 1973 that the National Research Council initiate a brief study of the Materials of Construction for Wet Oxidation Reactors. Such devices are currently under development for application to the shipboard waste processing problems. Thus, the study was to include consideration of the unique problems of shipboard installation, operation, and maintenance in addition to the temperature, pressure, and cost considerations inherent in this type of process equipment.

The assignment was accepted and implemented by the National Materials Advisory Board (NMAB) with the following stated purpose:

> "Conduct a short-time study (approximately two meetings) of the materials of construction for wet oxidation reactors of the type used on ships to reduce harbor pollution, including assessment of the materials available for use in relation to design limitation of space, weight, size, pressure and temperature; recommendations of criteria for selection of optimum materials for this use, considering both performance and cost; description of the problem areas that may require study in greater depth, where such exist."

A Committee was formed in April 1973 with the membership as shown on pages iii and iv.

In general, the primary goal of the study was to provide an evaluation and appropriate recommendations on the materials of construction for the reactors used in the wet oxidation process. This process is being developed for potential use aboard ships by the U. S. Navy. However, the results of their work may well be of direct interest to other governmental agencies and private ship owners and operators, all of whom are attempting to meet the same environmental quality requirements.

In the context of U. S. Navy operations, there are numerous operational aspects of the wet oxidation process to choose among and consider. Among these are, for example, whether or not to plan for salt or fresh water flushing and for adding catalysts or other chemicals. In performing this study, the Committee took cognizance of the need for long reliable life and ease of maintenance and operation aboard ship. Therefore, their discussions and recommendations are based on the following:

- that with reduced flow toilets and showers, fresh water would be the primary liquid feed material to the reactor, thereby minimizing chloride content,
- that air, rather than oxygen, or oxygen enriched air, would be used for aeration in the process,
- that chemical additives (such as acid) would not be added to the process, and
- that as low a combination of temperature and pressure would be used as is commensurate with effective processing of the wastes to the desired degree.

With this charter and guideline philosophy, a small five-man committee was organized to include several disciplines. The Committee operation was scheduled for a total of three meetings. The first was held at Florida Atlantic University on July 9 and 10, 1973, and the second and third were held at the National Academy of Sciences in Washington, D. C. on September 5 and 6, 1973 and on September 27 and 28, 1973.

The deliberations and studies of the Committee were greatly aided by the presentations given, especially by Messrs. Paul Schatzberg and Don Vreeland of the U. S. Naval Ship Research and Development Center at Annapolis, Maryland. The extremely effective diligence and creative contributions of Donald G. Groves, who served so well as the National Academy of Sciences-National Materials Advisory Board Staff Engineer on the Committee, are also greatly acknowledged and sincerely appreciated. To him and all the others who contributed, though unnamed, we give our thanks.

TABLE OF CONTENTS

TABLE OF CONTENTS (Continued)

FIGURES AND TABLES

I. SUMMARY OF CONCLUSIONS AND RECOMMENDATIONS

Preceding page blank

Introduction

This section of the report summarizes for the busy management-type reader the Committee's most salient conclusions and recommendations regarding the shipboard application of the wet oxidation process and the potential materials of construction for a reaction vessel to be used therein.

While the Committee did not attempt to compare all potential candidate processes for shipboard waste treatment, the information obtained on the wet oxidation process was sufficiently impressive to indicate that its further development for shipboard usage is highly warranted. It is felt that wet oxidation is a promising environmental protection process that has some very distinct advantages over the other candidate processes for this purpose. Such advantages include:

- the low energy requirements needed for the process because of the autogenic type reaction involved;
- the lack of any appreciable air pollution produced by the process; and
- the production of a sterile, primarily liquid effluent that can be effectively recycled for some shipboard uses.

The wet oxidation process requires the containment of corrosive products at elevated temperatures and pressures, which impose severe requirements on the reactor as well as the ancillary equipment. The chemical process operating temperature

and pressure range from 475 to 600°F and from 600 to 1850 lbs/in^2, respectively, while the material being processed can range from very acidic (pH = 2) to slightly basic (pH = 9) and over a broad spectrum of wastes. A maximum chloride content of approximately 0.3% can be expected. These severe conditions lead to difficult but solvable materials problems.

Additionally, it appears from our study of the problem that the shipboard wet oxidation process can be operated most effectively in a continuous operating system. For this reason and to best fit the processing equipment into ships, the reaction vessel should consist of a piping array configuration.

Based upon these considerations, the Committee's principal conclusions, observations and recommendations are summarized below. Some additional detailed conclusions and recommendations are presented in this report.

In the Design Area

Conclusion:

On the basis of its study of the problems related to the design of shipboard wet oxidation processing equipment, the Committee concludes that a continuous operating system consisting of an array of piping has definite advantages over the tank or tower system. In essence, we feel that the chemistry of the reaction can be successfully carried out in such a properly designed piping arrangement, thus eliminating the need for any one large mixing and pressure vessel container.

Discussion:

To support the above conclusion there is considerable first-principle evidence to indicate that the wet oxidation process can be operated in a continuous manner. Such a

method would be highly advantageous for a variety of shipboard applications. The piping configuration to be used can consist of several separate lengths of pipe made from materials that will meet existing boiler codes and the whole unit can be supplied in a modular form. Specifically, the waste processing portion of a flow-through wet oxidation system in the form of interconnected pipe sections has the following advantages:

- can be mass-produced in appropriate length (i.e., 10 foot) pipe sections along with U-bends needed and the whole unit assembled in various lengths and configurations;
- maximum shipboard "dead-space" utilization is feasible;
- pipe sections can be easily inspected and replaced, if necessary;
- pipe sections can be fabricated to include a sensing system to monitor corrosion, if desired; and
- pipe sections are easily adaptable to metallic and non-metallic coatings and liners.

Therefore, what is envisioned in this scheme is a series of linear and U-bend sections through which the waste water and air can pass at operating temperature. This piping can also be operated full or nearly full to minimize potential interface corrosion problems. The total length of the piping array will depend on the volume of waste to be processed and the residence time required for a particular degree of waste destruction. Appropriately designed baffles can be inserted in some or all the pipe sections to provide the mixing necessary for best oxygen utilization.

It should be recognized that there is a current requirement to investigate the most critical design parameters of this piping system approach. The problems relating to static

mixing devices, baffling plates, etc. within the piping plus those involving gaskets, penetrations, and couplings must be addressed in a systematic analytical manner.

Recommendation:

- It is recommended that the U. S. Navy first initiate a comprehensive design and analysis study of the continuous wet oxidation process of the type mentioned wherein a piping array is to be utilized. At the completion of such a design study, it is further recommended that a working prototype of the piping design be built and operated so as to evaluate both the various recommended prime candidate materials of construction as well as the efficiency of the process itself prior to its certification for shipboard installation and operation.

In the Materials Area

Conclusions:

- Of the various materials of construction that have been tested for service in the wet oxidation process, stainless steels do not appear to warrant further consideration because of their poor corrosion resistance.

- Commercially pure titanium (Ti) and the Ti-0.2% palladium (Pd) alloys offer excellent corrosion resistance and sufficient mechanical properties for use as the pressure vessel.

- Nickel-chrome-molybdenum alloys also appear to offer attractive properties and performance for this pressure vessel application.

- Tantalum has outstanding corrosion resistance in oxidizing chloride-containing applications, and should be considered as a lining material.

- Some non-metallic (oxide, glass and glass-ceramic) materials offer excellent corrosion resistance and should also be considered for use as linings or coatings.

Discussion:

In view of the conditions under which the process of wet air oxidation is carried out, and the influence of these strongly oxidizing conditions on corrosion rates and mechanisms, it is concluded that the most promising metals and alloys for this application are those that form erosion resistant, impervious, tenacious oxide films which are stable in the presence of chloride ions. Consideration should be given to the use of anodic protection to improve the corrosion resistance of the metallic materials. Lower corrosion rates are favored by milder conditions; therefore, it is recommended that consideration be given to an effort to achieve mild reaction conditions, for instance by the use of catalysts. A study of stress corrosion cracking rates of candidate metallic materials under various operating conditions is also recommended. These candidate materials are those metallics that can meet the lower temperature conditions and certain non-metallics for use in the upper temperature ranges. In this regard, three specific types of construction are presented below:

1. A completely titanium alloy (commercially pure or 0.2% palladium) pipe construction is considered

to be feasible for lower-temperature (475-500°F) usage. With the proper design, fabrication, and operation the equipment should last for several years.

2. To gain a longer operating life and to meet any "fail-safe" conditions for the 475-500°F operating temperature regime, a tantalum lining in commercially pure or palladium alloy titanium or nickel-chrome-molybdenum alloy pipe construction could be utilized. Such materials would provide both strength and redundancy from a corrosion damage standpoint. If this type of redundancy is deemed, upon further in-depth study of the problem, to be unnecessary, a low carbon steel pressure container should then be considered.

The tantalum-titanium system could expect a lifetime of 15 years at 500°F. At temperatures over 500°F, provision may have to be made to prevent back-side corrosion of the tantalum. This can be done by providing an inert gas flushing system between the tantalum and the substrate.

3. For higher-temperature (500-600°F) operation where corrosion of tantalum, titanium, or other metallics may restrict their usage, some non-metallics appear to be the best candidate materials. In such a system, some suggested components to consider are a titanium or perhaps low-carbon steel (glass or polymeric coated) outer pipe for resisting the pressure with an inner liner of a sintered oxide porcelain

such as one primarily of alumina or zircon or zirconia for resisting the corrosive environment and an insulating cement layer in the annulus between these two pipes. However, such a system would require careful analysis and design in order to select the proper materials and wall thicknesses so as to achieve the proper stress situations and keep the ceramic liner in compression.

A potentially valuable feature of this materials system is the possibility of installing an electrical sensor in the annular cement layer to ascertain the condition of the ceramic liner, especially with respect to leakage.

Overall, these types of construction should offer many years (approximately 15) of reliable elevated temperature life and with lower equipment weight and cost than any other approach.

Recommendations:

- The current usage of commercially pure (CP) and palladium alloys of titanium is endorsed as a useful approach for wet oxidation reactors intended to operate in the 475-500°F range.

- A more reliable and longer life system than the all-titanium construction wherein titanium or low-carbon steel piping is augmented with tantalum inserts and coatings is recommended.

- Some non-metallic lined, as mentioned above (viz., alumina, zirconia, glasses, etc.), metallic pressure vessels are recommended for further study since they offer a means of achieving suitable processing construction materials when the processing operation is in the 500-600°F range.

II. PROCESS DESCRIPTION

A. Introduction

Wet oxidation is a process whereby organic wastes dissolved or suspended in water are converted to water, carbon dioxide, small amounts of low molecular weight, organic acids and a very small amount of fine inorganic ash. This process is conducted with an excess of oxygen at temperatures ranging from 475-600°F in a pressure vessel which maintains the water as a liquid. Air overpressure can range from 50 to 300 lb/in^2. The resulting operating pressures range from approximately 600 to 1850 lb/in^2.

The advantages of this process are:

1. Aqueous waste streams with no or minimal preparation are converted directly into sterile, innocuous effluents.

2. Energy requirements are substantially less than for incineration, since only a small amount of the water being treated converts to steam.

3. Oxidation of the organic waste releases heat, permitting the process to be energetically self-sustaining.

4. The process is relatively rapid, and is particularly suitable where space is at a premium.

5. No contaminants are released into the atmosphere.

The disadvantages of the process are:

1. It is conducted at elevated pressures, requiring a pressure vessel involving stringent safety considerations.

2. Materials of construction for the pressure vessel and auxiliary equipment must be carefully selected to be corrosion resistant.

3. Heavy duty air compressors are required to supply air against the operating steam pressure.

B. The Chemistry of Wet Oxidation

The chemistry of wet oxidation adequately obeys first-order kinetics. Thus,

$$-\frac{dC}{dt} = kC \qquad (1)$$

where C is the concentration of organic wastes which can be expressed as the chemical oxygen demand (COD) in mg/liter and k is the reaction-rate constant. Equation (1) states that the rate of decrease (destruction) of the wastes is directly proportional to the concentration of the wastes. First-order kinetics for this process is valid only when an excess of the stoichiometric oxygen requirement is maintained throughout the reaction.

Rearranging equation (1) and integrating with appropriate limits yields

$$\ln \frac{Co}{C} = kt \qquad (2)$$

where Co is the concentration of organic wastes at the start of the reaction. Equation (2) can be expressed graphically by plotting the logarithm of Co/C against time, t. The slope of the resulting straight line can be used to calculate the reaction-rate constant.

Experiments to verify the reaction kinetics have been conducted in a mechanically stirred one-gallon-capacity pressure vessel. Water and air or oxygen are introduced into the vessel.

When operating temperature (500°F) and pressure are reached, a sample of waste is injected into the vessel. Samples are removed from the reaction vessel at various time intervals and analyzed for chemical oxygen demand by a standard method. A typical result of such experiments is shown in Figure 1.

Results show two first-order reactions in sequence. The first one is rapid, signifying the hydrolysis and oxidation of large molecules such as proteins, carbohydrates, and cellulose. This results in the formation of water, carbon dioxide, and low-molecular-weight organic residues consisting primarily of acetic acid and its homologs. The wet oxidation of these organic residues occurs at a much lower rate. Reaction rate constants for the rapid reaction range from approximately 0.1 to 0.2 $minute^{-1}$ while those for the slow reaction range from 0.003 to 0.008 $minute^{-1}$. The change in slope of the data in Figure 1 occurs when the large-molecular-weight materials have been consumed and the rate of oxygen consumption has slowed to that associated with the oxidation of the low-molecular-weight products.

Measurements of hydrogen-ion concentration (pH) of samples removed from the reaction vessel show a rapid drop from approximately 7.0 before injection of waste to 2.5 and 3.5 within 30 seconds after injection. This is attributed to the rapid formation of low-molecular-weight carboxylic acids and carbon dioxide. When organic nitrogen is present in a waste sample, hydrolysis of this nitrogen is also present. The hydrolysis of this nitrogen to ammonia, a slow process, gradually raises the pH to approximately 6.0.

While the reaction-rate constants of the fast reaction are influenced by the nature of the waste, experiments performed with sewage sludge, oil-in-water emulsions, cellulose, food products and human waste have shown that the reaction generally follows the pattern described by Figure 1. That is, in the presence of excess oxygen, at 500°F organic wastes in water are destroyed rapidly so that in most cases a 70-80% reduction in COD is achieved in 15 minutes. The organic residue remaining is relatively innocuous and difficult to destroy further, an additional 5-10% reduction requiring an additional 60 minutes of reaction time.

C. Catalysts

The wet oxidation reaction can be catalytically accelerated. This may be done by the addition of an inorganic acid reducing the pH to approximately 1.5. While the addition of an inorganic acid alone can accelerate the process, particularly by accelerating the hydrolysis of large organic molecules, the decrease in pH which occurs due to the formation of low molecular weight organic acids may achieve that purpose. Considerable potential exists for the use of numerous catalysts, both heterogenous and homogeneous. These materials are solid metals, oxides, and carbon as well as dissolved metal ions. The broken lines in Figure 2 illustrate how a catalyst system may influence the rate of wet oxidation. The possible influence of catalysis is illustrated in two ways. First, the change from the fast to the slow step of the reaction can be delayed and second the slow step can have a significantly higher rate with catalysis than without.

D. Various Systems

Considerable data on the wet oxidation process have been developed by use of the one gallon type batch reactor vessel at several research laboratories. Additional effort is currently under way in these laboratories using a flow-through continuous wet oxidation system. These systems consist of a pressurizing pump, an air compressor, heat exchanger, central processor, and gas-liquid separation chamber, as well as minor ancillary equipment. The most significant differences in these systems are in the design of the central processor. These differences are noteworthy since the flow-through systems serve as a prototype or model for future systems designed for shipboard application. At present, three different designs exist:

1. Vertical bubble tower. The preheated, pressurized waste stream along with air is introduced in the bottom of the tower. Mixing is by the action of the gas bubbles. Product and gas are removed at the top of the reactor. The height-to-diameter ratio may be large.

2. Packed tower. The preheated, pressurized waste stream, mixed with air, is introduced at the top, trickling through the packing which serves to mix the components. Product is removed at the bottom. Considerable reactor volume is taken up by the packing material.

3. Horizontal tank series. The preheated pressurized waste stream is introduced in the first of a series of two to six horizontal tanks. Each tank is mechanically stirred. Air passing through the tank is vigorously mixed with the liquid. Product from each tank becomes the feed for the next tank in the series.

Current understanding of wet oxidation chemistry as described in this report establishes the maximum rate and degree of waste destruction that can be achieved by this process. The design of a wet oxidation waste destruction system for shipboard application will be primarily influenced by:

1. space and weight constraints,
2. operational requirements,
3. process conditions,
4. materials of construction, and
5. reliability and life cycle cost.

Design innovation can play a significant role in a successful shipboard wet oxidation system.

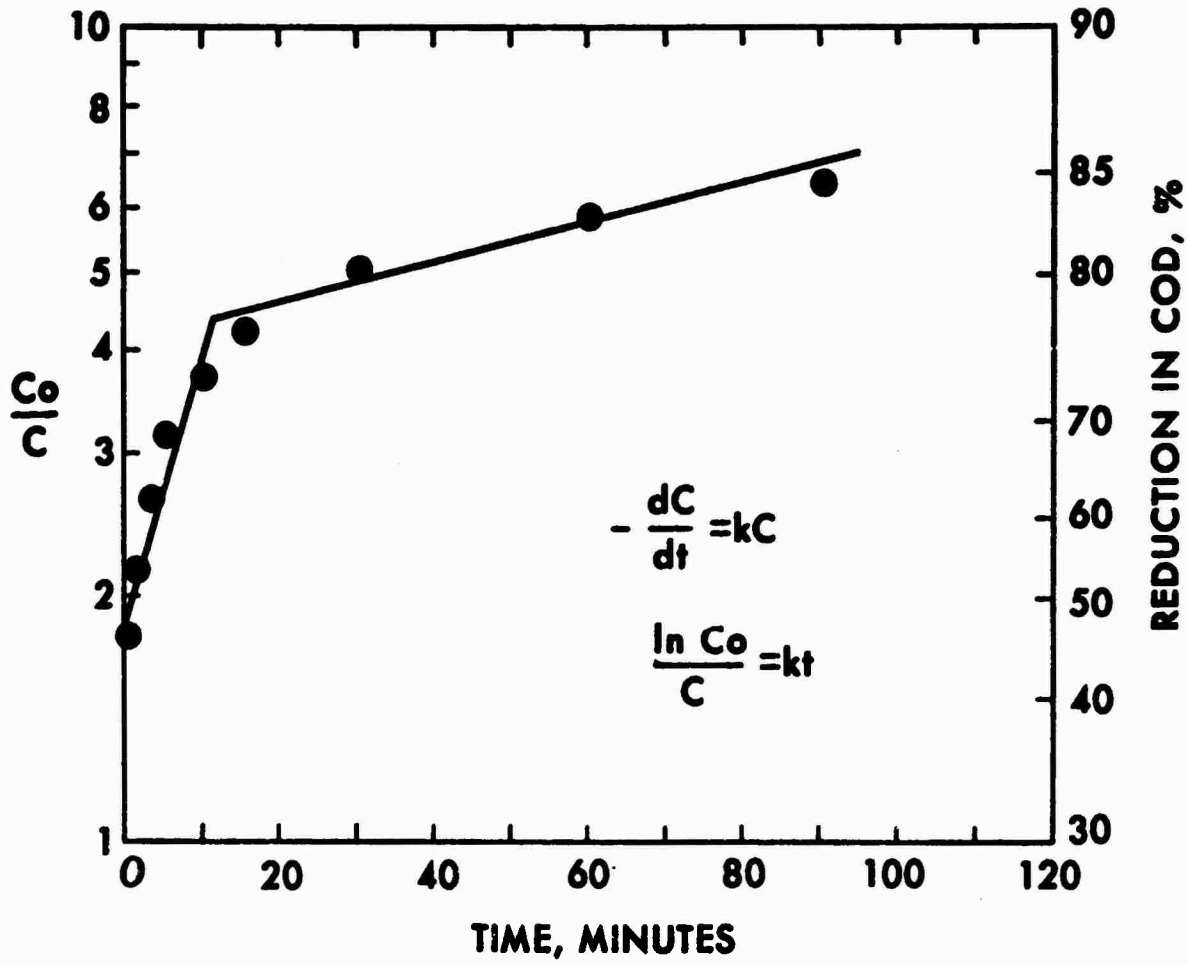

Figure 1. Wet Oxidation Rate Data

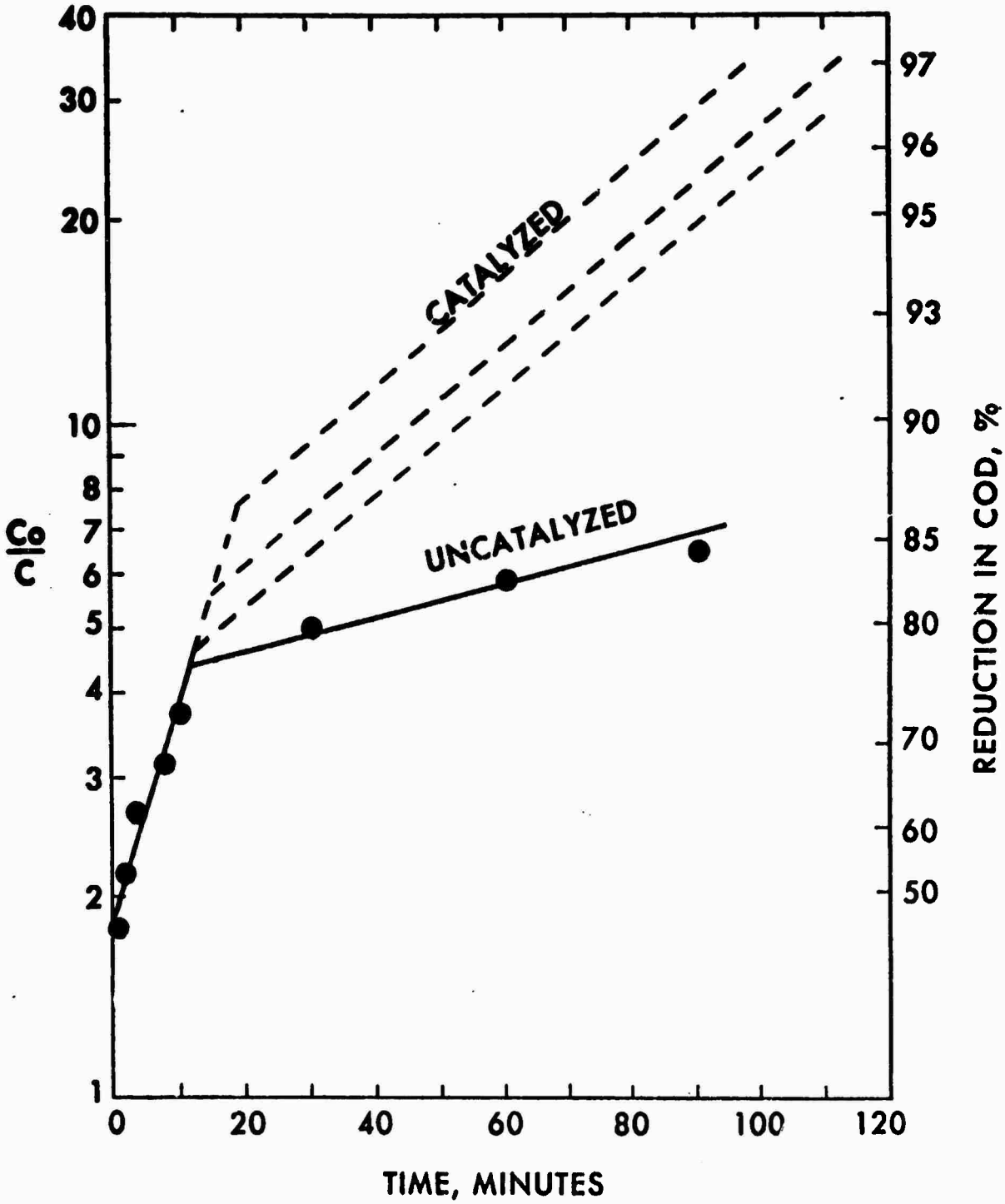

Figure 2. Wet Oxidation Rate Data (With Catalysts).

III. DESIGN CONSIDERATIONS

A. Introduction

The mechanical design of the process chamber pressure vessel will be governed by many factors, but these factors can be categorized by two major criteria. The criteria are the design function and the safety factor, with their product resulting in a design specification. This can be illustrated in Figure 3, showing the components of each of the two major criteria.

The basic data required to determine the design function come from the operational requirements. One such requirement is the volumetric capacity of the pressure vessel and its associated configuration. The vessels' weight-to-internal-volume ratio can be one parameter used in selecting the configuration. For example, in a long unpenetrated cylinder subjected to internal pressure (P_i), the unit-weight-to-internal-volume ratio is

$$\frac{W_c}{V_{ci}} = \left[1 + \frac{b^2}{a^2}\right] \rho_c \left[\frac{P_i}{\sigma_{max}}\right]$$

where ρ_c is the density of the cylindrical shell material, σ_{max} is the allowable stress, and a and b are the internal and external radii respectively.

If the same materials and pressure are involved, a sphere is more efficient, based on the weight-to-volume ratios for any geometry of $b/a < 2$. Since the geometry will have ratios of $b/a \ll 2$, then a sphere will theoretically be the most

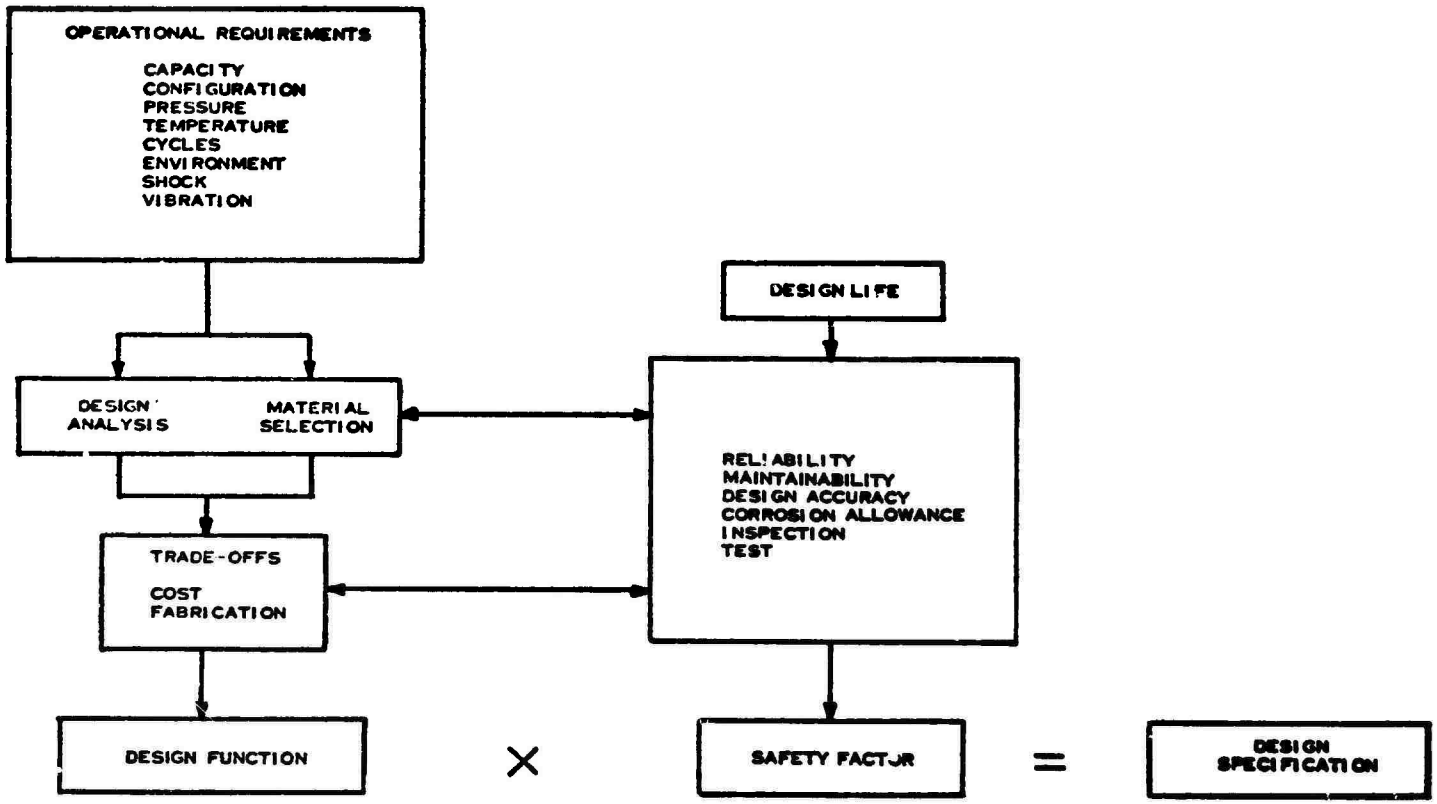

Figure 3. Design Criteria

efficient shell based on weight and volume. However, for arrangements purposes, a long cylinder will be more advantageous. Once a configuration is chosen, the scale of this geometry will not greatly affect these weight-to-volume ratios very much, since the b/a ratio will not differ much with size. Therefore, once the overall pressure vessel configuration is chosen, the selection of diameters and lengths should be dictated by other considerations, such as volumetric capacity, physical arrangements in the ship, and the like.

One such attractive arrangement is a series of cylinders or pipes with long length-to-diameter ratios. These cylinders could be interconnected by U-bend sections made in the shape of segmented toroids. In this arrangement, there are not only long lengths of reasonably small diameter cylinders being used, but a single cylinder could be removed for inspection, repairs or replacement without disrupting the total system.

Many of the other operational requirements will be set by the selection of the specific process conditions. These will include the normal operating pressure and temperature. If the design of the vessel due to these set parameters results in a vessel that is too costly, the process might have to be altered to one with lower temperatures and pressures. For the purpose of the design of process chambers, a range of operating temperatures of 475-600 °F and the associated pressure range of 600-1850 lb/in^2 is reasonable to assume. These pressures include overpressures required by the process.

The environment inside the pressure vessel is another operational function that is set by the process. Ideally, this process would go on continually without cyclic change.

Since this is impractical, the number of thermal and associated pressure cycles must be set before the design begins. This number will most likely be less than 10^4 cycles. For most of the candidate metals, this number of cycles is low, but if the vessel is lined with non-metallics this number of cycles may be of concern.

Finally, there is the operational requirement of shock and vibration loads due to shipboard installation. The shock and vibration specifications are essentially the same for all naval ships. The spectra for various ships vary but not the tests and design procedures. MIL-S-901-C is the current shock specification and MIL-STD-167B is the current vibration specification. A report, "Shipboard Shock and Navy Devices for It's Simulation," by E. W. Clements, Naval Research Laboratory Report 7396, dated July 1972, explains the shock specifications and all Navy design procedures and tests required by the Navy.

B. Design Analysis

The ability to design efficient pressure vessels has been greatly enhanced by the advent of the computer. In pre-computer days, handbook designs were normal, but because design techniques were simplistic, the factors of safety (actually factors of ignorance) were necessarily high. The state of the art today permits detailed design analysis of complex shell structures and their penetrations. The term "design analysis" has also come into common use, because there is no clear-cut distinction between design and analysis. Most designs are performed by first selecting a geometry, analyzing it, and iterating on the design until an optimum configuration is approached.

C. Stress Analysis

The primary stresses imposed on the vessel are the normal and shear stresses, due to internal pressure, which are necessary to satisfy the laws of equilibrium. Obviously, if the primary stresses exceed the yield strength, distortion and possible failure will occur. Thermal stresses, which are not primary stresses, are developed in the vessel whenever the vessel is prevented from assuming the size and shape that it normally should under a change in temperature.

Secondary stresses are defined as the normal and shear stresses developed by the self constraint of the vessel or by the constraint of adjacent structures, such as foundations. Unlike primary stresses, which are not self-limiting, secondary stresses are self-limiting. Local yielding can satisfy the conditions which caused the stress and a single cycle load normally will not cause failure.

Peak stresses are stresses that do not cause any noticeable distortion. These are only significant in consideration of failure by means of fatigue, stress corrosion cracking or by brittle fracture.

D. Failure Theory

A theory of failure is essential to the establishment of design specifications. For pressure vessels fabricated from ductile materials, the theory of failure is the maximum shear stress theory. This is the theory used by the American Society of Mechanical Engineers Boiler and Pressure Code, Section VIII, Division 2. This Code, with special amendments, is generally accepted for most pressure vessels used on board naval ships.

The maximum shear stress is equal to one-half the difference between the algebraically largest and smallest of the principal stresses. The stress intensity at a point on the vessel is the difference between the algebraically largest and smallest principal stress and this value is a major parameter governing the design of the vessel. The ASME Code noted above places five basic stress intensity limits on the vessel:

1. General primary membrane stress intensity. This stress intensity governs the average through thickness stress produced by internal pressure and any primary mechanical loads.

2. Local membrane stress intensity. This stress intensity, whose allowable is 50% more than in 1 above, governs average through thickness primary local membrane stresses. These stresses are caused by discontinuity effects in the vessel.

3. Primary membrane plus bending stress intensity. This stress governs the highest value across the shell thickness of the primary membrane plus bending stresses, and its allowable is 50% higher than in 1 above.

4. Primary plus secondary stress intensity. This stress governs the highest value across the shell thickness of primary stresses (membrane plus bending) plus secondary stresses caused by mechanical and thermal loads. This allowable stress value is three times that given in 1 above.

5. Peak stress intensity. This value governs the highest value of the combination of all primary, secondary, and peak stresses. Its allowable will vary depending on fatigue considerations.

E. Penetrations

Penetrations into the pressure hull are inevitable, but their numbers and sizes should be minimized wherever possible. The stresses in the area of penetrations are difficult to determine analytically and many empirical techniques have been used to develop design specifications for them. In most specifications, including the ASME Boiler Code, the use of stress indices is commonly used for design of typical penetrations. This method uses various design formulas in combination with empirical data based on extensive testing. The term "stress index" is generally defined as the ratio of the normal stresses in the penetration to the membrane stress intensity in the unpenetrated or unreinforced pressure vessel.

The location and number of penetrations is a major factor in the design. It is advantageous to locate penetrations in areas that the resulting stresses are axially symmetric, but this is not usually practical. Since it is not always possible to pick the best locations from a stress point of view, the penetrations and reinforcements could be located almost anywhere in the vessel.

F. Material Selection

The pressure vessel material selection will be governed by many criteria, some of which are listed in Table 1. The general criteria listed are obvious. Availability of the materials, at a reasonably low cost, together with the technology to readily fabricate a vessel, are criteria common to pressure vessels. The matter of low weight is of concern only if the ship in which the system is to be installed is weight critical.

High yield strength is desirable in order to keep the shell thickness reasonably thin. The cost and fabrication difficulties will increase with increasing wall thicknesses. A material whose ultimate strength is high compared to its yield strength is desirable so that the burst pressure is substantially greater than the pressure required to initiate yielding.

Stress corrosion cracking is cracking caused by the presence of tensile stress field in the vessel containing a corrosive medium. Parameters affecting stress corrosion cracking are temperature, medium composition, metal composition, the type of structure, and the stress field. The stress field can either be an imposed stress, such as that caused by internal pressure, or a residual stress, such as that caused by forming.

Generally, the areas of the highest tensile stresses are the most likely areas of crack developments. These cracks can propagate through the shell thickness, reducing the effective thickness sufficiently to cause catastrophic failure. Most corrosive environments lower the fracture toughness, rendering cracks in this state more dangerous than in air. By reducing the design allowable stress imposed on the pressure and temperature, the stress corrosion resistance can be improved. Stress relief treatments can be used to reduce residual stresses. Surface tensile stresses should be minimized. Techniques such as shot peening, which introduces surface compressive stresses, are often used.

Low-cycle fatigue considerations are based on a comparison of peak stresses with strain cycling fatigue data. Stress amplitudes are calculated on the assumption of elastic behavior

and do not represent a true stress in some areas where stress concentrations may cause the material to yield locally. Also, fatigue curves are normally derived from uniaxial tests. Therefore, the data can only approximate the condition in a pressure vessel where there is a triaxial stress field. Many times the curves are adjusted empirically to compensate for these conditions.

TABLE 1. Material Selection Design Criteria

General	Design Strength	Metallurgical
Availability	High Yield Strength	Toughness
Fabricability	High Ultimate Strength	Ductility
Low Cost	Stress Corrosion Cracking Resistance	Corrosion Resistance
Low Weight	Low Cycle Fatigue Resistance	

Fatigue strength reduction factors are commonly used, particularly in areas of local discontinuities. Except in areas of known defects, fatigue strength reduction factors seldom exceed five.

High fracture toughness is a very desirable feature and a very necessary design consideration. A decrease in toughness may exist at elevated temperatures or after cooling to room temperature. This condition could be accentuated by prior cold working during fabrication. This problem is more evident when heavy sections are used.

When corrosion is involved, the interaction of temperature, stress, corrosive medium and time normally makes specific design procedures most difficult to define. Economic considerations frequently determine whether corrosion is combatted by a change in material, corrosion allowance thicknesses, or the use of a protective material in contact with the corrosive medium.

G. Trade-Offs

Cost and fabrication are the major trade-offs affecting the design function. If they are deemed to be unacceptable, then the design-function cycle must begin anew, beginning with operational requirements. These requirements are primarily governed by the process. Certainly capacity, pressure, temperature, cycles, and the environment are process-related. Other operational requirements, such as the configuration, shock and vibration requirements, will mostly be governed by shipboard requirements.

If the operational requirements are fixed, the design/analysis and material selection function must be changed if the trade-off requirements dictate a new design function. In most instances, the design/analysis function is set by a standard or a code. Therefore, a change in material selection often is made to satisfy the design-function requirements.

H. Safety Factor

The initial, and most important, requirement affecting the safety factor is the design life. If the normal twenty-year shipboard life is expected, the safety factor will tend to be high. This is particularly true of a high-temperature, high-pressure vessel containing a corrosive medium.

Maintainability and inspection are requirements normally set by the vendor and accepted by the operator. It is always a compromise situation because it affects, on one side, the cost of fabrication and, on the other side, the cost of operations.

Reliability, design accuracy, corrosion allowances, tests, etc. are usually design functions. The designer usually is required by codes and standards to meet certain minimum requirements.

All these requirements feed into a safety factor. The factor could justifiably be called a factor of ignorance since, in the ideal case, the factor will be unity. This is far from the case and a factor of safety between 1.5 and 4.0 is usually set.

Finally, the product of the safety factor and the design function results in the design specification that the vessel must be designed to meet.

I. Inspection and Tests

Variations in present test and inspection requirements will be inevitable for the process chamber pressure vessel since this type of vessel has never been used on naval ships before. These deviations from the norm depend on the sophistication of the vessel design. Obviously, a vessel with a corrosion-resistant liner and a thermal barrier will require more testing and inspection than an unlined vessel. For the unlined vessel, the standard requirements of Section VIII of the ASME Boiler and Pressure Vessel Code should cover most of the Navy's needs. Under these rules, the manufacturer:

- obtains authorization to design and fabricate to a specification (ASME or Mil-Spec),
- provides drawings and design calculations,
- provides material certification data,
- allows inspection of plant facilities,
- maintains a defect and tolerance measurement program,
- performs impact tests,
- maintains qualified welding procedures,
- performs non-destructive test (NDT) examinations, and
- subjects vessel to hydrostatic and thermal tests.

Special inspection and test procedures will have to be developed as the designs increase in sophistication. For instance, corrosion resistant liners will have to be tested and inspected to assure their tightness. Instrumentation and tests will have to be devised to test for leakage while in use. One such test could involve passing a gas through a porous insulation layer separating a corrosion-resistant liner and the pressure hull. The gas could then be constantly monitored for purity and the detection of leaks could be linked to a warning or alarm system. All these special tests will have to be written into a Mil-Spec that uses the ASME Boiler and Pressure Vessel Code as a base but adds on requirements due to the particulars of the design or due to the normal shipboard shock and vibration specifications.

J. Conclusions and Recommendations

It is concluded that the design of process chamber pressure vessels for naval shipboard application is quite feasible. Obviously, the lower temperatures and pressures (475°F and 600 lbs/in^2 respectively) present lower problems for the

designer, and the first-generation systems may be kept at these temperatures and pressures, even though the process efficiency may suffer. Unlined vessels will probably be used for the lower temperatures and pressures. The best configuration appears to be the use of long cylinders with U-bends connecting the ends of the cylinders. This lends itself to reasonable structural efficiency as well as attractive shipboard arrangements. The system can also be inspected and repaired easily, since one cylinder can be worked on independently of the others. The major problem could be high erosion/corrosion of the U-bends. This may cause the designer to overdesign the U-bends or to specify special inspection/replacement requirements.

As the temperatures and pressures increase to the higher levels (600°F and 1850 lbs/in^2 respectively), liners will probably be required. The multiple cylindrical configuration will not change for the higher temperatures and pressures. The liners will actually result in a redundant system from the point of view of corrosion and stress corrosion cracking. If the liners do not leak, the metal pressure vessel will act only to resist temperature and pressure. If a leak occurs, the metal shell must also resist corrosion and stress corrosion cracking. The designer must determine a reasonable design life for the liner with some probability of no leakage throughout that life. He must also specify a metallic shell material to resist corrosion/stress corrosion cracking for a reduced design life in case of leakage in the liner. Ideally, the design life for the worst-case situation should be the specified ship's overhaul interval.

It is recommended that a preliminary design of an unlined process chamber vessel be conducted for a temperature of 475°F and a pressure of 600 lbs/in^2. It is also recommended that a preliminary design of a lined process chamber be conducted for temperatures up to 600°F and a pressure of 1850 lbs/in^2.

Based on these designs, a cost estimate to fabricate and install these systems onboard a pre-selected naval ship should be made. The estimated cost of these two vessels must then be factored into the respective total systems costs and efficiencies for the processes and compared with each other.

IV. CORROSION MECHANISMS AND CORROSION PREVENTION

A. Introduction

This section of the report deals with the mechanisms by which corrosion occurs and the means that can be employed for the prevention of corrosion. Because of the high temperatures and high oxygen pressures involved in the wet oxidation process, only a few metals and some ceramics can be seriously considered as candidate materials of construction for wet oxidation reactors. Metals are to be preferred because of their generally superior mechanical properties. Therefore, the main emphasis of this section will be upon the corrosion of metals, and the effects of temperature and oxygen pressure on the corrosion rate.

The corrosion of metals usually involves oxidation and/or electrochemical reactions (both oxidation and reduction reactions). The rates of corrosion reactions are influenced by a large number of variables, some of which can be used to advantage in reducing the rate of corrosion. The variables influencing the rate of corrosion include the composition of the material, its metallurgical state, temperature, concentrations (or pressures) of the reactants and products of the corrosion reactions, the electrochemical potential, the geometry of the material being corroded, its state of mechanical stress, the presence of protective films, the rate of mass transfer of reactants and products, the presence of materials which catalyze or inhibit corrosion reactions, and contact with dissimilar metals.

B. Types of Corrosion

The particular situation, with regard to the variables noted above, determines the type and rate of corrosion that will take place. The types of corrosion can be categorized as follows:

- uniform corrosion
  - simple oxidation
  - uniform dissolution (chemical or electrochemical)
- localized corrosion
  - pitting
  - grain boundary attack
  - crevice corrosion
  - stress corrosion cracking and corrosion fatigue
  - hydrogen cracking and blistering

The simple oxidation of metals by oxygen or air to form their oxides is a very common type of corrosion. This type of attack is relatively uniform and in some cases results in a dense, relatively pore-free film which serves to protect the metal from further attack. The rate of oxidation of the metal may follow any of a number of courses. If a protective film is formed, as with titanium or aluminum, the rate decreases with time and may become negligible following a logarithmic growth law. A parabolic film growth law (rate decreasing parabolically with time) is followed by metals for which the oxygen diffuses through a compact oxide film. As the temperature is raised, the film may break and become porous with further oxidation following a linear rate law (amount of oxidation directly proportional to time). Because of the

high oxygen pressures involved in wet oxidation, it is expected that oxidation of the metals of construction will take place. Metals which form protective oxide films under process conditions are to be preferred; these include tantalum, titanium, and some titanium- and nickel-base alloys. While some other alloys may also be suitable, there is a paucity of data on the oxidation of metals and alloys under wet oxidation conditions.

Electrochemical corrosion, both uniform and nonuniform, can be understood on the basis of the voltage versus current density (current per unit of electrode area, A/cm^2) relationship in the appropriate liquid environment (water, sea water, etc.). Figure 4 shows a schematic voltage versus current density curve for a metal which shows passivation behavior (such as titanium in aqueous chloride solution). The ordinate increases in the anodic direction, the higher voltages representing a greater driving force in the oxidation direction.

Starting at zero volts in Figure 4 (the potential of the electrode versus a hydrogen reference electrode), as the voltage on the sample of metal is increased, the metal is oxidized to form metal ions (e.g., M+) which move into the electrolyte, resulting in a flow of current, as indicated by the active dissolution region in Figure 4. A continued increase in voltage results in an increase in the current density, until a maximum is reached, followed by a continued decrease of current density as a film (of oxide or hydroxide) forms on the surface of the sample, interfering with the dissolution process. The current density reaches a minimum value with continued increase in voltage. This minimum current density represents the current which passes through the film and

through imperfections in the film, and represents an acceptable low corrosion rate for some materials under some conditions (e.g., titanium in aqueous chloride solution). Because the protection film has been formed anodically, the intentional formation of such films is called anodic protection, and is a suitable means of corrosion control (or prevention) in some situations. Beyond the voltage region labeled passive in Figure 4 lies the transpassive region, which displays a current density. This increases with the anodic voltage. In aqueous environments, this region usually corresponds to the electrochemical evaluation of oxygen, and sometimes the disruption of the oxide film and continued corrosion of the sample.

The corrosion of a sample may display highly localized attack, as evidenced by pitting. Pitting results from the preferential attack of small areas of metal such as individual grains or zones of composition, such that they are in an anodic state. Other portions of the sample, by virtue of their composition and the availability of reducible reactants (such as oxygen), can act as local cathodes, providing the driving force for the electrochemical reactions of the shorted electrochemical cell formed by the sample and the aqueous phase. Metal is dissolved (electrochemically oxidized to form metal ions) from the pit, and may be deposited in a locally cathodic zone of the sample, or may remain dissolved in the aqueous phase. Pitting is a particularly undesirable form of corrosion because the sample may be completely penetrated by pits after only a small percentage of the sample has reacted.

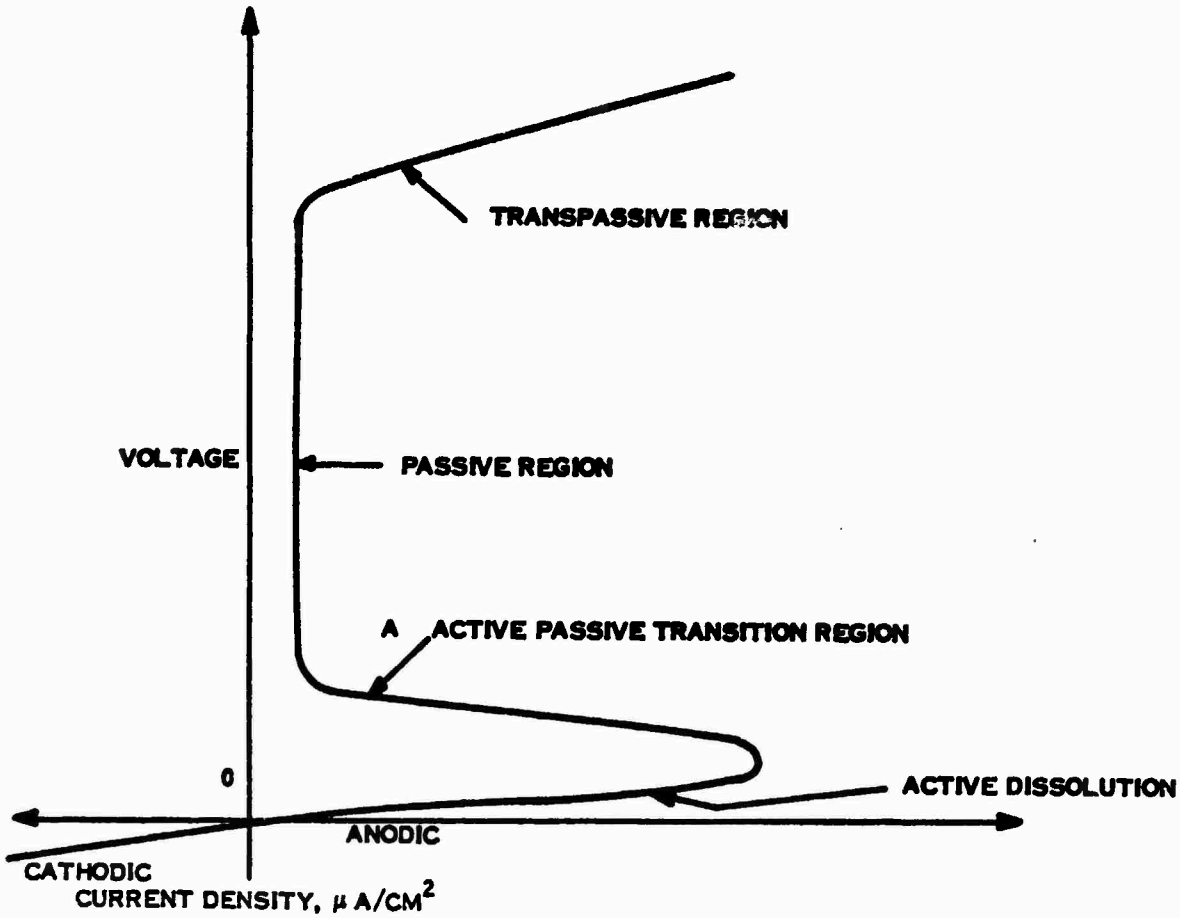

Figure 4. Schematic Voltage versus Current Density Curve for a Metallic Sample in an Aqueous Electrolyte.

The segregation of certain constituents in the grain boundaries of a sample may cause preferential attack because of a greater tendency of the grain-boundary material to react with the aqueous phase. This type of localized attack is very destructive because the corrosion rate can be very high, resulting in complete destruction of the structural properties of the sample by removal of the grain boundaries through preferential anodic attack (the grains act as the cathode), leaving a group of loose grains in place of the previously solid sample. In such cases, it is important to control the impurity levels in and metallurgical state of the grain boundaries, avoiding the formation of new phases which are corrosion-prone.

Crevice corrosion, the localized electrochemical attack of metals in small cracks and crevices, is commonly caused by the creation of a cathodic zone outside of the crevice (where there is an adequate supply of oxygen) and an anodic zone in the crevice (where the concentration of oxygen has been depleted). This localized attack may be particularly troublesome because it can go unnoticed, and because special attention is required in design and fabrication to avoid the occurrences of crevices at welds and joints.

Stress corrosion cracking is another form of localized corrosion, however, it differs from those discussed above in that it involves the presence of a mechanical (tensional) stress, either externally applied or present because of mechanical deformation of the sample. The combined action of corrosion and mechanical stress causes the corrosive effect to be more severe than that which would result from the separate actions of corrosion and stress. The cracks which form may

be either intergranular or transgranular, the former being more common. For example, stainless steel is susceptible to stress corrosion cracking in the presence of chloride, especially near welds. The tendency for stress corrosion cracking may, of course, be reduced by the avoidance of highly stressed areas in zones where corrosion can occur. Because chloride will be present in the wet oxidation process, perhaps at concentrations approaching 2% (from urine), it will be important to assess the stress corrosion situation for the leading candidate materials of construction.

C. Corrosion Prevention

Corrosion fatigue involves a cooperative action between stress (in this case, cyclic) and electrochemical corrosion similar to that for stress corrosion. The life of the sample may be terminated by a very small loss of material from stress concentration points. The cracks tend to direct the electrochemical attack, as in stress corrosion cracking. In some cases, the rate of failure caused by stress corrosion cracking and by corrosion fatigue has been reduced significantly by applying a cathodic potential to the sample, thus minimizing the rate of anodic dissolution of material in the cracks. This corrosion prevention method does not appear to be especially promising for application in wet oxidation reactors because a high oxygen activity at a high temperature is involved. This condition would be expected to result in very high currents being required for cathodic protection, since the cathodic current due to oxygen reduction would be high.

Hydrogen cracking and blistering, which is caused by diffusion of hydrogen (atoms) into the metal and the formation of hydrogen molecules there, can take place in the presence of a relatively high hydrogen overvoltage, such as might be encountered during cathodic protection. As indicated above, cathodic protection does not appear to be promising for application to wet oxidation reactors; therefore it is unlikely that hydrogen cracking and blistering would contribute to failure of these reactors.

In systems which contain flowing or agitated corrosive fluids, it is important to consider the effects of the fluid motion on the rate of corrosion. Fluid motion has the effect of enhancing both the rate of supply of reactant to the sites of corrosion, and the rate of removal of products, causing an increase in the corrosion rate. In addition, an erosion is brought about by the mechanical action of the fluid on loosened grains of metal and films which may be present on the metal surface. It will be important to take these effects into account in the design of the wet air oxidation reactor, taking care to avoid sharp protrusions and bends, and employing good hydrodynamic design. Passive stirring design will be particularly critical. Cavitation should be avoided.

Among the important variables affecting the rates of corrosion reactions are the temperature, the concentration of the reactants, and the potential (voltage). Although the results available on the kinetics and mechanisms of many of the reactions are insufficient, the results seem to be consistent with a rate expression of the type:

$$\text{rate} = k\, c_A^m c_B^n \left(\exp \frac{-\Delta E^{\ddagger}}{RT}\right) \left(\exp \frac{\alpha n' F\eta}{RT} - \exp \frac{-(1-\alpha) n' F\eta}{RT}\right) \qquad (2)$$

where c_A and c_B are the concentrations of the reactants (e.g., oxygen), $\Delta E^{\ddagger}$ is the activation energy, α is the transfer coefficient for the electrochemical reaction (usually, 0.4 to 0.6), and η is the driving force, or overvoltage for the electrochemical corrosion reaction. If the corrosion reaction under consideration is nonelectrochemical, then the terms in which η appears should be deleted. m and n represent the numbers of molecules (or ions) of A and B involved in the reaction, and are usually unity. n' is the number of electrons involved in the electrochemical reaction, and k is the reaction rate constant.

Equation 2 indicates that the effect of temperature on the corrosion rate is expected to be significant, since T appears exponentially. The effect of concentration, since it appears as a simple multiplicative factor, is smaller than that of temperature. The overvoltage, η , has an exponential effect on rate; therefore, the rate of corrosion is strongly affected by the local composition variations in a metal, which affect the value of the local overvoltage. Because of the strong effect of temperature on corrosion rate, it will be important to minimize the operating temperature of the reactor, consistent with acceptable reactor size. The concentration of oxygen in the solution will probably be proportional to the oxygen partial pressure. A trade-off investigation should be made of the desirable effects of high oxygen concentration on the rate of waste oxidation, and the undesirable effect on the rate of oxidation of materials of construction.

With regard to non-metallic materials, most of the types of corrosion are similar to those for metals, except those involving electrochemical reactions (e.g., electrochemical, dissolution, crevice corrosion) and hydrogen cracking and blistering. This difference in corrosion behavior eliminates some important mechanisms from consideration for ceramic materials, suggesting that the corrosion rates of some ceramics, properly chosen, should be markedly lower than those of metals.

D. Conclusions and Recommendations

It can be concluded from the above discussion of the types and rates of corrosion reactions, and the effects of some variables on them, that the most promising metals and alloys for wet oxidation reactors are those that form impervious, tenacious oxide films which are stable in the presence of chloride, at temperatures in the vicinity of 500°F, at oxygen pressures of tens of atmospheres, and which resist the erosive effects of rapid fluid movement. Since it is important to have a system of long life (10 to 20 years) and high reliability (perhaps a 6-month inspection interval), it is appropriate to seek the mildest oxidation conditions consistent with reasonable equipment size and throughput. In this respect, some continued effort on means for achieving mild reaction conditions (e.g., catalysis) may be appropriate. With respect to the use of already-known materials in the present process, the employment of anodic protection (with titanium, for example) should be investigated as a means for improving reactor lifetime. The concentration of chloride ion on reactor lifetime should be studied under conditions simulating reactor operation (including appropriate fluid flow). Stress corrosion cracking

is expected to be an important aspect of this work. Based on previous results, a logical starting point is the study of titanium, titanium-based alloys, and nickel-chromium-molybdenum alloys.

In view of the conditions under which wet air oxidation is carried out, and of the influence of these strongly oxidizing conditions on corrosion rates and mechanisms, it is concluded that the most promising metals and alloys for this application are those that form erosion-resistant, impervious, tenacious oxide films which are stable in the presence of chloride ion. Consideration should be given to the use of anodic protection to improve corrosion resistance. It is recommended that the candidate materials include titanium, titanium-rich alloys, tantalum and nickel-chromium-molybdenum alloys, as well as certain non-metallics. A study of stress corrosion cracking rates of candidate metallic materials under operating conditions is recommended. Lower corrosion rates are favored by milder conditions; therefore, it is recommended that consideration be given to an effort toward achieving mild reaction conditions, for instance, by the use of catalysts.

V. MATERIALS SELECTION

A. Introduction

Proper choice of materials for shipboard wet air oxidation reaction systems is important. In any selection process, the properties of various candidate materials must be considered and analyzed, not only relative to one another but also with regard to system design and intended performance. Material properties that should be considered are:

1. Physical properties
2. Mechanical properties
3. Electrical properties
4. Magnetic properties
5. Nuclear properties
6. Thermal properties
7. Chemical properties

B. Application of Materials Selection Criteria

For the specific case of shipboard wet oxidation reactors, properties listed as 3, 4, and 5 above are probably not significant. With regard to physical properties only density of the material need be considered. This is important as it influences weight of the reactor and strength-to-weight ratio. The thermal properties of prime concern are conductivity and expansion, the latter only as it might contribute to differential thermal expansion between various components.

With regard to structural integrity, mechanical properties are of utmost importance. Yield strength, ultimate strength,

elastic modulus, Poisson's ratio, ductility, toughness and fracture toughness and resistance to fatigue must be considered.

The most critical aspect of materials selection for the present application relates to chemical properties. There is little that existing technology can contribute to prediction of material response in the specific environment and service conditions for shipboard wet oxidation reactors. Of particular concern here are 1) resistance to corrosion, 2) resistance to high-temperature oxidation, and 3) influence, if any, of exposed, internal material surfaces upon the processing reactions. Forms of corrosion damage that are considered relevant to this specific selection process include uniform and galvanic attack, selective leaching, erosion corrosion, crevice corrosion and pitting, intergranular corrosion, stress corrosion cracking, hydrogen embrittlement, and corrosion fatigue. Types of corrosion attack which are localized are often the most damaging and difficult to detect. For example, a stress corrosion crack can penetrate a pressure vessel, but the associated corrosion weight loss may be negligible.

As for high-strength, low-toughness materials, it is often advantageous to refer to fracture mechanics analysis for evaluating the latter three forms of damage (stress corrosion cracking, hydrogen embrittlement and corrosion fatigue). By this procedure, small flaws or cracks are assumed to be present initially,* and so no time in service is consumed by

* A most critical analysis recognizes that cracks are invariably present in commercially fabricated materials. Even if it can be guaranteed by thorough non-destructive testing and inspection that no flaws are present at the time of installation, there is no way of ensuring that they will not develop subsequently in service. Thus, the above assumption refers to the most pessimistic circumstances possible.

crack initiation processes. While such defects may be dormant in an inert environment, they may grow in a corrosive medium. This is commonly termed subcritical flaw growth, and it may take place by any one or more of four mechanisms: stress corrosion, hydrogen embrittlement, fatigue, and corrosion fatigue. For such an analysis the parameters of importance are:

- the maximum initial flaw size,
- the rate of subcritical flaw growth, and
- the flaw size to which a crack must grow to initiate brittle or terminal fracture.

The first factor is generally related to either material processing or pressure vessel fabrication techniques, whereas the latter two are inherent material properties.

Additional selection considerations are those involved with economics and design. Such factors as cost, availability, and fabricability of materials must be weighed and thus can be accomplished wholly in terms of information available in standard handbooks and from various producers. Related considerations include ease of maintenance and repair and avoidance of problems such as stagnation, which can lead to accelerated corrosion during shutdown. These latter factors are closely linked to system design and to performance in service, in which existing technology can help very little.

C. Specific Candidate Materials

This section will summarize presently available technical information which pertains to the suitability of existing engineering materials for wet air oxidation service. The

discussion focuses only upon the pressure vessel itself and upon related structural components. In terms of existing materials technology it appears that metals are now the only realistic choice for such a load-bearing application. Consequently, in this section we will weigh the advantages and disadvantages of likely metallic materials and identify the best candidate among these.

The feasibility of using coatings so that the metal members of the reactor are isolated from the environment is discussed later in this report. Coatings generally constitute a means of upgrading material performance, rather than providing total and complete isolation. This is so since flaws are present in these coatings, and, consequently, some small areas of the underlying material are still exposed. For such cases, the use of protective coatings will probably not influence selection of a pressure vessel material. If, on the other hand, a coating can be considered 100 percent protective, then chemical properties of the various candidate materials are not nearly as important.

For structural applications in which resistance to corrosion is required, the following classes of alloys are generally considered:

1. aluminum-base alloys,
2. copper-base alloys,
3. nickel-base alloys,
4. stainless steels, and
5. titanium and titanium-base alloys.

Although some candidates in category No. 1 (aluminum alloys) possess excellent corrosion resistance for numerous types of exposure, it is anticipated that because of their relatively low melting temperature (1220°F) the mechanical properties are unacceptably low for the service temperatures presently in question. Consequently, this alloy class is not considered further. Copper-base alloys exhibit "normally active" (non-passive) corrosion response for aqueous exposure, and so their corrosion rate may be high for wet air oxidation service temperatures (corrosion rate for active electrodes generally increases exponentially with temperature). Also, with regard to mechanical properties these alloys offer little that cannot be achieved by the remaining three classes (stainless steels and nickel and titanium alloys).

It was pointed out earlier that existing data can provide only limited assistance in materials selection for wet air oxidation reactors. Two recent investigations (see Table 3) into the corrosion response of certain stainless steels, nickel alloys, and titanium have been carried out, however, and are particularly noteworthy. The alloys investigated are listed in Table 2. Both projects were of the simple "batch reactor" type, as compared to a more complex, flow-through procedure. The first program employed a 10 percent by weight sewage sludge at 550°F and 2200 lbs/in^2, whereas, in the second, the sludge was diluted to 10 to 20%, both using synthetic seawater. Mean temperature for the latter tests was 580-600°F and mean pressure was in the range 1500-3800 lbs/in^2. Exposure time varied for different tests but was usually one to two weeks in duration. A limited number of tests were for

as long as six weeks. On the basis of these two test programs, Table 3 lists likely candidate materials for wet air oxidation service. Comments with regard to the suitability of each are included.

While corrosion resistance is a necessary property for wet air oxidation materials, other factors must also be considered in the final selection. For the purpose of emphasizing these, Table 4 rates qualitatively the materials in Table 3 for the various properties that are thought to be important. On the basis of Tables 3 and 4, it can be concluded that commercially pure titanium (alloy No. 19) or the titanium-1% nickel alloy (alloy No. 20) appear as logical and justifiable choices for wet air oxidation reactors. Alloy 20 does not, at present, have ASME pressure vessel code approval. Certain of the nickel-base materials (alloys 8 and 13) show promise and cannot be disregarded. The stainless steels, on the other hand, are categorically viewed with disfavor because of their generalized suceptibility to the localized forms of corrosion damage.

Commercially Pure Titanium and Titanium-1% Nickel. With the recommendation of commercially pure titanium or the titanium-1% nickel alloy as the structural material for reactor use, it is worthwhile to consider properties of this alloy class and to direct attention toward specific problems that may arise in conjunction with this selection. One negative feature of commercially pure titanium is its loss of mechanical strength at elevated temperatures. For example, at 600°F the 0.2% yield strength of commercially pure titanium is about 60% lower than for ambient temperatures. By way of comparison,

the complex nickel base alloys, such as Nos. 7 and 8 in Tables 2 and 3, experience only a 10% decrease for the same temperature differential. The elevated temperature mechanical properties of titanium can be enhanced by alloying, but lack of corrosion data for wet air oxidation environments* prohibits their immediate application. The feasibility of using titanium alloys will be discussed in greater detail subsequently.

A related potential problem is creep; however, titanium and many of its alloys are unusual in that they exhibit good general resistance to creep in the temperature range 300-700°F and for stress levels below yielding. For temperatures either below or above this range, creep deformation can occur.

Pitting and/or Crevice corrosion. At ambient temperatures, titanium and its alloys exhibit excellent resistance to pitting and crevice corrosion in aqueous environments. The two significant variables that can influence this are temperature and chloride ion concentration, as depicted for commercially pure stock in Figure 5. Thus, for sea water exposure titanium retains its resistance to localized attack to at least 250°F. At higher temperatures, immunity is evidently retained, provided the chloride ion concentration is sufficiently low (% NaCl $\lesssim$ 1.5%). On this basis, the suitability of using titanium with a fresh-water reactor becomes evident, and the 1.5% salt concentration limit appears as a useful design parameter. (A factor of safety should also be included, of course.)

---

* Of course, this point does not apply to the titanium-1% nickel alloy discussed above.

Where commercially pure titanium does not provide adequate resistance to localized corrosion, the alloy titanium-0.2% palladium is often recommended. As small amounts of corrosion take place for this alloy, palladium accumulates on the metal surface, resulting in anodic polarization and protection. Elevated-temperature corrosion exposures for this latter material have shown that the curves in Figure 5 defining the various regions of corrosion response are displaced to the right (higher temperatures) by 50-100°F. It was in search of a less expensive substitute for palladium that the titanium-1% nickel alloy mentioned earlier has evolved. Figure 5 and Table 2 suggest that commercially pure titanium (also, the 1% nickel and 0.2% palladium alloy of titanium) may be serviceable at temperatures approaching the 600°F limit of wet oxidation reactors. This assumes that the chloride ion concentrations are below the limiting value discussed above. High-temperature aqueous service experience with titanium makes it unclear, however, whether this is actually the case. For this reason, it is recommended that any shipboard titanium reactor not exceed the approximate temperature range of 475-500°F, until more detailed tests can better define serviceability at the higher temperatures (500-600°F). For reactors that are to experience the latter temperature range, a coating or composite material system seems at this time to be the more appropriate candidate for investigation.

Other Titanium Alloys. In view of the relatively low strength of commercially pure titanium and its reduced mechanical properties at increasing temperatures, it may be advantageous to consider higher-strength titanium alloys for wet air oxidation service. These alloys are generally divided

into two classes, depending on whether the alloying additions stabilize the low-temperature α (hexagonal close-packed) or the high-temperature β (body-centered cubic) phase. The former (α alloys) are characterized by intermediate strength, toughness, and weldability, whereas the latter (β alloys) are heat-treatable to high-strength levels; but this is often at the sacrifice of other properties, toughness and weldability in particular. Additionally, an intermediate series of alpha-beta alloys exists that contains both phases. Table 5 lists mechanical properties for a number of the more promising titanium alloys at both ambient temperatures and 600°F. Each material is designated according to its primary alloying constituents. Undoubtedly, additional alloys with improved properties will become available in the future; and it must be ensured that any stock breakthroughs are incorporated into the present treatment system.

D. Stress Corrosion, Hydrogen Embrittlement, and Corrosion Fatigue.

A most significant factor that must be taken into account if higher-strength alloys are employed is the possibility of environmental cracking (stress corrosion, hydrogen embrittlement, fatigue, and corrosion fatigue). For both service and laboratory conditions it is difficult to separate stress corrosion failure from failure caused by hydrogen embrittlement. In titanium alloys the mechanism of what is commonly termed stress corrosion is actually thought by many to be due to hydrogen pickup and cracking resulting therefrom. Commercially pure titanium and the 0.2% palladium alloy mentioned earlier do not generally crack under static loads. On the other hand,

the occurrence of stress corrosion (and/or hydrogen embrittlement) in some of the higher-strength alloys corresponds to one of two exposure conditions.* The first of these pertains to hot-salt-bath environments, where titanium alloys are widely recognized as undergoing accelerated cracking. While the temperature range for this susceptibility overlaps that of wet air oxidation reactors, the environment chemistry is notably different; and so this case is probably not of concern. A potential problem that could arise for the present application, however, relates to a system design which would allow salt to deposit or accumulate in air spaces.

The second condition for stress corrosion cracking requires that a "pre-crack" or crack-like flaw be initially present. If the size of this crack and the magnitude of tensile stress are such that the threshold stress intensity parameter K_{Iscc} for stress corrosion is exceeded, then rapid crack growth can be expected. For this reason it seems advantageous to rigorously inspect any higher-strength titanium alloy used as a reactor material for surface flaws that could contribute to this. Also, it must be assured that the threshold stress intensity value K_{Iscc} is high for the alloy selected. For the purpose of rationalizing the susceptibility to stress corrosion of the higher-strength titanium alloys in Table 4, values of plain strain-fracture toughness K_{Ic} and for K_{Iscc} are listed for each. The closer K_{Iscc} is to K_{Ic} for a particular alloy, the greater its resistance to stress corrosion cracking. The latter data were obtained using a 3.5% NaCl-distilled water

---

* A third condition involves exposure of stressed titanium to methanol - HCl solutions. This, however, is not considered germane to the present circumstances.

solution at room temperature. At best, this permits only a qualitative prediction of behavior under wet air oxidation conditions; but it is not unrealistic that the same relative order of merit may prevail at higher temperatures. On this basis, the Ti-3Al-2.5V, the Ti-6Al-2Cb-1Ta-1Mo (Ti-6211), and the Ti-6Al-4V-ELI (Extra Low Interstitials) alloys seem especially promising.

E. Conclusions and Recommendations.

Analysis of available data for existing materials warrants that commercially pure titanium, the titanium-0.2% palladium or the titanium-1% nickel alloy be recommended for wet air oxidation service. Because of uncertainties with regard to these materials at temperatures above 500°F, additional tests are recommended to better define temperature and pressure limitations. Specifically, these experiments should determine the resistance of commercially pure titanium and the two alloys to 1) localized corrosion (pitting and crevice attack), 2) cavitation, impingement, and erosion corrosion, and 3) stress corrosion and/or hydrogen embrittlement for the service temperatures in question. Further, it is recommended that differential-temperature cell corrosion experiments be performed to determine the magnitude of any galvanic potentials and currents generated between titanium surfaces at different temperatures.

In view of the relatively low mechanical properties of commercially pure titanium (and probably also for the 1% nickel alloy) at 600°F, it is also recommended that comparable corrosion experiments be performed on the alloys Ti-6Al-4V,

Ti-3Al-2.5V and Ti-6Al-2Cb-1Ta-1Mo. Also, because certain nickel-base alloys appear competitive, a similar investigation of these seems worthwhile. Therefore, it is recommended that the test programs outlined above for titanium be expanded to include these latter alloys (Nos. 8 and 13) shown in Tables 2, 3, and 4.

TABLE 2. Chemical Composition of 20 Various Alloys Investigated for Wet Oxidation Reactors.

		Nominal Chemical Composition									
Alloy No.	Condition	Ni	Cu	Cr	Mo	Fe	Co	Ti	Al	W	Other
1	ANN	9	-	19	-	69	-	-	-	-	C=0.08max, Mn=2.0max, Si=1.0max
2	ANN	12.5	-	22	2.3	Bal	-	-	-	-	Mn=5, N=0.3, C=0.06max, Cb=0.2, V=0.2
3		10-14	-	16-18	2-3	Bal	-	-	-	-	Si=1.0max, Mn=2.0max
4		34	3.5	20	2.5	33	-	-	-	-	Mn=2.0, Si=1.0
5	ANN	-	-	25	1.0	Bal	-	-	-	-	Mn=0.4, Si=0.4, Ni+Cu=0.5
6	HRAP	25	-	21	4.5	Bal	-	-	-	-	C=0.03, Mn=1.7, Si=0.5, Cb=0.3
7	HRAP	56	-	16	15.9	6.2	1.2	-	-	4	C=0.08 max, Si=1.0 max
8	HRAP	54.5	-	15.5	16.0	6.0	2.3	-	-	3.34	C=0.008, Si=0.02
9	ANN	60	-	1	28	5	2.5	-	-	-	
10	HRAP	72	-	7	16.4	4	0.1	-	-	-	V=0.3
11	ANN	47	-	22	9.3	17.6	1.7	-	-	-	
12		76	-	16	-	7	-	-	-	-	
13	CRA	62	-	22	9.1	1.7	-	0.2	0.2	-	Cb+Ta=4.3
14	ANN	53	0.1	18	3.1	18.0	0.1	0.9	0.6	-	Cb+Ta=5.2
15		-	4	22	3	28	-	-	-	-	Ni+Co=42, Mn=1.0
16	ANN	60	2.6	20	4.8	6.0	-	-	-	-	
17	ANN	50	-	19	10	5	11	3	1.5	-	
18		35	-	20	10	-	35	-	-	-	
19		-	-	-	-	-	-	Bal	-	-	
20		1	-	-	-	-	-	Bal	-	-	

NOTE: ANN = annealed
HRAP = hot rolled, annealed, pickled
CRA = cold rolled and annealed

TABLE 3. Properties of Some Candidate Alloys for Wet Oxidation Reactors

Alloy No.	Comments
7	Uniform corrosion rate determined as ~ 0.5 MPY (mils per year) for both fresh and salt water. Reference 1* concluded that this is the best candidate. Reference 2** noted stress corrosion cracking, however. In view of the latter result, it is concluded that stress corrosion or intergranular attack limit serviceability, particularly for a welded system.
8	Uniform corrosion rate ~ 0.5 MPY. This alloy generally exhibits less susceptibility to stress corrosion than alloy 7 and may eliminate localized damage problems. It is felt, however, that additional testing is necessary to confirm this prior to using.
13	Uniform corrosion rate in seawater sludge ~ 0.1 MPY. No localized attack observed.
19	Uniform corrosion rate ~ 0.2 MPY. Some etching observed at crevice sites.
20	Similar to alloy 19 but showed more resistance to localized corrosion.

* "Design and Development of a Prototype Wet Oxidation System for the Reclamation of Water and the Disposition of Waste Residues Onboard Space Vehicles," NASA Report CR-112151.

** "Corrosion Studies for Wet Air Oxidation Program," D. C. Vreeland, NSRDC Report 28-548.

TABLE 4. Qualitative Ratings of Candidate Alloys Shown in Table 3.

	Alloy Number				
Property	7	8	13	19	20
Strength*	G	G	G	G	G
Ductility	E	E	E	G	G
Density	F	F	F	E	E
Impact Resistance	G	G	G	G	G
Corrosion Resistance	P	F	G	G	G
Weldability	G	G	G	G	G
Fabricability	F	F	F	G	G
Cost	G	F	G	F	F
Availability	G	G	G	G	G
Pressure Vessel Code Approval	Yes	Yes	Yes	Yes	No

Code

E = Excellent F = Fair
G = Good P = Poor

* The present rating is with regard to ambient temperature data. At 600°F alloys 19 and 20 do not appear as favorable.

TABLE 5. Mechanical Properties of Some Candidate Alloys

Alloy	Micro-structure	Tensile Properties								Weldability	Tough-ness (Charpy ft-lbs)	K_{Ic} Fract. Toughness ksi $\sqrt{in.}$	K_{Iscc} ksi $\sqrt{in.}$
		Room Temperature				600°F							
		$Ex10^{-6}$ psi	YS ksi	TS ksi	EL %	$Ex10^{-6}$ psi	YS ksi	TS ksi	EL %				
99.5 Ti	Alpha	14.9	27	38	30	12.1	10	20	50	Completely Weldable	-----	--------	-------
99.2 Ti	"	14.9	45	60	28	12.3	13	28	45	"	25-40	--------	-------
99.0 Ti	"	15.0	60-75	75-90	25	12.5	19-27	33-43	23-28	"	15-35	--------	-------
98.9 Ti	"	15.5	85	100	17	12.6	30	47	25	"	11-15	--------	-------
Ti-0.2 Pd	"	14.9	46	62	27	12.3	13	28	30	"	-----	--------	-------
5Al-2.5 Sn	"	16	110	115	20	13.4	65	82	19	Weldable	19	112	50
7Al-12 Zr	"	6	159	165	14	14.3	119	130	18	"	-----	108	42
7Al-2Cb-1Ta	"	17.7	120	126	17	15.1	81	100	25	"	-----	100	35
8Al-1Mo-1V	"	----	130	141	18	----	85	107	19	"	-----	54	18
6Al-4V	Alpha-Beta	16.5	128	138	12	13.5	95	105	11	"	10-20	101	80
6Al-6V-2Sn 1(Fe. Cn)	Alpha-aged	16.5	180	190	10	14.5	132	180	15	Only under Special Conditions	15	111	96

CODE:

$Ex10^{-6}$ = modulus of elasticity
YS = yield strength
TS = tensile strength
EL = elongation

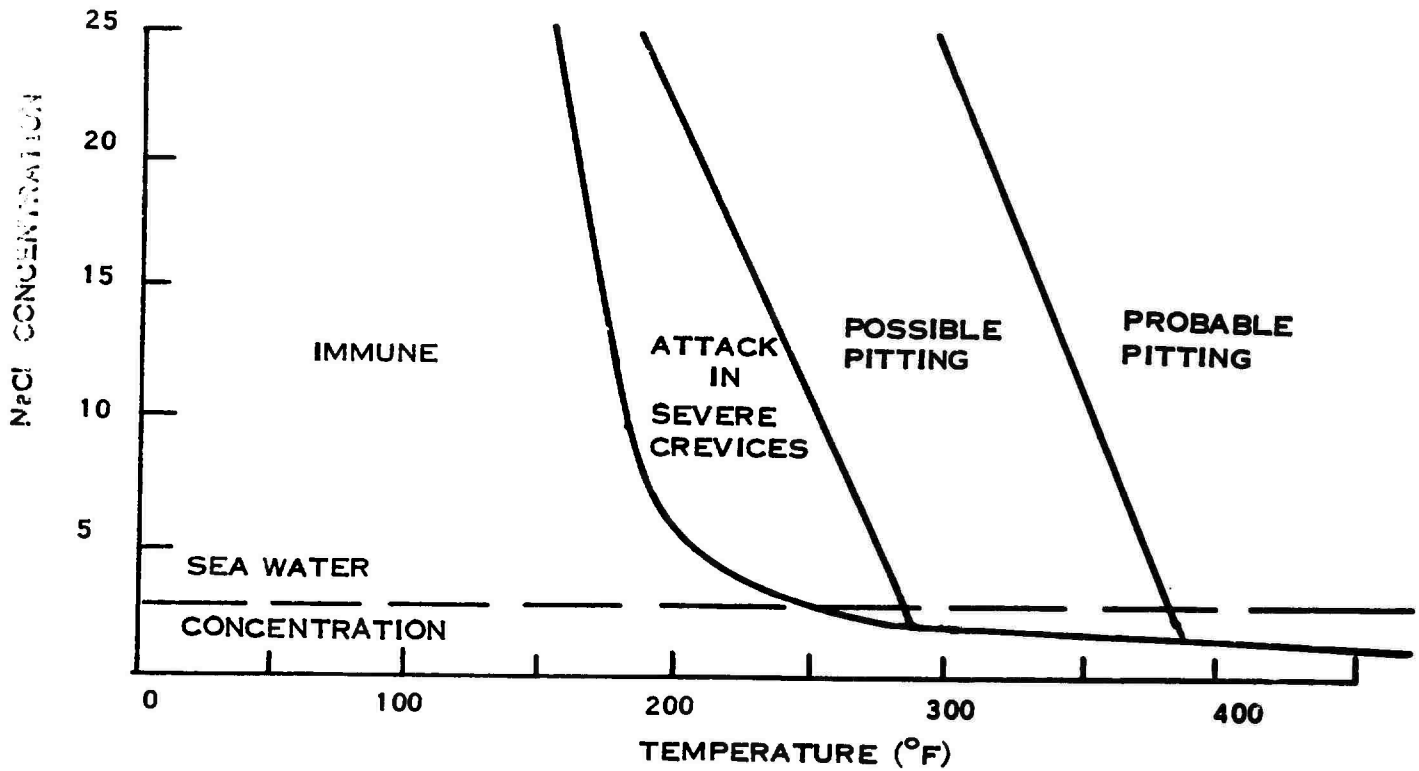

Figure 5. Corrosion Response of CP Titanium (Ti-50A) as a Function of Temperature and Sodium Chloride Concentration. The Titanium-0.2% Palladium alloy shows these three degrees of attack at about 50-100°F higher temperatures.

VI. COMPOSITE MATERIALS

A. Introduction

The wet oxidation process under development demands very high corrosion resistance of the materials so that the reaction and associated parts may be made to withstand the mechanical, thermal, and other chemical needs of the system for 10-20 years. Further, there is a need to make the system cost effective, which places further restraints upon the technical requirements. The position taken in this section is that, although one single material will be capable of withstanding the lower temperature and pressure environments of this process, the more severe requirements would require composite construction. Another section of this report deals with the metallic materials and their usefulness in this application. It is the purpose of the present section to build on these other portions of this report and deal with the possibility of using a multiple layer construction. Each of the layers of this construction would perform a specific function more efficiently than a single material can perform the multiple functions required.

The development of composite materials has taken a dramatic step forward within the past 10 years. It is now possible to engineer composites to meet advanced mechanical requirements. To a limited degree there has been development in composites which will meet other advanced combined requirements of corrosion, thermal and mechanical severity. However, these latter developments have not received the same attention as the previous category involving the mechanical aspects.

There is a large spectrum of materials that might be considered for their use in a composite approach for wet oxidation application. There is no intention to deal with all these possible materials in this section of the report. However, there will be an attempt to deal with certain presently known composites which should hold some promise for this wet oxidation application, and to go from there to some more speculative composites which may be of use in the future.

There are three major categories of materials: metals, ceramics, and polymeric materials. The subject of metals has been dealt with elsewhere in this report and hence will only be discussed here in the context of composites. The properties of the polymerics do not favor their use over the other two types of materials; therefore, only a limited discussion of these materials is contained in this section of the report.

B. Coatings, Linings, and Laminates

Ceramic materials are known to have high intrinsic resistance to many kinds of corrosion. Glass laboratory ware is standard for carrying out experimental reactions where corrosion is involved. The resistance of certain ceramic materials extends to fairly high temperatures. Many of the materials may also exhibit fairly good strength at these high temperatures. However, the design shortcoming of ceramics is their brittleness, and thus low impact resistance. Metals, quite in contrast to this, usually have good ductility and thus have high impact resistance. Metals may have deficiencies in corrosion resistance. Therefore, it seems logical to try to combine the best properties of each of these materials in such a way

that the final metal-ceramic composite will withstand the total environment better than either of the single components would do alone.

Several composite materials having possible use for this wet oxidation environment are:

- ceramic coatings on metals,
- composite: ceramic-metal-plastic-metal,
- metal and metalloid coatings on metals, and
- loose metallic linings.

In the chemical-process industry, coatings are usually applied to base metals either because a single material of construction is deficient technically or the use of a single material presents severe cost or weight penalties. For example, a coating of glass or glass-ceramic is placed on a steel substrate when one of the super alloys will not perform adequately or when the refractory metal would be too expensive. However, there are also conditions so severe that it is necessary to use a multiple coating where each layer performs its own special service.

Corrosion resistant composites able to withstand environments of pH 2-9 and high temperatures and pressures are compared in Table 7.

C. Ceramic Coatings on Metals

The improvement that may be derived from a coating may be of two types: flaw-free or with minor flaws. There is place in the processing industry for both types. However,

only the flaw-free-type coatings are candidates for this wet oxidation usage because of the exacting nature of the corrosion environment.

Flaw-free coatings can be made to withstand severe processing environments even though the substrate may exhibit fast destruction in this environment. For example, it is possible to coat a good grade of steel with a glassy material and make the combination resistant for long periods of time (15 years). In this case, the acidic environment would consume the steel substrate in a fairly short period of time. Thus, it is necessary that the coating protect the steel at all times.

If glass or glass-ceramic coatings are to be used on the steel substrate, then it is usually recommended that the environment remain on the acidic pH side for most of the life of the reaction vessel.* Glass or glass-ceramic is quite resistant to most acids (except hydrofloric acid) through a wide range of concentrations. The temperature and pressure of the vessel have to be considered and, as both of these increase, the life of the vessel is reduced.

The ceramic-steel vessel is used mostly in the flaw-free condition; therefore, the inspection and testing of these units has to be comprehensive. The integrity of the coating is tested with a high-voltage A.C. tester. Any flaws or pinholes are detected in the dielectric coating to the base steel with a

---

* "Glassed Steel," W. B. Crandall, in the book: Composite and Engineering Laminates, A.G.H. Dietz, ed., MIT Press Cambridge, Mass, 1961.

flash over. In this way, the flaw may be found and repaired or the unit returned for reprocess. Tantalum plugs are used for repair with certain limits.

Ceramic Steel Applications. An attempt is made by the manufacturer of the equipment to make a universally acceptable type of coating for the vessel. The coating is generally made to withstand rather severe acid attack (except hydrofloric acid) but not much alkaline attack.

The wet oxidation process under consideration here meets about the usage limits of pH range on the high side, i.e., up to pH 9. Acidic use is usually well within the proper range. The present intended pressure and temperature, however, exceed the capabilities of almost any ceramic coating on steel in production today. The normal range of application for this type of equipment usually does not exceed 450°F and 300 lbs/in^2. The present application may operate at 600°F and over 1000 lbs/in^2. It can be seen from Table 6 that this higher temperature and pressure of operation is beyond the acceptable limits for the ceramic corrosion resistance in the present state-of-the-art of this manufacturer.

In Table 7 it is shown that the metal ceramic system has poor impact strength and thermal shock resistance when compared with the other systems described. The poor impact strength usually results from the fact that the applied impact on the ceramic-metal locally yields the metal under the ceramic coating, thus cracking the ceramic. Another way of stating this is to say that the compressive strength of the ceramic coating is usually higher than the yield strength of

the supporting metal and will not fail until the bending of the metal (through yielding) under the ceramic exceeds the strain limit of the ceramic.

The thermal-shock resistance of the ceramic-metal system is lower than the others for slightly different reasons. Thermal shock of the ceramic coating can come about because of the mismatch in the coefficient of expansion of the two materials and/or the exceeding of the lower tensile strength of the ceramic coating through the generation of high thermally induced stresses.

It is not the intention of this Committee to urge the use of this untested, beyond the state-of-the-art vessel, but rather to point out how this equipment may be used with other linings.

In a later portion of this section of the report, there is a description of a composite lining using a ceramic-steel construction as a backup or redundant lining of resistance. This type of construction should have definite advantages for this new area of wet oxidation application where present process vessels are still experimental.

D. Multi-Component Reactors (Composite: Ceramic-Metal-Plastic-Metal)

There has been a minor development in the chemical processing industry of multi-component equipment construction. This is a further development of the idea that one should use only the most desirable corrosion-resistant material in contact with the processing fluids and a series of material, if necessary, in the backup. In this case, the inner material

in contact with the process fluids is usually a ceramic. This ceramic may be a chemical resistant tile which will resist the fluids but will not be liquid-tight. Therefore, the ceramic tile will allow some fluids to pass by and come in contact with the next lining. The temperature of the fluid, however, has been reduced by the time it reaches the next lining. This means that the second material need not be as corrosion-resistant at high temperatures as the inner lining. This second lining may be some metal like lead, which can be formed easily into the reactor shape and be yielding to the ceramic tile in the inside, i.e., take up certain thermal expansion mismatches, etc. To add some more redundancy to the system, it is possible to add one more barrier to the corrosive fluid before it might reach the pressure containing vessel. This next lining may be a polymeric material like a silicone rubber. This polymeric will stop any seepage which may pass the lead lining, and will have a long life similar to that of the other materials of construction because the temperature will be reduced again. Finally, the outer shell of the vessel is constructed according to pressure codes and is usually made of steel.

The technology of this particular system has not reached a high degree of development; however, there is much to be said for the basic concept because it allows one to mix materials optimally. The selection of the best composition of ceramic tile, metallic lining, polymeric lining, and metal shell should be made after a careful consideration of many parameters taken from all portions of this report. However,

it is easy to see that this type of construction is quite bulky and heavy. This may exclude it from certain weight or volume-sensitive uses.

E. Metal and Metalloid Coatings on Metals

A number of techniques have been developed for applying metal and metalloid to metal substrates. The salt-bath process and the gas-plating process are two of the current methods used. Also, metalloids and mixed metalloids may be applied to substrates by slurry coating, hot spraying, pac cementation, and fluidized bed.

The flame-sprayed coatings present a permeability problem where leak-free coatings are required. However, many of the materials which may be applied by this method have a high intrinsic resistivity to the wet oxidation environment.

The salt-bath and vapor-deposition processes are very interesting because they do not require high temperatures for processing like the ceramic coatings. This means that the thermal-expansion mismatch in the composite materials will not build up such high stresses upon cooling and use and cause possible destruction. With these coatings, there is a problem of coating adherence and coating integrity which is required for a fluid-tight coating. Further, it is extremely difficult to inspect and test an electrical conduction coating to prove its integrity before use.

Pac cementation and fluidized bed coatings are usually a fairly high-temperature process. Reaction takes place between the pac or bed process ingredients and the surface of the substrate. These coatings are controlled by the ingoing

ingredients and the temperature and time of the process. Silicide, alumide, chromide, and other mixed coatings can be produced this way. The integrity of the coating may be quite high but, because there is a diffusion process for the substrate and the coating materials, the composition and thus the microstructure and other properties usually vary over the thickness of the layer. The chemical resistance of these materials has not been tested very thoroughly as it is the oxidation resistance at elevated temperature that is usually desired and evaluated. Both the metallic and metalloid coatings are put on by processes which do not lend themselves easily to scale-up. Salt baths, pacs, or fluid beds at present are limited in size. Thus, it would be difficult to make a large reactor with a high integrity from these coatings at the present state of the art.

F. Loose Linings

It is possible to protect a steel pressure vessel with a loose lining material. Many years ago, a loose lining of plastic was placed in a steel pressure vessel; however, at high temperatures and pressures there was permeability of the lining causing deterioration of the metal shell. The polymeric material had a high intrinsic resistance to the corrosive environment in the reactor but the high-temperature permeability caused the destruction of the shell. Thus, the lining must have high intrinsic resistivity to the corrosive medium and must also be more than pinhole-free if the shell is unprotected. It is possible to protect the shell from any seepage through this loose lining by placing a ceramic coating on this

outer shell. If the severity of the corrosion environment is reduced somewhat by the loose lining, the ceramic metal shell would offer an excellent backup system.

The loose linings would need to be pressure formable (yielding) to the shell shape. The fitting of this loose lining would need to be good enough so that when this forming takes place no flaws are opened in the lining. The generous radii used on all openings and turns in the ceramic steel construction favor this process.

Tantalum has been constructed in loose linings for severe corrosion applications. It is probably the best material for this type of pressure vessel. Tantalum and other reactive and refractory metals suffer from oxidation corrosion as the temperature increases above about 500°F in an air or oxygen environment. Tantalum is equal or superior to ceramic materials in other corrosion resistance, but is nearly five times as expensive to produce in pressure-vessel form as an equal-size ceramic steel unit. However, where the combined corrosion, pressure, temperature, time requirements are so demanding, perhaps having a redundant system of a tantalum loose lining on the inside and a ceramic steel or a titanium shell to back it up is not too expensive. It should be possible to test the loose lining for flaws because the space between the lining and the shell would be available for limited examination after a pressure test with water. Also, scale-up should be no real problem because large sizes are already in use. Thus, it seems that this method of construction for the wet oxidation process offers one of the possible alternatives for composite materials.

G. Conclusions and Recommendations

This section has described a number of composite type coatings, linings, or laminates which may be able to withstand the severe environment of a wet oxidation process at elevated temperatures and pressures for extended periods of time. In all cases, there are trade-offs to be made in the material selection based upon technical requirements, bulk weight, and cost. This can be seen in Table 7. This Committee takes the position, however, that, considering all these factors, the best solution of the materials of construction for this process will come from a composite construction in which each portion of the composite performs a service when combined with the other materials of the composite, which is superior to any single material. The tantalum loose lining in the ceramic-coated or titanium shell seems like the best near-term solution if a composite is to be used. The "back-side" oxidation of tantalum must, however, be considered. There are at least two methods of circumventing or correcting this situation. One way would be to keep the temperature of operation sufficiently low so that the back-side oxidation would be eliminated, i.e., less than 500°F. A second possibility would be to flush the space between the layers with an inert gas, preventing oxidation. The second method would also have the advantage of making continuous inspection of the integrity of the inner lining by "sniffing" the gases through this inner space to check for any possible leak that might occur. A heat-exchanger-type reactor that might be used on shipboard can be made from ten-foot-long tubes of metal with incorporated

baffling to control reaction conditions within at required low flow rates. If this unit were to be made in a composite construction, it is recommended that the outside pressure shell be either a good grade of steel coated with ceramic or an uncoated titanium. The next inner layer would be a noncrushable porous ceramic. This porous annulus area could be used to contain the inert gas and also to detect the presence of a leak by proper gas detection systems (a "sniffer").

TABLE 6. Corrosion Resistance of #3300 Glass

Acid	Conc. % wt.	Temp. F°	Corrosion Rate mdd*	mpy**
HCl	5	325	26.0	14.6
HCl	20	325	47.5	26.7
HCl	30	325	31.3	17.6
HNO_3	5	300	8.9	5.0
HNO_3	10	300	14.2	8.0
HNO_3	30	300	22.2	12.5
HNO_3	50	300	15.6	8.8
HNO_3	60	300	8.4	4.7
HNO_3	70	300	3.6	2.0
H_2SO_4	5	300	10.1	5.7
H_2SO_4	20	325	28.8	16.2
H_2SO_4	50	375	6.9	3.9
H_2SO_4	50	425	35.2	19.8
H_2SO_4	90	450	10.7	6.0
H_3PO_4	5	300	7.1	4.0
H_3PO_4	10	300	9.1	5.1
H_3PO_4	40	300	25.1	14.1
H_3PO_4	50	300	40.2	22.6
H_3PO_4	60	275	21.8	12.3
H_3PO_4	80	266	29.9	16.8
H_3PO_4	86	250	31.4	17.7
H_3PO_4	100	176	7.6	4.3
H_3PO_4	115	176	3.4	1.9
CH_3COOH	5	350	21.5	12.1
CH_3COOH	10	350	19.0	10.7
CH_3COOH	20	350	17.6	9.9
CH_3COOH	40	350	11.2	6.5
CH_3COOH	50	375	29.9	16.8
CH_3COOH	70	400	15.5	8.7
CH_3COOH	70	450	23.3	13.1
CH_3COOH	90	425	10.8	6.1
CH_3COOH	90	450	10.7	6.0

*Mils per square decimeter per day; ** Mils per year

TABLE 7. Composite Materials Trade-Off Chart for Wet Oxidation Application.

Composite Materials	Corrosion Resistance		Mechanical Properties			Thermal Properties		Fab. Ease (Scale-up)	Bulk Wt.	Insp. Tests	Cost
	$Cl+O_2$ +pH 2.0-3.0	$Cl+O_2$ +pH 8-9	Strength	Impact Strength	Abrasion Resistance	Thermal Shock	Temp. Limit				
1. Ceramic Metal	E	F	F	P	F	P	E	F	E	E	M
2. Metal-plastic Metal-ceramic	E	E	F	F	E	F	E	P	P	F	M
3. Metallic Coatings (Ta)	E	E	E	F	F	E	E	P	F	P	H
4. Metalloid coatings	E	E	F	F	E	E	E	P	E	P	H
5. Loose Metal Linings (Ta)	E	E	E	F	E	E	E	P	F	F	H

KEY

Properties

E = Excellent
F = Fair
P = Poor

Cost

H = High
M = Medium
L = Low

BIBLIOGRAPHY

Preceding page blank

BIBLIOGRAPHY

Ault, N. N. and W. M. Whieldon, "Modern Flame Sprayed Ceramic Coatings," in the book: Modern Materials, H. H. Hausner ed., Academic Press, N.Y., 1960.

Bradstreet, S. W., "Refractory Coatings," in the book: High Temperature Materials and Technology, I. E. Campbell and E. M. Sherwood eds., Chap. 16, Wiley, 1967.

Burns, R. M. and W. W. Bradley, "Protective Coatings for Metals," Am. Chem. Soc. Ser., Reinhold, N.Y., 1967.

Coatings of High Temperature Materials, H. H. Hausner ed., Plenum Press, N.Y., 1966.

Colombire, L. and J. Hochman, "Stainless and Heat Resisting Steels," in the book: Mechanisms of Corrosion, Chap. 3, St. Martin's Press, N.Y., pp. 132-195, 1968.

Evans, V. R., The Corrosion and Oxidation of Metals: Scientific Principles and Practical Applications, St. Martin's Press, N.Y., 1960.

Holland, L., "Surface Chemistry and Corrosion of Glass," in the book: The Properties of Glass Surfaces, Chap. 3, Wiley & Sons, N.Y., 1964.

"How Materials Stand Up to Corrosion," Special Issue of Materials Engineering, Vol. 73, No. 1, pp. 36-60, Feb. 1971.

McDonald, D. P., "Corrosion Resisting Materials and Their Applications," Brit. Chem. Engrg. and Proc. Techn., Vol. 16, No. 9, Sept. 1971.

Powell, C. F., J. H. Oxley and J. M. Blocher, Vapor Deposition, Wiley & Sons, N.Y., 1966.

Schussler, R., "Tantalum Immune to Most Corrosive Attack," Mtrl. Engrg., Vol. 4, pp. 24-25, 1973.

Uhlig, H. H., Corrosion and Corrosion Control, Wiley & Sons, N.Y.-London, 1963.