

The Corrosion Resistance of Nickel-Containing Alloys in Sulfuric Acid and Related Compounds

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PREFACE

Corrosion Engineering Bulletins are published by Inco so that Industry may have up-to-date corrosion data upon which a more knowledgeable selection of nickel-containing alloys may be based for use in a variety of corrosive media including acids, caustics, seawater and numerous other industrial environments.

Data in this bulletin on sulfuric acid, as in other Inco Corrosion Engineering Bulletins in this series, are gathered from a variety of sources, including laboratory and field exposures as well as the literature, technical bulletins of the alloy producers and actual plant experience.

Much of the laboratory data is from our own research. The laboratory data, while admittedly produced under stringently controlled conditions which quite often do not represent real life situations in industry, nonetheless provide a useful guide toward alloy selection. Such data are most useful when supplemented by corrosion data obtained in field exposures under actual operating conditions, as presented in the later sections of this bulletin.

Inco field test data are obtained by exposing selected alloys in duplicate on spool type test racks in accordance with ASTM Recommended Practice G4. These are placed in operating equipment, such as pipes, process and storage tanks

or other plant components of interest. The exposure locations and conditions are usually those selected by the participating plant operating personnel and such information becomes part of the exposure history of the test materials.

These laboratory and field data, when properly interpreted by trained corrosion specialists, usually prove useful in determining the class of alloys likely to perform well under closely related process conditions.

Conditions, and hence corrosion rates, may be quite different under heat transfer, where velocity is high and erosion may occur or where contaminants are present. Thus, it is critical before utilizing these data for alloy selection to learn the details of proposed operating conditions, as well as the possibility of an "upset" which would result in significant changes in exposure conditions. These corrosion data are most appropriately used to identify several alloys suitable for further evaluation under specific conditions.

Within the guidelines which have been outlined, it is hoped that designers, chemical and process industry personnel, alloy producers and researchers will find these corrosion data even more useful in the future than they have proven in the past.

A 1200 ton-per-day, energy efficient, sulfuric acid plant under construction with the first all-austenitic nickel stainless steel converter in the center. The hot SO₂ and SO₃ gas lines in this plant will also be austenitic nickel stainless steel and the coolers will be anodically protected Type 316L shell and tube units. Pumps and valves will make liberal use of cast LEWMET alloy 55.



(Photograph courtesy of Chemetics International Ltd.)

PART I - INTRODUCTION

A. USE AND PRODUCTION

Worldwide, more sulfuric acid (H_2SO_4) is produced than any other chemical. It used to be that the annual consumption of sulfuric acid could serve as an economic indicator as so many chemicals and their derivatives are based on its use. However, this relationship is now only coincidental because the use of sulfuric acid for the acidulation of phosphate rock to produce phosphoric acid overshadows its other uses. In the United States sulfuric acid is used as follows:¹

Industry	Percent
Fertilizer	59
Chemical	24
Pigment and paint	5
Petroleum	5
Textile and film	3
Iron and steel	1
Other	3

While major use areas have been given above, specific uses to indicate the utility of the acid include the manufacture of dyes, drugs, rayon, cellulose products, the alkylation of petroleum products to increase octane rating, the pickling (descaling) of ferrous and nonferrous alloys, the extraction of uranium from ore, the production of hydrogen fluoride from fluorospar; in process use in copper, zinc and nickel refining, and the treatment of organics in the production of alcohols and detergents. Some H_2SO_4 is also used for the inclusion of sulfur values which lend special properties to the finished product such as surfactants.

Almost all of the sulfuric acid is now produced by the Contact Process where sulfur dioxide (SO_2) is oxidized to sulfur trioxide (SO_3) in the presence of a catalyst; sulfuric acid is used to absorb the sulfur trioxide thereby increasing the strength of the acid. There are a number of variations in the process with regard to the source of the SO_2 . The burning of elemental sulfur is the most common; but sulfur values are also obtained from oil, natural gas, pyrite, smelting of sulfide ores, and more recently, by recovery from stack gases as a pollution control measure.

A small amount of sulfuric acid is produced by the much older Chamber Process where oxides of nitrogen are reacted with sulfur dioxide, oxygen, and water vapor to form nitrosulfuric acid, which, in turn, is reacted with water to form sulfuric acid. This process was once the most important source of H_2SO_4 , but accounts for less production each year as these plants are replaced by the more modern Contact Process plants.

Weak or spent acids are often utilized to recover their acid value from which new acid is regenerated or reconstituted by adding fresh acid or fortified by adding oleum (100% acid containing sulfur trioxide). Some acid is recovered from petroleum refinery alkylation unit sludge and other refinery sludges, as well as from miscellaneous dilute sulfuric acid solutions where concentrations are well below levels useful for most applications.

B. GRADES OF SULFURIC ACID

Sulfuric acid is produced and shipped in a number of concentrations and grades:

78% Acid (60°Bé) is popular since it represents the maximum strength made by the Chamber Process. (Chamber Process acid includes that produced by the Chamber Process, as well as that produced by other means in the 62-78% concentration range).

93% Acid (66° Bé) is the most popular commercial shipping concentration as its low freezing point and low corrosivity permits outdoor storage in steel containers. The name, "oil of Vitriol", is sometimes applied to this grade.

Oleum or fuming sulfuric acid is a solution of SO_3 in H_2SO_4 . It is produced in several concentrations, 20%, 40% and 65% oleum. In the United States, production is reported in three categories: oleum 40%, oleum under 40% and oleum over 40%.

"*Technical*" grade sulfuric acid is intended for large scale industrial use and need not be of high purity.

USP grade* is a high purity acid that meets specifications of the United States Pharmacopoeia and is used in drug manufacture.

Electrolyte Acid (high purity) for storage batteries is usually supplied at strengths between 27.24 and 93.19% (sp. gr. 1.2001.835) to meet customer specifications.

Chemically pure or reagent grade acid is supplied at a strength of 95-96% to meet ACS specifications.

The relationship between acid concentration in percent, specific gravity, degree Baume, and grams per liter is given in the Appendix.

The Armed Services and other government agencies as well as some consumers have established specifications delineating acceptable acid purity limits. Many rayon producers specify a maximum iron content of 50 ppm for commercial 66°Bé H_2SO_4 . Battery manufacturers specify a maximum of 42 ppm iron for 1.835 sp. gr. electrolyte acid. These values are easily met by modern plants using corrosion resistant materials of construction. When specifications are not presented, producers usually detail acid purity levels available.

C. CORROSION IN SULFURIC ACID

Sulfuric acid is unique in comparison to other mineral acids. Reference to the freezing point of sulfuric acid solutions in the Appendix shows that it varies in an apparent anomalous manner. Peculiarities also extend to the corrosion area, especially where austenitic stainless steels are concerned. Reference to the literature will show radically different corrosion rates for the same alloy in sulfuric acid at the same concentration and temperature, large variations in corrosion rate with only slight variations in exposure conditions and occasions when laboratory data do not correlate with equipment experience.

Acid concentration and temperature are important variables but sometimes the presence of oxidizing or reducing impurities, the presence of chlorides, velocity or heat transfer may drastically affect corrosion rates of alloys. Laboratory test results may be affected by the length of exposure because

*See Appendix for Abbreviated Nomenclature

of a buildup of corrosion products or depletion of oxygen in the test solutions; in another case the amount of oxygen in the test solution may be different for different types of condensers used in the test apparatus. *It is important that there is a thorough knowledge of exposure conditions, including not only the temperature and concentration of the acid but also the presence or absence of oxidizing agents and other impurities, acid velocity and heat transfer effects before selecting a material of construction for a sulfuric acid environment.*

A number of isocorrosion charts from various sources are included in this bulletin. The corrosion rates shown pertain to the isocorrosion lines. These were based upon laboratory tests in chemically pure acid and are only intended as guides for the selection of candidate alloys for further investigation in your specific system. There are conditions under which both higher and lower corrosion rates than indicated by these charts may be obtained.

The nominal composition of alloys cited in the tables and text are shown in the Appendix. Some of the proprietary alloys have been improved by compositional modifications. Where data exist for the newer modification they are included; however, some data on the obsolete alloys are included. Lacking data for the newer modification, corrosion rates may be assumed to be approximately equivalent to the earlier alloy since they are usually equivalent or lower. Tradenames of proprietary alloys have been used in the text and trademarks are also listed in the Appendix. All materials are in the mill annealed condition unless notations to the contrary are shown.

The cast counterparts of wrought alloys have not always been included in the corrosion tests. However, the corrosion resistance of cast counterparts is usually equivalent and sometimes superior to the wrought versions.²

The order in which alloys are listed in the Table of Contents and presented in the text does not have particular significance. A section on corrosion theory introduces the stainless steels to aid in an understanding of the subsequent information. This section is appropriate in the first Inco Corrosion Engineering Bulletin and has application in corrodents covered in subsequent Corrosion Engineering Bulletins, where alloys can exhibit either active or passive behavior.

All percentages expressed in these data are in weight percent unless another basis is specifically stated. Corrosion rates are reported in millimeters per year (mm/y) followed by the corrosion rate in mils per year (mpy), (one mil = 0.001 inches). As a final note, metric values were usually derived from English units, therefore, they are the least precise unless otherwise stated.

PART II - ALLOY RESISTANCE TO SULFURIC ACID

A. GENERAL

Although steel and cast iron can sometimes be used for concentrated sulfuric acid, there are numerous reasons for choosing more corrosion resistant alloys based on a need for reduced maintenance costs, freedom from product contamination, greater equipment flexibility, or the necessity of great-

er corrosion resistance under more stringent conditions. A number of iron, copper and nickel base alloys are available for sulfuric acid service. The order of merit of each alloy varies considerably according to the specific conditions of each application and the function of the particular component under consideration.

Alloy additions are an economical approach to achieving improvement in corrosion resistance. The alloying elements that enhance corrosion resistance in sulfuric acid include nickel, molybdenum, copper, silicon and chromium. While single element additions of these elements are of scientific interest, multiple element additions are much more common and advantageous and result in the commercial alloys discussed subsequently.

The alloys most noted for corrosion resistance in sulfuric acid are the "20 Type" alloys discussed in Section E and the nickel-base iron-chromium-molybdenum-copper alloys discussed in Section F. Considerably more information is given on the stainless steels (Sections B, C and D) because, although these alloys are used extensively, they have limitations which have to be defined.

B. WROUGHT AUSTENITIC (300 SERIES) STAINLESS STEELS

1. General (Corrosion Theory)

The 300 series austenitic stainless steels, especially Types 316 or 316L, find widespread use in sulfuric acid solutions for specific applications. Their cast counterparts are also used. Usually these applications are either in dilute solutions or concentrated solutions at moderate or low temperatures. The 300 series austenitic stainless steels display active-passive behavior in sulfuric acid solutions. This type of behavior is most readily explained by mixed potential corrosion theory. Exhaustive treatment of this subject is beyond the scope of this bulletin; however, a limited amount of theory will be included to allow interpretation of corrosion data which follow. (For a more comprehensive review of corrosion theory, the reader is referred to several texts.³⁻⁶)

Corrosion in sulfuric acid environments is electrochemical in nature and the total amount of metal corroded (at the anode) is related to the total corrosion current according to Faraday's law. The corrosion rate is proportional to the current density of the corroding metal if the corrosion is uniform over the metal's surface. An anodic polarization curve for an active-passive alloy, which is a plot of electrical potential vs. logarithm of the current density, is shown in Figure 1. The current density corresponding to the tip of the "nose" is known as the critical current density. A region of active corrosion (and possibly high corrosion rate) exists below the nose of the curve; a region of passive corrosion (and usually low corrosion rate) exists between the "nose" and the onset of oxygen evolution which is marked with a rapid increase in current density at noble potentials. This rapid increase in current density is called "transpassive behavior". In the presence of chloride, a "breakout" will occur at a less noble potential which is then called "pitting potential" or "rupture potential".

FIGURE 1
ANODIC POLARIZATION CURVE

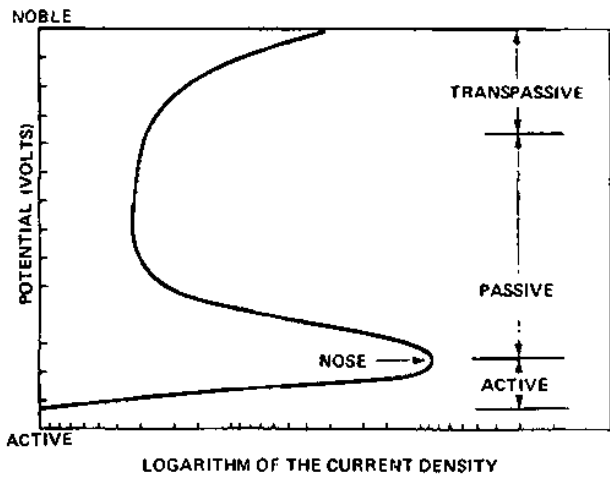


Figure 2 illustrates the effect of increasing temperature, increasing chloride concentration, or both, on the anodic polarization curve for a stainless steel in a sulfuric acid environment. Typical potential and current density values have also been added for perspective. As temperature or chloride ion concentration increases, the critical current density increases, the region of passivity decreases and pitting occurs at less noble potentials. These effects can be quite large because the abscissa is a logarithmic plot.

The anodic polarization curves alone do not indicate corrosion rates. An alloy exposed to sulfuric acid reaches a rest or corrosion potential fairly quickly at which time the total



This DURIMET alloy 20 valve handles 93 percent H₂SO₄ at ambient temperature.

(Photograph courtesy of The Duriron Company, Inc.)

FIGURE 2
EFFECT OF TEMPERATURE OR CHLORIDES

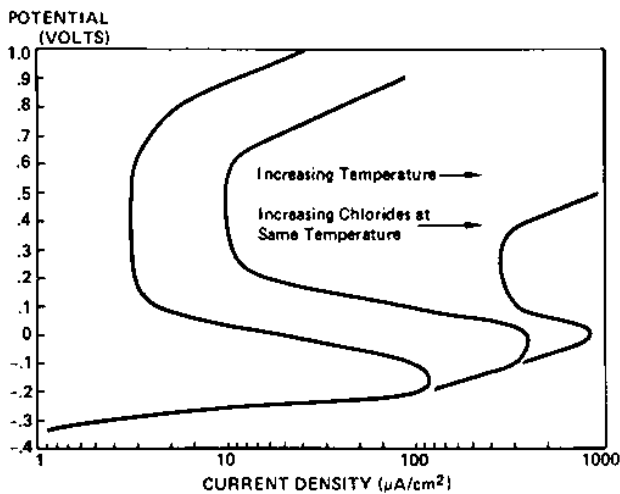
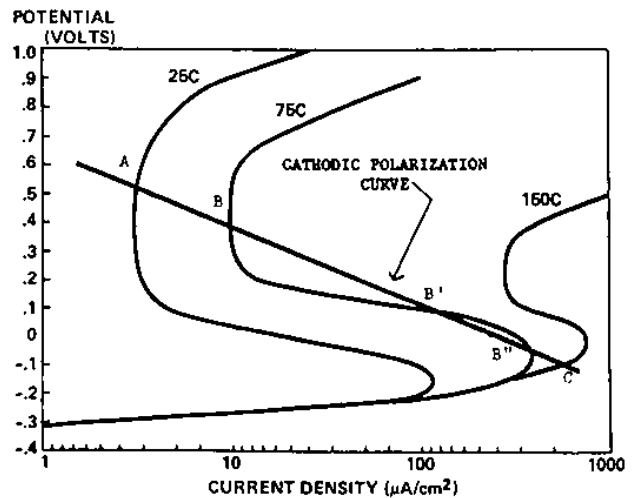


FIGURE 3
EFFECT OF TEMPERATURE



cathodic and total anodic current densities are equal. This is defined as an intersection of the cathodic polarization curve with the anodic polarization curve. The corrosion rate is proportional to the corrosion current density associated with that intersection.

In Figure 3 a cathodic polarization curve has been added to further demonstrate possible effects of increasing temperature. At 25°C (77°F), stable passivity and a low corrosion rate is indicated (see intersection A). At 75°C (167°F), the cathodic polarization curve intersects the anodic curve at 3 points (B, B', B''). Intersection B' is usually unstable. When multiple intersections exist, the corrosion potential may occur in the passive region (with an attendant low corrosion rate); it may occur in the active region (with an attendant high corrosion rate) or, it may oscillate between the active and the passive region, in which case the corrosion rate will be somewhere between the extremes of its active and passive corrosion rates, depending upon the period and frequency of oscillations between the two potentials. This is sometimes referred to as "borderline passivity". At 150°C (302°F), the cathodic polarization curve intersects the anodic polarization curve in the active region at location C and a high corrosion rate is obtained.

The anodic polarization curves shown here are the ideal theoretical curves; in actual practice it is often not possible to obtain the complete curve.⁷

Figure 4 was taken from laboratory studies on the corrosion of Type 316 stainless steel in 93 percent sulfuric acid from a plant producing sulfuric acid from a metallurgical plant stack-gas. The acid contained impurities, mainly sulfur dioxide, which tended to make it more aggressive than reagent grade sulfuric acid. The open circuit or corrosion potential was found to be stable-passive at 25°C, occasionally active at 75°C and, at 95°C, the sample became active for a short period of time about every minute. The corrosion rates associated with these conditions were less than 5 mils per year at 25°C, about 50 mils per year at 75°C and greater than 200 mils per year at 95°C.

FIGURE 4
OPEN CIRCUIT POTENTIAL BEHAVIOR
Type 316 Stainless Steel in Contaminated, 93% Sulfuric Acid

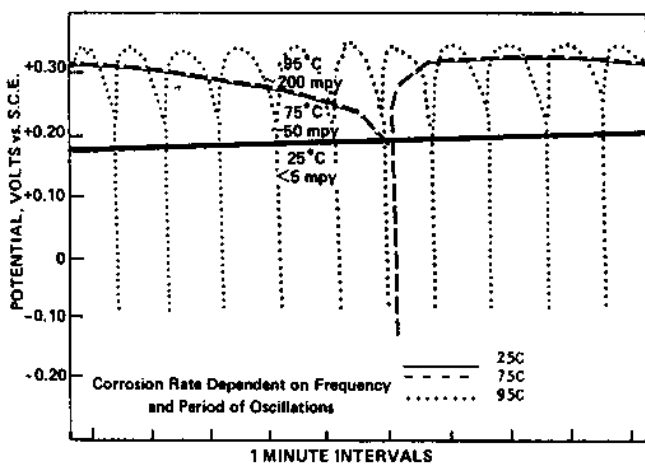


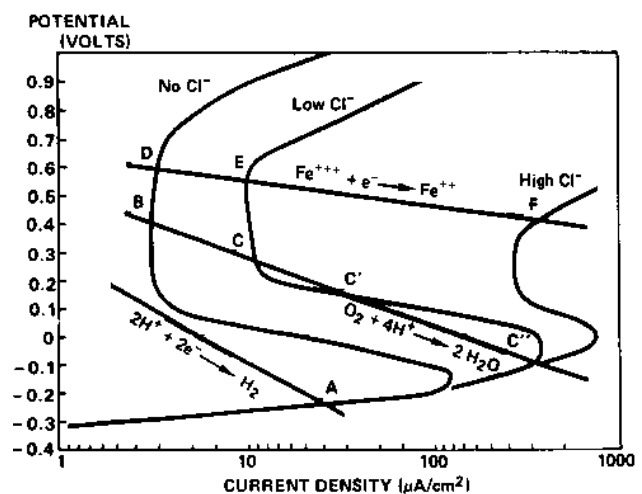
Figure 5 shows the effect of oxidizing agents on the corrosion of active-passive alloys in sulfuric acid containing chloride. The primary effect of oxidizing agents is revealed by cathodic polarization. In the absence of oxidizers, hydrogen reduction and active corrosion will result as shown (see intersection A). If air is present in the acid, the reduction of oxygen will occur at cathodic sites on the metal surface which takes place at more noble values than hydrogen reduction (see intersections B, C, C', C''). Contamination of the environment with a stronger oxidizing species than oxygen will have an even greater effect on corrosion. When ferric ions are reduced to ferrous ions at the local cathodes, the corrosion potential shifts even further in the noble direction (see intersections D, E and F). Thus, the addition of oxidizing agents may act as inhibitors by shifting the corrosion potential into the passive region, however, in the presence of chlorides oxidizers can cause pitting as a consequence of an intersection of the anodic and cathodic polarization curves in the pitting region.

Since the presence of an oxidizing agent tends to raise the corrosion potential to more noble values, the possibility also exists that a limited amount of oxidizing agent might increase corrosion rates in the active region before reaching a concentration that would cause passivity.

It is not necessary to add oxidizing agents to sulfuric acid to obtain passivity; passivity can be obtained electrochemically by means of a potentiostat and is known as anodic protection. This topic is covered in greater detail in later sections of this bulletin.

Discussion thus far has centered on electrochemistry. There is one metallurgical aspect that should always be taken into account when stainless steels are considered for sulfuric acid service. Chromium depletion associated with carbide precipitation in the grain boundaries (sensitization) caused by heating a regular carbon (0.08C max) stainless steel within the range of 425-760°C (800-1400°F) may lead to severe intergranular corrosion in sulfuric acid. Exposure of the stainless steel in

FIGURE 5
EFFECT OF OXIDIZING AGENTS AND CHLORIDES



this temperature range might result from adverse heat treatment during fabrication but is most commonly caused by welding. Although sensitization does not always occur during welding because sensitization is a time-temperature dependent phenomenon, experience has shown that it is a wise precaution to utilize only a low carbon (0.03C max) or stabilized grade of stainless steel if weld fabrication is to be employed in sulfuric acid service, unless it is known through experience in very dilute or concentrated solutions that intergranular corrosion will not occur in a particular application. (Sensitization is discussed in greater detail in another publication).⁸ A lot of the corrosion data that follow were obtained on annealed, regular carbon grades of stainless steel and hence, they are identified in the text. The corrosion rates of these annealed grades are comparable to their low carbon counterparts.

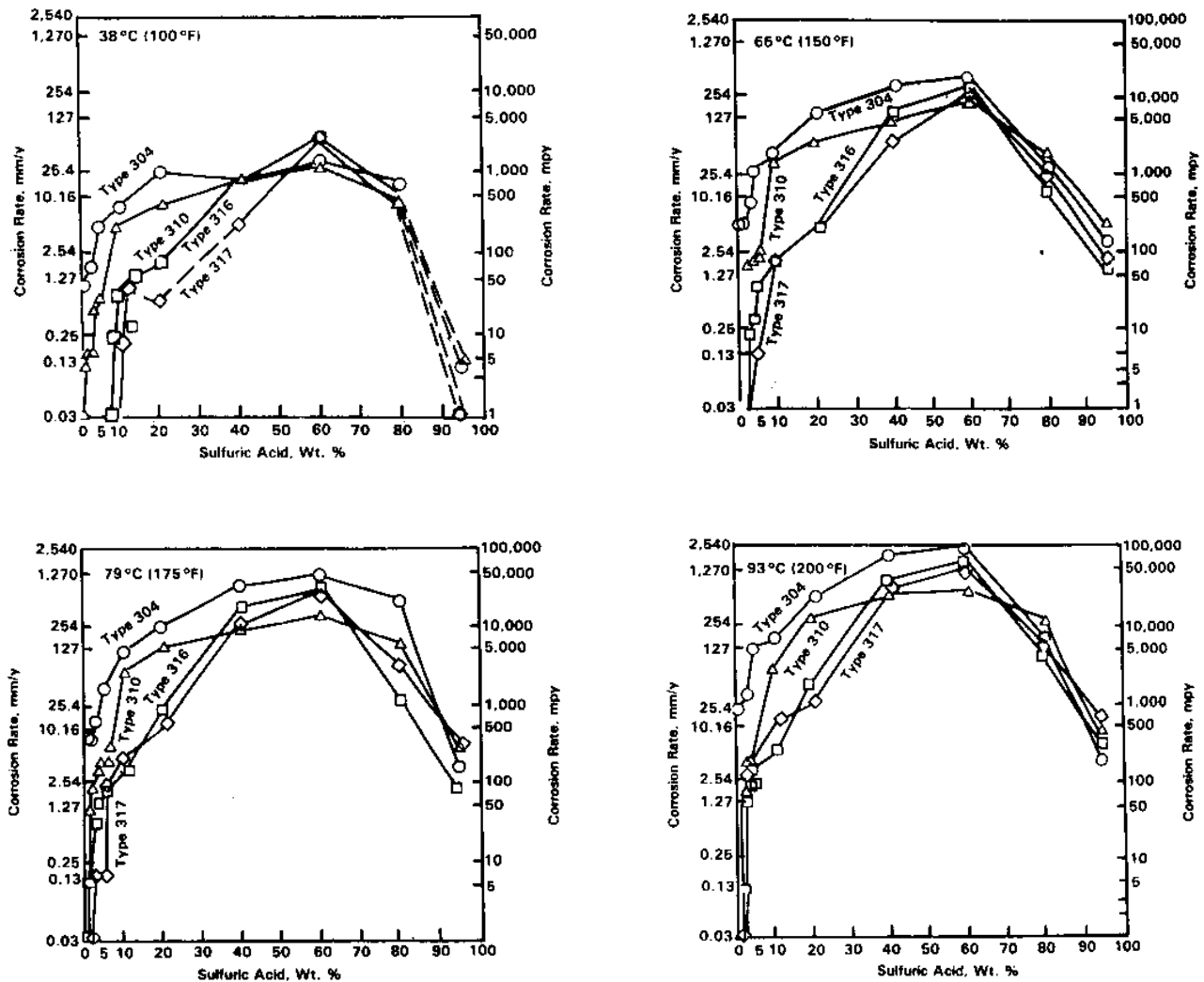
Thus, corrosion in sulfuric acid is complex and corrosion rates are affected by the variations in conditions of exposure. Since these alloys exhibit active-passive behavior, the change in corrosion rate from one condition to another may be very

marked. Austenitic stainless steels are generally less expensive than more highly alloyed iron and nickel base alloys discussed subsequently. Because of very low corrosion rates under certain passive conditions and their economy, stainless steels are being utilized more and more in sulfuric acid service.

2. Effect of Temperature, Acid Concentration and Alloy Composition

Kiefer and Renshaw made an extensive evaluation of Types 304, 310, 316 and 317 stainless steels in sulfuric acid of various concentrations from one-half percent to 95 percent at 38, 65, 80 and 93°C (100, 150, 175 and 200°F).⁹ The results of duplicate samples in two-hour tests are shown graphically in Figure 6. Dashed lines were used in areas of uncertainty. These tests were run using "as-mixed" acid and the samples were activated in 15 percent hydrochloric acid at 65°C (150°F) just prior to testing. This activation treatment removed the protective oxide film from the surfaces and a new film had to form under the test conditions if passivity was to be achieved. In this

FIGURE 6
CORROSION OF STAINLESS STEELS IN AS-MIXED SULFURIC ACID

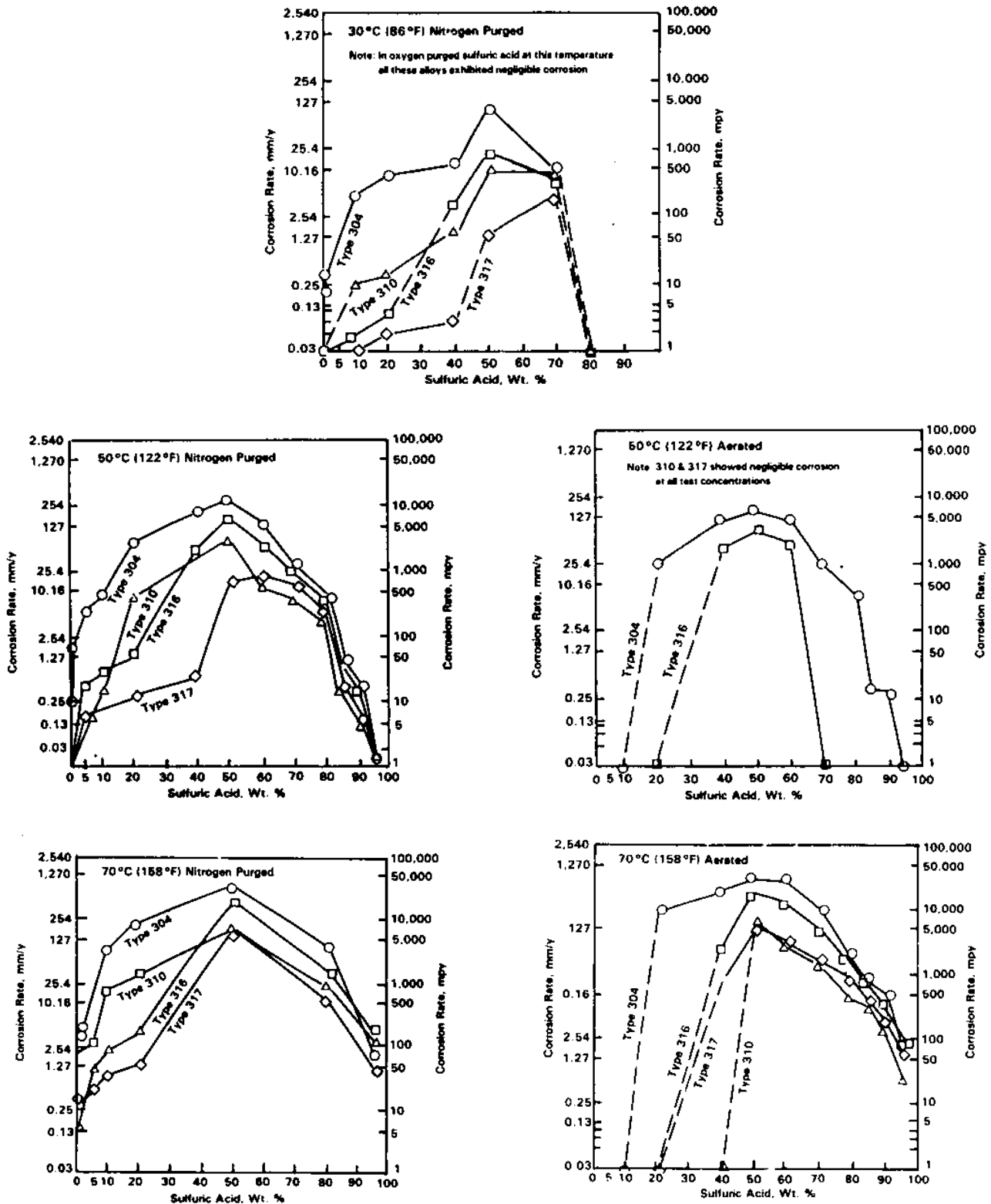


respect, their laboratory test did not duplicate industry exposures where an air-formed oxide film would be present on the surface of stainless steel components prior to exposure.

Helps and Vreeland later experimented with these same alloys in sulfuric acid of various concentrations from 0.1 per-

cent to 96 percent at 30, 50 and 70°C (86, 122 and 158°F).¹⁰ Single specimens of each alloy were exposed simultaneously for 96 hours, but specimens that corroded very rapidly were removed after 24 hours. Since high corrosion rates were experienced on some of the specimens, the possibility exists that

FIGURE 7
CORROSION OF STAINLESS STEELS IN NITROGEN-PURGED OR AERATED SULFURIC ACID



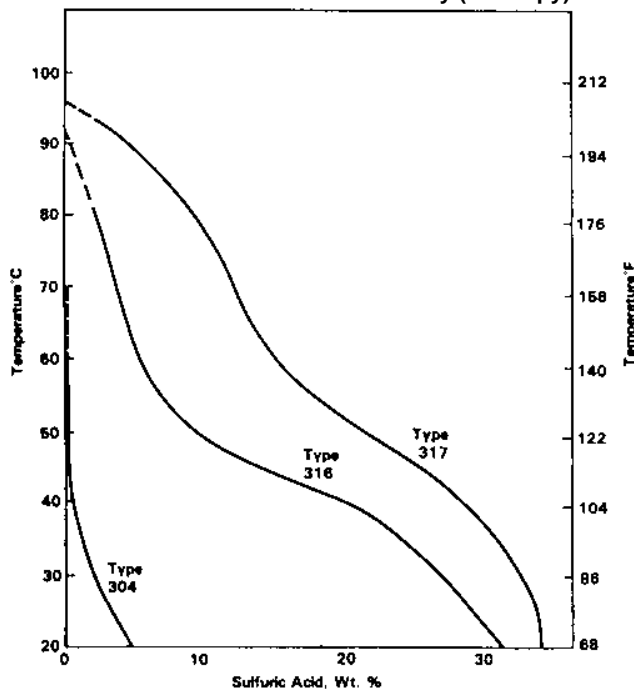
corrosion products affected the results of the remaining specimens. All tests were repeated with duplicate specimens. These tests were run in air-tight vessels using either a nitrogen purge or an oxygen purge; the samples were ground to a 120 grit finish and cleaned in nitric acid at 60°C (140°F) for 20 minutes followed by rinsing and drying before the test. Their test results are shown graphically in Figure 7. Stabilized Types 321 and 347 stainless steel were also investigated and the corrosion rates of these grades were approximately the same as those for Type 304.

Shreir¹¹ has reported the effect of sulfuric acid concentration and temperature for a number of stainless steels including Types 304, 316 and 317 in "static solutions, not deliberately aerated" which corresponds to the as-mixed acid used by Kiefer and Renshaw. However, the specimens were not activated in hydrochloric acid prior to exposure and the test results, some of which are shown in Figure 8, indicate corrosion rates which are usually intermediate between the Kiefer and Renshaw data and the corrosion rates in oxygenated acid obtained by Phelps and Vreeland.

Abo, Ueda and Noguchi tested a series of stainless steels which included the Japanese Industrial Standard equivalents of AISI Types 304, 316 and 317L.¹² They concentrated their efforts at lower concentrations with tests in 0.1, 0.5, 1, 5, 10, 30 and 50 percent sulfuric acid at 20, 40, 60 and 80°C (68, 104, 140 and 176°F) and at the boiling point. Their data was presented on semilogarithmic plots, as shown in Figure 9, which accentuate the limiting conditions at low concentrations, under their test conditions. The samples were polished through 600 grit emery paper, degreased in alcohol, rinsed in water and dried before testing. The tests were conducted in a flask with a reflux condenser using as-mixed acid. The isocorrosion lines on their figures were drawn at 0.1, 1 and 10 g/m². hr. which have been recalculated to mm/y and mpy for consistency in this publication.

FIGURE 8

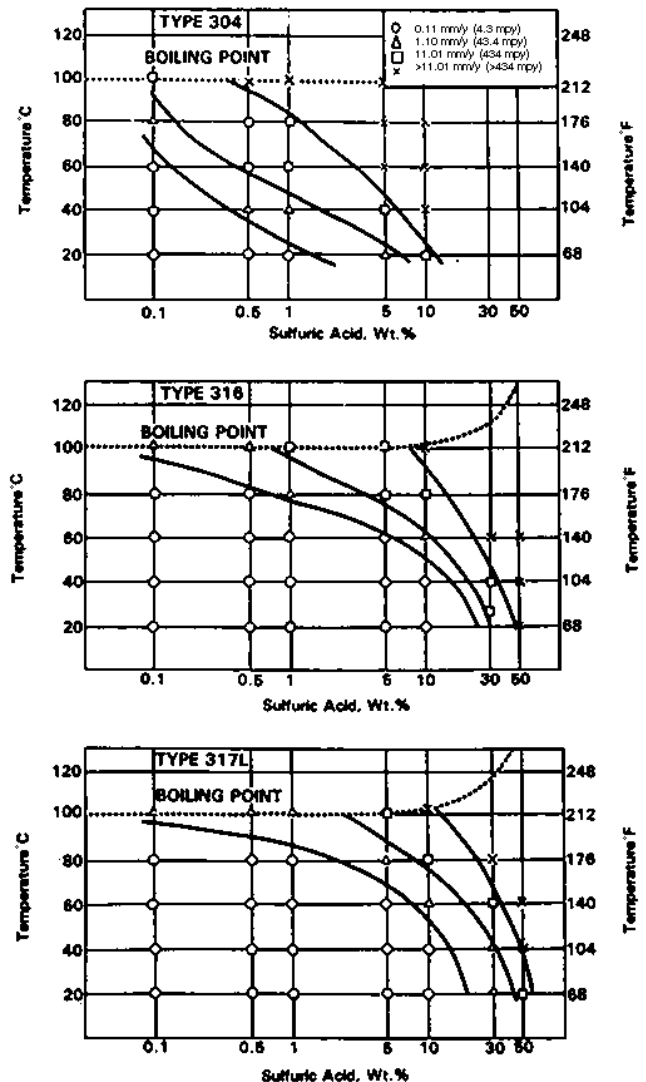
STRENGTH AND TEMPERATURE OF SULFURIC ACID SOLUTIONS AND TYPE OF STAINLESS STEEL TO GIVE A CORROSION RATE OF 0.113 mm/y (4.46 mpy)



All of these investigations were performed under strictly controlled laboratory conditions but the results sometimes appear to be contradictory. In addition to acid concentration and temperature, one must consider other variables concerned both with specimen preparation and test procedures. Because of these variations, it is difficult to reach positive conclusions based on a comparison of these data. Some generalizations are apparent:

- Aerated solutions are much less aggressive than either as-mixed or nitrogen-purged sulfuric acid solutions. Indeed, aeration has been successfully employed commercially to reduce corrosive attack on stainless steel components. (The effect of oxidizing agents will be discussed further in a subsequent section).
- Temperature is an extremely important variable; an increase of 10°C (18°F) can cause a 2 to 20 fold increase in corrosion rate. Thus temperature control in actual applications may be critical.
- The drastic increase in corrosion rate at some limiting temperature and sulfuric acid concentration is a result of moving out of the regime where passivity is maintained.
- The molybdenum bearing grades of stainless steel (Types 316, 317 and their low carbon counterparts) are more resistant

FIGURE 9



to dilute concentrations of as-mixed or nitrogen-purged sulfuric acid, than the molybdenum free grades. However, Type 310 stainless steel with a nominal composition of 25 percent chromium - 20 percent nickel, but containing no intentional molybdenum addition, is more resistant than these molybdenum bearing grades when an oxidizing agent is present in sulfuric acid. (This is attributed, in large part, to the higher chromium content of Type 310).

3. Effect of Oxidizing Agents

The beneficial effect of oxygen in reducing stainless steel corrosion rates has been shown in the preceding section. Cations that are easily reducible, such as ferric, cupric, stannic, ceric etc., are oxidizing agents that can inhibit the attack of stainless steels in sulfuric acid solutions. Apparently this effect was first observed by Hatfield in 1924.¹³ Streicher later investigated the inhibition of corrosion in a number of acids by ferric salts and explained the effect as resulting from the depolarization of cathodic areas shifting the corrosion potential in the noble direction with resultant passivity.¹⁴ Although he did not measure this potential shift, he did refer to such a change being observed by Uhlig and Geary.¹⁵ Streicher found that 0.19 grams of ferric ion per liter was sufficient to cause passivity and low corrosion rates of Types 304 and 316 stainless steel in boiling 10 percent sulfuric acid but that 0.115 grams of ferric ion per liter did not give complete inhibition.

Tables I and II show the corrosion inhibiting effect of divalent nickel (ic) and cupric ions in 10 percent sulfuric acid solutions.

Cations in their lower valence state and those that have a single valence are much less effective as corrosion inhibitors as shown by Figure 10 where only the cupric iron is in its higher valence state.⁹ At higher temperatures and acid concentrations, the effect becomes much less pronounced with all of the cations shown except the cupric and stannous ions, as shown in Figure 11. If a cation in its lower valence state is reduced to its elemental form, it will raise the corrosion potential and may cause passivity. (This may account for the efficacy of the stannous ion.) Although arsenious oxide (As_2O_3) is usually considered a reducing agent, the addition of As_2O_3 to dilute 1M H_2SO_4 at 25°C (77°F) prevented the corrosion of Type 304 stainless steel because arsenic was reduced to the metal and deposited on the surface.¹⁶

The effect of metal ions in solution should always be taken into account when planning laboratory corrosion tests in sulfuric acid. It has been observed that utilization of the same solution for extended tests leads to lower corrosion rates than when the test solution is periodically replaced, not because of depletion of acid but because of the oxidizing effect of the metal corrosion products.

TABLE I
Corrosion Test Data

	Penetration Rate			
	Exposure No. 1		Exposure No. 2	
	mm/y	mpy	mm/y	mpy
ALOYCO-316 (CF-8M)	3.81	150.0	0	0
ALOYCO-20 (CN-7M)	0.90	35.5	0	0

Exposure: 1. 10% Sulfuric acid, no impurities
2. 10% Sulfuric acid + nickel sulfide impurities (exact amount unknown)

Temperature: 1. 107°C (225°F)
2. 93°C (200°F)

Exposure Hours: 1. 240 (Five 48-hour exposures. New solution after each exposure)
2. 672 (Continuous)

TABLE II
Effect of 40 Grams Per Liter of Copper Sulfate On Corrosion of Various Alloys By 10% Sulfuric Acid At 66°C (150°F)

Alloy	Corrosion Rate			
	Cupric Sulfate 40 g/l		Air Free, No Oxidizing Salts	
	mm/y	mpy	mm/y	mpy
Type 304 S/S	0.06	2.3	66.0	2600.0
Type 316 S/S	nil*	nil	2.13	84.0
MONEL alloy 400	5.16	203.0	0.18	7.0
Silicon bronze	destroyed specimen		0.38	15.0

* nil = less than 0.00635 mm/y (0.25 mpy)

FIGURE 10
30% SULFURIC ACID AT 38°C (100°F)

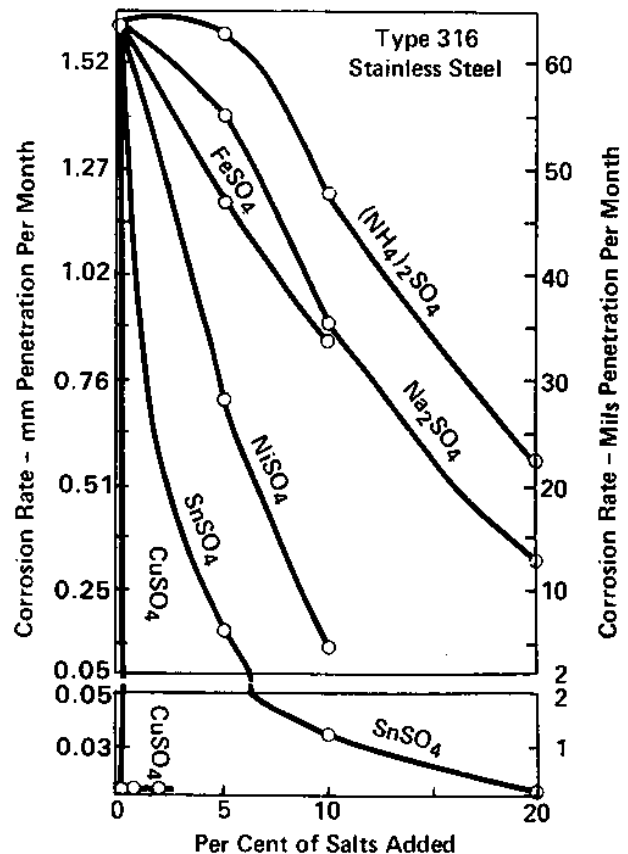


FIGURE 11

30% SULFURIC ACID AT 93°C (200°F)

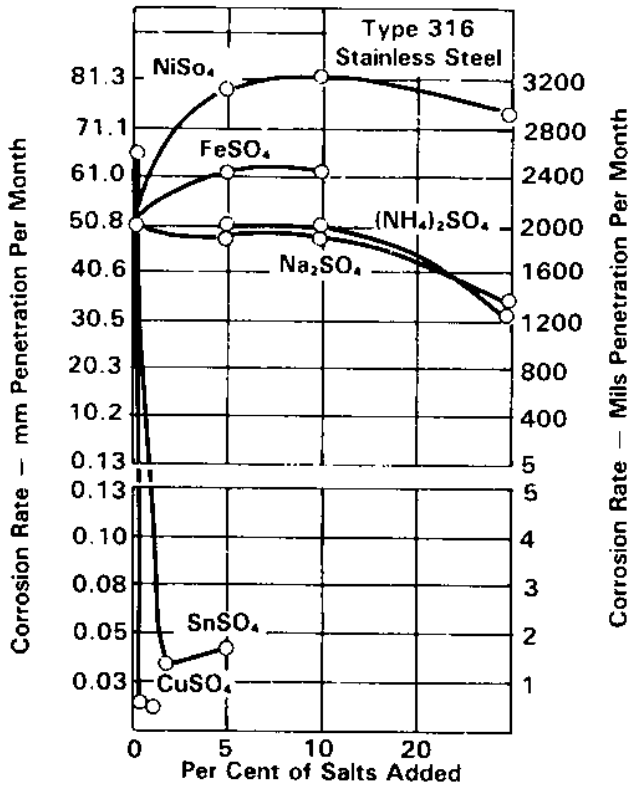


FIGURE 12

30% SULFURIC ACID AT 93°C (200°F)

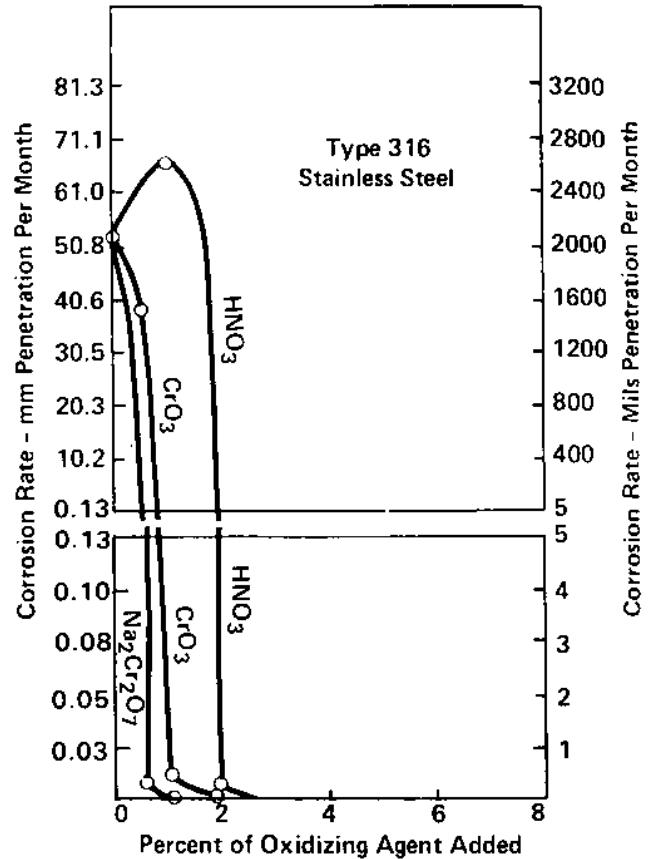


Table III shows the results of Kiefer and Renshaw regarding the amount of cupric sulfate that caused passivity and low corrosion rates with Types 304 and 316 stainless steels in 5 and 30 percent sulfuric acid. These authors also showed that other oxidizing agents are effective in reducing corrosion rates, if present in sufficient quantity, as shown in Figure 12. Note the increased corrosion rates associated with an insufficient amount of nitric acid.

Monypenney has shown the inhibiting effect of nitric acid over a wide range of sulfuric acid concentration at 15.6°C (60°F)¹⁷ (see Figure 13). These data appear to be at variance with the Phelps and Vreeland data at 30°C (86°F) where passivity was maintained throughout the sulfuric acid concentration range of 0.1 to 96 percent by aeration, since nitric acid is a stronger oxidizing agent than oxygen.

There are four precautionary notes in regard to adding an oxidizing agent as an inhibitor to allow the use of a stainless

steel in a sulfuric acid environment where it is not normally passive:

1. Sufficient oxidizing agent must be present or higher corrosion rates may result than if no inhibitor were present.
2. The oxidizing agent must be present in sufficient quantity continuously or active corrosion may result.
3. The presence of oxidizing agents may still lead to high corrosion rates, pitting or crevice corrosion if chlorides or other reducing impurities are present. (See subsequent section on impurities).
4. If corrosion tests are performed to assess the effect of oxidizing agents, the ratio of the exposed stainless steel surface area to the solution volume is an important variable that should be taken into account, because of possible depletion of the oxidizing agent.

TABLE III
Amount of Cupric Sulfate Causing Passivity
With Types 304 and 316 Stainless Steel in
Sulfuric Acid Solutions

Acid Concentration (Wt. %)	Temperature		Weight Percent of Cupric Sulfate to cause Inhibition*	
	C	F	Type 304 S/S	Type 316 S/S
5	38	100	0.20	none required
5	66	150	0.25	0.01
5	79	175	1	0.5
5	93	200	1	0.5
30	38	100	1	0.5
30	93	200	2	1

* Passive corrosion rate less than 6 mils per year

4. Effect of Impurities in the Acid

The effect of aeration and oxidizing agents on the corrosion of stainless steels in sulfuric acid solutions has been covered in the preceding section. In general, oxidizing agents in sulfuric acid solutions are beneficial but the presence of reducing agents, such as sulfur dioxide (sulfurous acid), hydrogen sulfide or sodium sulfite, is detrimental.^{16, 18}

Halides in sulfuric acid make it more difficult to achieve and maintain passivity with the stainless steels and higher nickel alloys as well. Working with 10M H₂SO₄ (about 64%) at room temperature, an extremely severe environment where stain-

FIGURE 13

EFFECT OF SMALL ADDITIONS OF NITRIC ACID ON CORROSION OF TYPE 304 STAINLESS STEEL IN SULFURIC ACID AT 16°C (60°F)

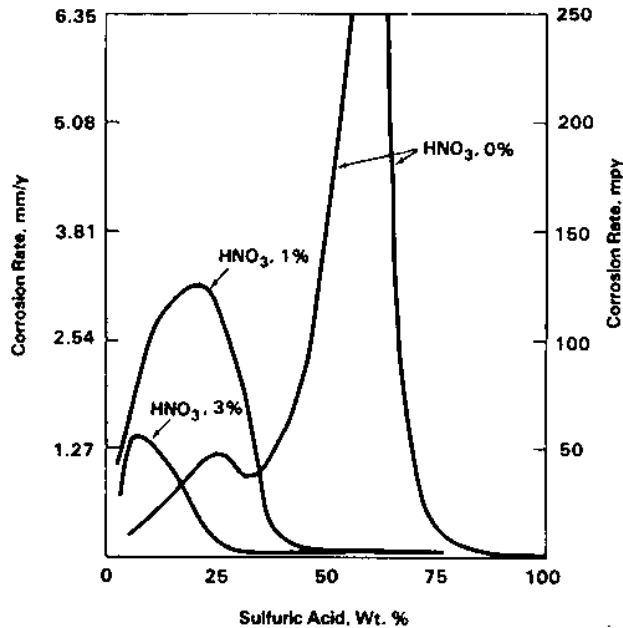


TABLE IV
Effect of Oxidizing Agents and Chlorides on the Corrosion of Stainless Steels and High Nickel Alloys

Alloy	Corrosion Rate					
	10% H ₂ SO ₄		10% H ₂ SO ₄ + 5% HNO ₃		10% H ₂ SO ₄ + 5% NaCl	
	mm/y	mpy	mm/y	mpy	mm/y	mpy
Type 316L stainless steel	0.74	29	0.13	5	17.04	671
INCOLOY alloy 825	0.03	1	0.05	2	5.16	203
CARPENTER alloy 20Cb-3	0.03	1	0.05	2	4.60	181

Conditions: 20 hr. tests in aerated 10% H₂SO₄ @ 66°C (150°F)

TABLE V
Effect of Surface Preparation on Average Corrosion Rate of Annealed, Passivated Stainless Steels in Air-Saturated Sulfuric Acid at 70°C (158°F)

Sulfuric Acid wt. %	Type 304 Stainless Steel				Type 310 Stainless Steel				Type 316 Stainless Steel			
	Specimen Prepared On Dry Grinder	Specimen Prepared On Wet Grinder	Specimen Prepared On Dry Grinder	Specimen Prepared On Wet Grinder	Specimen Prepared On Dry Grinder	Specimen Prepared On Wet Grinder	Specimen Prepared On Dry Grinder	Specimen Prepared On Wet Grinder	Specimen Prepared On Dry Grinder	Specimen Prepared On Wet Grinder	Specimen Prepared On Dry Grinder	Specimen Prepared On Wet Grinder
40	41.91	1650	nil*	nil*	nil	nil	nil	nil	6.10	240	nil	nil
50	60.96	2400	nil	nil	12.95	510	nil	nil	35.81	1410	nil	nil
60	53.34	2100	11.94	470	5.59	220	nil	nil	26.67	1050	nil	nil

* nil is less than 0.00254 mm/y (<0.1 mpy)

less steels would not normally be employed, Riggs demonstrated that prepassivated Type 316 stainless steel could remain indefinitely passive but the introduction of 5 ppm chloride ion into the acid destroyed the passivity and active corrosion resulted.¹⁹

Table IV shows the results of a laboratory test demonstrating the deleterious effect of chloride. If an oxidizing agent is present in addition to chlorides, pitting or crevice corrosion may result. There is, unfortunately, no rule of thumb in regard to the amount of chlorides that will cause difficulty. The amount varies with acid concentration and temperature; investigations have not been sufficiently extensive to determine "safe" chloride concentrations.

Several investigators have shown that chloride ions intensify the attack of austenitic stainless steels when the alloys are in the passive state but can inhibit corrosion when the alloys are actively corroding. However, the use of chlorides to inhibit corrosion is impractical because under conditions which bring about a minimum corrosion rate the stainless steels appear to be subject to stress-corrosion cracking and localized attack.²⁰⁻²²

5. Effect of Surface Grinding

Grinding can have an influence on the corrosion resistance of stainless steels in H₂SO₄ as shown in Table V.¹⁰ In all but one instance, the specimens prepared on a wet-belt grinder had lower corrosion rates than specimens prepared on a dry-belt grinder. The reasons for the higher rates for the dry ground specimens was not entirely understood but were attributed to a combination of a highly stressed surface and high surface temperature reached during grinding.

6. Effect of Velocity

The effect of velocity on the corrosion of austenitic stainless steels can be complex, as shown schematically in Figure 14. This type of behavior has been observed with a series of alloys dynamically tested in accordance with NACE Standard TM-02-70 (see Figures 15 and 16). In this test, specimens are held in a PTFE specimen holder and an impeller causes the acid solution to rotate past the specimens. Although not intentionally aerated, the apparatus is open to air and as the speed of rotation increases, a vortex develops, contributing to aeration

FIGURE 14
EFFECT OF VELOCITY ON THE CORROSION OF
SELECTED ALLOYS

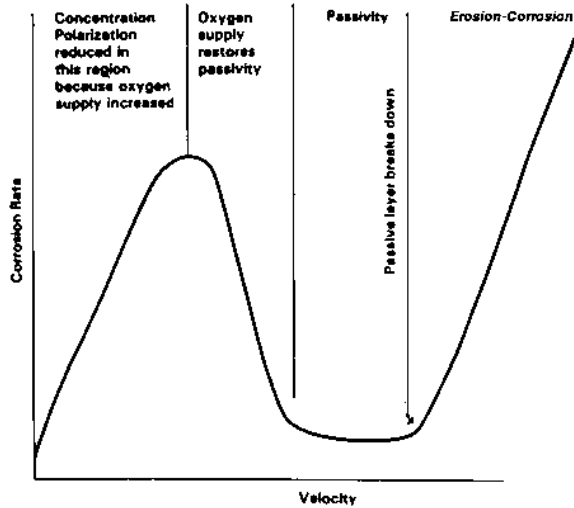
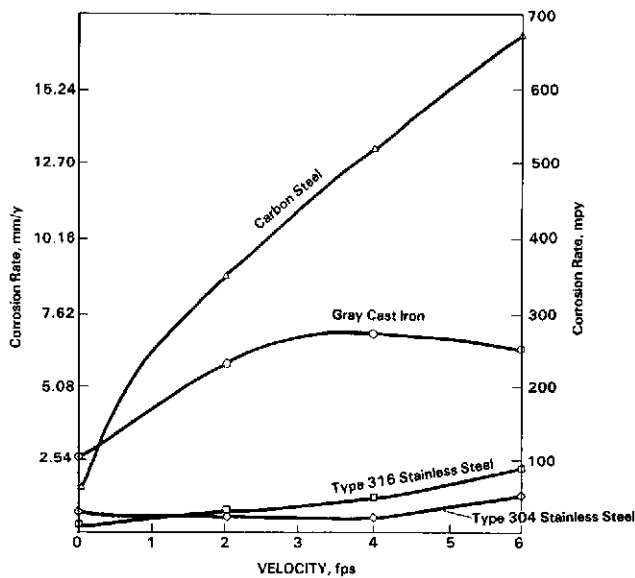


FIGURE 15
EFFECT OF VELOCITY ON CORROSION IN
95% H₂SO₄ AT 49°C (120°F)*

* Average of duplicate specimens for 3 twenty-four hour test periods. Tested in accordance with NACE standard TM-02-70.

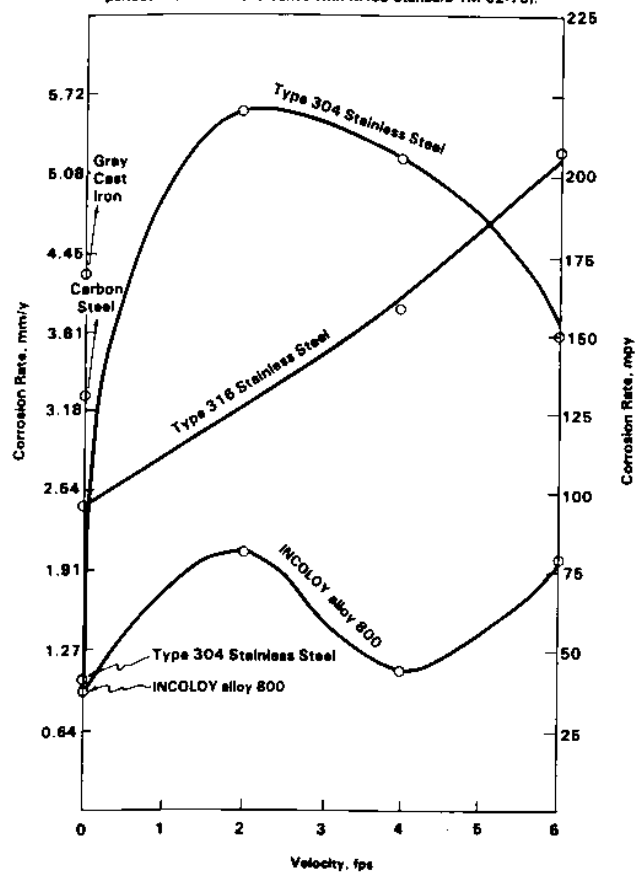


Of the acid. Occasionally, all the zones shown in Figure 14 are observed, but more often just portions of the curve are exhibited according to the resistance of the alloy and the velocity. Thus, increasing velocity may cause an increase in corrosion rate followed by a decrease; or a low, fairly uniform rate may be observed until the passive layer breaks down and erosion-corrosion begins. This may result in some unexpected "crossovers" in which the more resistant alloy under quiescent conditions is less resistant after some velocity is reached.

Extrapolation of these data to plant process conditions does not appear to be warranted because of the oxygen effects and differences between the flow of acid in a pipeline and the test

FIGURE 16
EFFECT OF VELOCITY ON CORROSION OF WROUGHT
ALLOYS IN 95% H₂SO₄ AT 71°C (160°F)*

* (Average of duplicate specimens for 3 twenty-four hour test periods. Tested in accordance with NACE Standard TM-02-70).



method. However, these data do show superior corrosion resistance for the austenitic alloys under dynamic conditions in comparison to carbon steel and gray cast iron, which generally confirms field experience. This same test has generally shown cast stainless steels and higher nickel alloys to be more resistant to velocity effects than their wrought counterparts, as reported in Part II, Section C.

These data also suggest that dynamic tests under field conditions may show alloys such as Type 304 stainless steel or INCOLOY alloy 800 (see Part II, Section M) to be worthy of consideration in concentrated sulfuric acid environments. In fact, plant acid streams usually contain oxidizing agents in the form of corrosion products which could reduce the corrosion rates of these alloys under dynamic conditions to tolerable levels. If tests are run, they should be carried out utilizing "plant acid" rather than CP acid.

Although carbon steel tanks are utilized for the storage of 93-98% sulfuric acid, velocities of 0.6 m/sec (2 fps) or even less greatly accelerate corrosion. Table VI shows the results of tests on full-sized pipe sections at 2 m/sec (6.5 fps) carrying 90-95 percent process (black) sulfuric acid at ambient temperatures.²³

Under such conditions, the stainless steels offer sufficient economical advantage to make them the alloy of choice.

TABLE VI
Corrosion Rates In Flowing
90-95% "Black Acid"

Alloy	Corrosion Raft	
	mm/y	mpy
Type 304 stainless steel	nil*	nil*
Type 316 stainless steel	nil	nil
Gray Cast Iron	<1.52	<60
Carbon Steel	25.4	1000

* nil <0.00254 mm/y (<0.1 mpy)

Conditions: Corrosion rates determined from exposure of spool specimens in 90-95% H₂SO₄ at 2 m/sec (6.5 fps) at ambient temperature. Exposure time not indicated.

7. Effects of Heat Transfer

Experiments utilizing heat transfer showed that a distinction should be made between bulk fluid temperature and metal temperature when considering corrosion rates. This is illustrated in Figure 17 from the work of Fisher who utilized a soldering iron and suitable equipment to transfer 5,000 to 30,000 BTU per hour, per square foot through specimens exposed to 93 percent sulfuric acid on the opposite side.²⁴ The temperature of the metal was obtained from a thermocouple

reading in the center of the 6.35 mm (1/4-inch) thick test coupon and the corrosion rates for these specimens are plotted as triangles in Figure 17. The lower bulk temperature of the sulfuric acid was also measured and coupons exposed separately without heat flux showed corrosion rates as indicated by the circular data points. Low corrosion rates were obtained until at some "critical temperature" passivity was no longer maintained. The critical metal temperatures appear to be approximately 80°C (176°F) and 72°C (162°F) for Type 304 and Type 316 stainless steels respectively. In view of the corrosion rates shown in Figure 17, it appears that "plant acid" containing corrosion products that acted as an inhibitor was used for these tests. The scatter in the data close to these temperatures was probably caused by corrosion potential oscillations between active and passive behavior.

Heat transfer can sometimes be used to advantage; although bulk acid temperature may be high, it is sometimes possible to cool the stainless steels so that tolerable corrosion rates are obtained. Bergstrom and Ladd have indicated that in process tanks containing 88-92 percent H₂SO₄ the free acid is drawn off and the product is water washed, raising the temperature of dilute acid to 160°C (320°F).²⁵ Corrosion test results with and without water cooling are shown in Table VII. Of course, the risk of high corrosion rates in the event of failure to maintain coolant flow has to be considered.

FIGURE 17
HEAT TRANSFER TESTS
93% H₂SO₄ WITH VELOCITY OF 0.1 foot/second

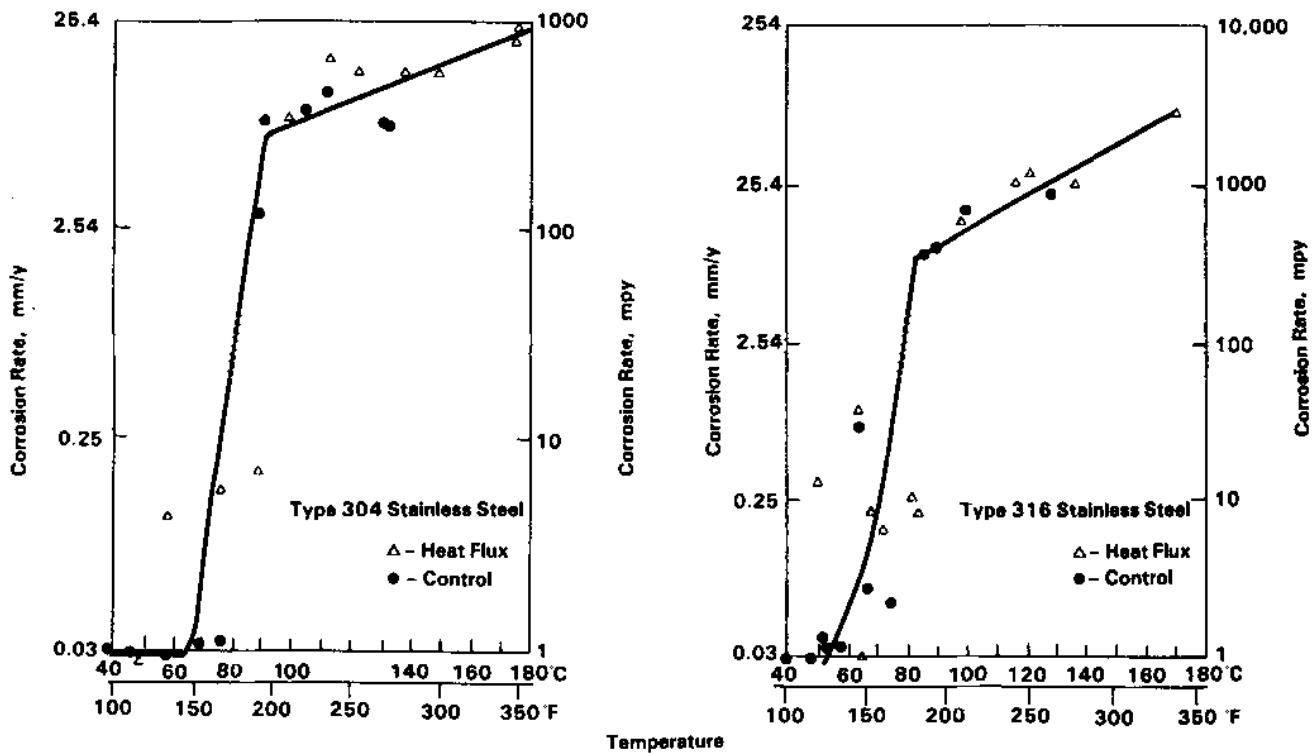


TABLE VII
Comparison of Corrosion Rates in Wash Tank

	Corrosion Rate			
	Normal		Cold-Wall	
	mm/y	mpy	mm/y	mpy
Type 316 stainless steel	6.55	258	0.38	15
CARPENTER alloy 20 Cb	3.18	125	0.13	5
INCOLOY alloy 825	3.43	135	0.13	5

8. Cathodic Protection

Cathodic protection is not usually applicable in aggressive environments such as sulfuric acid. In general, current requirements for impressed current systems and replacement costs for sacrificial anodes have been found to be excessive.

However, cathodic protection was successfully used to minimize intergranular attack of weld heat affected zones of Type 302 stainless steel in dilute sulfuric acid.²⁶ A Type 302 stainless steel, weld fabricated tank was improperly chosen for a process involving dilute (1.5 to 2.5 pH) sulfuric acid at temperatures ranging from 60-100°C (140-212°F). Intergranular corrosion in the heat-affected zones caused failure after one year of service. Repair welds were protected with an impressed current cathodic protection system utilizing silicon cast iron anodes to supply a current density of 12 to 15 ma/ft² and a polarized potential of -.2 to -.25 volts (SCE).

Although cathodic protection was useful in this instance to extend the life of the tank, it would have been more economical to have originally utilized a low carbon stainless steel such as Type 304L.

9. Anodic Protection

Anodic protection is a practical means of extending the useful range of stainless steels and other alloys in many corrosive environments and it has been successfully applied to minimize corrosion of carbon steel and stainless steel in sulfuric acid service.²⁷⁻³⁴

Edeleanu was the first to suggest the use of anodic protection.³⁵ Austenitic stainless steels such as Types 304, 304L, 316, 316L and 321 can be anodically protected at practically all concentrations of sulfuric acid at temperatures up to the boiling point.^{35, 36} The reduction in corrosion rate that can be obtained in going from the freely-corroding active-state to the protected passive-state can be startling. A 100,000 fold reduction in corrosion rate is possible!²⁰ The efficiencies achieved are not always this high but even in the 20% to 60% sulfuric acid concentration range where maximum corrosion rates are obtained with stainless steels, anodic protection appears to reduce corrosion rates by a factor of at least 500.³⁷

One misconception about the passive state is that it always leads to low corrosion rates. It is possible to have fairly high corrosion rates in the passive condition and thus, there are practical limitations in regard to anodic protection. Foroulis studied the anodic protection of Type 316 stainless steel in the concentration range of 3% to 92% sulfuric acid at temperatures of 34-121°C (94-249°F). He concluded that anodic protection is practical for the entire range of concentration studied at temperatures as high as 75°C (167°F) and for the concentration

ranges of less than 20% and greater than 60% anodic protection is feasible to 100°C (212°F).³⁷ If anodic protection is utilized in some of the more aggressive environments suggested by Foroulis, the consequences of a power failure should be considered. In a critical installation, the costs associated with an emergency alternate power supply might be compared with the cost of more corrosion resistant alloys. Figures 18-21, from the work of Foroulis, show how critical and passive current densities vary with concentration and temperature. Notice the small current density requirements to maintain passivity.

Critical current density is important because the equipment used to control potential must have the power to drive the potential past this point to obtain the more noble potentials associated with passivity. Therefore, an alloy with a low critical current density under the intended operating conditions is preferred (and sometimes required) to other alloys exhibiting high critical current densities. Figure 18 also suggests that passivity could be readily obtained while the acid is cold and then maintained while the equipment is brought up to operating temperature. Fyfe, et al. have indicated that another possibility to minimize the current requirement of the power supply is to progressively passivate by bringing the corroder into contact with the equipment one section at a time or by slowly filling a storage tank or heat exchanger.³⁴

FIGURE 18
EFFECT OF TEMPERATURE ON CRITICAL CURRENT FOR TYPE 316 STAINLESS STEEL IN 63.5% H₂SO₄

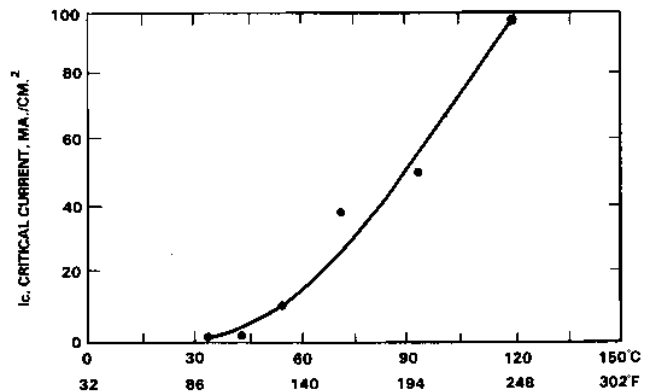
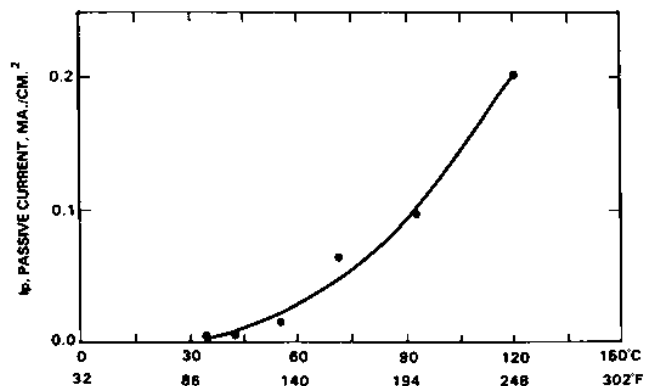


FIGURE 19
EFFECT OF TEMPERATURE ON PASSIVE CURRENT FOR TYPE 316 STAINLESS STEEL IN 63.5% H₂SO₄



Another important consideration with regard to anodic protection is throwing power in the solution of interest. Fortunately, sulfuric acid is generally a good conductor of electricity; Sudbury et al. obtained anodic protection in 18.3m (60 ft.) of 3/4-inch Type 304 stainless steel tubing that had thirteen 180 degree bends and two 90 degree elbows when circulating 67 percent H_2SO_4 at 24°C (75°F).²⁷ In less conductive solutions, the voltage output from the cathode must still be able to “throw” current to all parts of the equipment for protection to be obtained.

Still another consideration is cathode current density which will be limited by concentration polarization. The cathode to anode surface area ratio must be large enough to passivate the anodic surfaces at a reasonable rate. Both platinum and HASTELLOY alloy C-276 have been used as cathodes for anodic protection systems.

The electrical potential range for anodic protection has been selected by anodic polarization curves determined by conventional techniques.³⁴ However, because of inherent difficulties with these techniques, the optimum potential may not always be apparent. This is because there may be contaminants present in process acids which undergo anodic (electron releasing) reactions unrelated to the achievement of passivity. Kain and Morris developed a technique involving an active-to-noble potential scan followed by a noble-to-active potential

scan at a rate of 60 V/hr. that apparently overcomes these difficulties.³⁸ A low current region was obtained on the reverse scans and the authors suggested control at the midpoint of these regions. The optimum potentials selected by their technique were verified by corrosion rates determined by the weight loss of controlled potential test electrodes.

A large potential gradient exists in crevices during anodic polarization because of the high electrical resistance of the narrow electrolyte path. For this reason, France and Greene have suggested choosing alloys with small critical current densities which will both reduce the current requirements for initial passivation and improve the crevice-passivating ability of the system.³⁹

The deleterious effect of chlorides in sulfuric acid may sometimes be overcome by anodic protection. Table VIII shows the results of laboratory tests on Types 304 and 310 stainless steels in I Normal (5 percent) and 10 Normal (50 percent) sulfuric acid at 30°C (86°F) with various chloride additions. It is interesting to note that stress-corrosion cracking of Type 304 stainless steel in the strongest acid and chloride concentration was prevented by anodic protection. Several

An anodically protected sulfuric acid plant drying column sulfuric acid cooler. Both shell and tubes utilize Type 316L stainless steel. Sulfuric acid is on the shell side of this unit and cooling water is on the tube side. The electrical connections to the HASTELLOY alloy C-276 cathodes are visible at the channel cover. The cathodes run the entire length of the bundle and occupy the space that would normally be used for two 3/4-inch O.D. tubes in the bundle. Anodically protected Type 316L coolers are also used for Absorber and Product acid cooling at this plant.

FIGURE 20
DEPENDENCE OF CRITICAL CURRENT
OF TYPE 316 STAINLESS STEEL ON PER CENT H_2SO_4

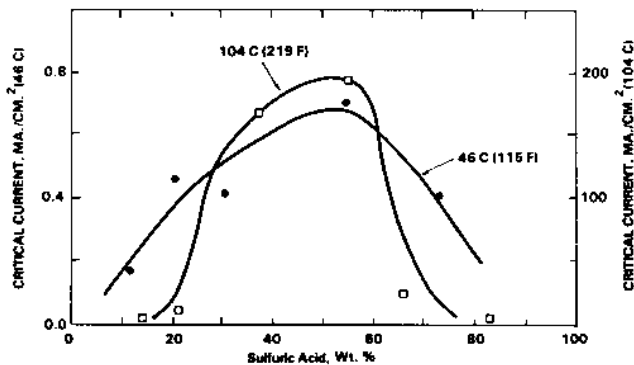
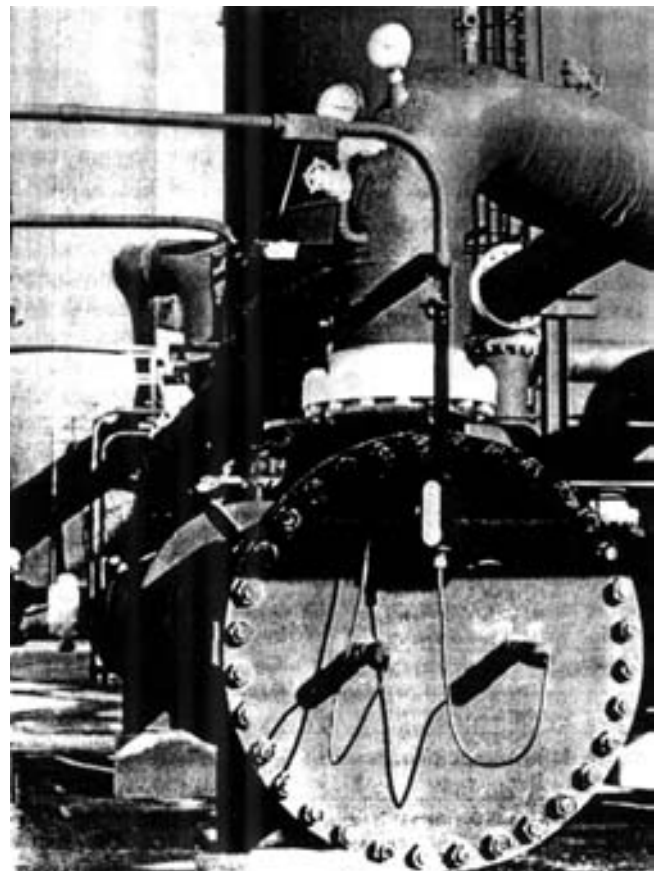
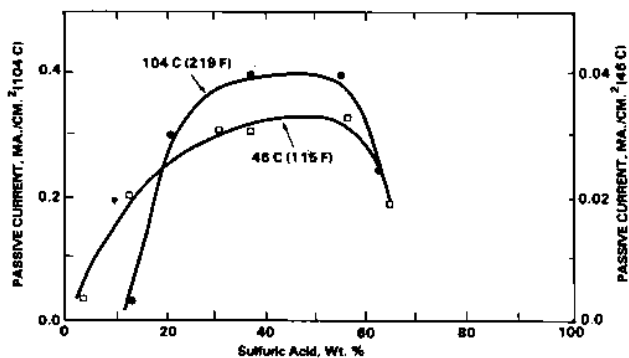


FIGURE 21
DEPENDENCE OF PASSIVE CURRENT
OF TYPE 316 STAINLESS STEEL ON PER CENT H_2SO_4



investigators have suggested that anodic protection could sometimes be used for protection of stainless steel equipment handling chloride contaminated sulfuric acid.^{20, 21} However, care should be taken to stay below the pitting potential.

There are references in the literature that indicate anodic protection can sometimes be used to prevent intergranular corrosion in sensitized stainless steel. Juchniewicz et al. working with severely sensitized 2H18N9 (a Polish stainless steel similar to AISI Type 302) containing 0.2 percent carbon was able to anodically protect the alloy from intergranular corrosion and preferential corrosion of second phase ferrite which developed with this alloy, in 30 percent H₂SO₄ + 1% NaCl at 20-30°C (68-86°F).³³ Corrosion was considerably reduced but not eliminated. France and Greene showed that it was possible to prevent intergranular corrosion of sensitized Type 304 stainless steel in 1N H₂SO₄ (5%) plus 5 g/l Fez (SO₄)₃ • 6H₂O by maintaining a potential of 0.6V (SCE).⁴⁰ However, if the sample was allowed to become active, intergranular attack occurred. It was hypothesized that once intergranular corrosion was initiated at an active potential, it could continue at a passive potential where the attack would not be initiated. Thus, the use of anodic protection to increase the life of improperly selected or heat treated stainless steel may be possible.

TABLE VIII
Comparison of Corrosion Rates With
And Without Anodic Protection in
Chloride Contaminated Sulfuric Acid²⁰

Stainless Steel Type	Environment	Corrosion Rates			
		[Air Exposed @ 30°C (86°F)]		Protected	
		Unprotected	Protected	mm/y	mpy
		mm/y	mpy	mm/y	mpy
310	N H ₂ SO ₄	0.01	0.35	–	–
	N H ₂ SO ₄ + 10 ⁻³ N NaCl	0.01	0.27	nil	nil
	N H ₂ SO ₄ + 10 ⁻³ N NaCl	**	**	nil	nil
	N H ₂ SO ₄ + 10 ⁻¹ N NaCl	0.05	2.1	nil	nil
	N H ₂ SO ₄ + 0.5N NaCl	0.05	2.1	–	–
310	10N H ₂ SO ₄	7.49	295.0	–	–
	10N H ₂ SO ₄ + 10 ⁻⁶ N NaCl	8.38	330.0	nil	nil
	10N H ₂ SO ₄ + 10 ⁻³ N NaCl	0.23	9.0	nil	nil
	10N H ₂ SO ₄ + 10 ⁻¹ N NaCl	0.64	25.0	nil	nil
	10N H ₂ SO ₄ + 0.4N NaCl	–	–	0.01	0.2
	10N H ₂ SO ₄ + 0.5N NaCl	0.66	26.0	–	–
304	N H ₂ SO ₄	0.40	15.7	–	–
	N H ₂ SO ₄ + 10 ⁻⁶ N NaCl	0.36	14.0	nil	nil
	N H ₂ SO ₄ + 10 ⁻³ N NaCl	0.07	2.9	nil	nil
	N H ₂ SO ₄ + 10 ⁻¹ N NaCl	0.08	3.2	0.01	0.2
	N H ₂ SO ₄ + 0.5N NaCl	0.06	2.5	–	–
304	10N H ₂ SO ₄	34.04	1340.0	–	–
	10N H ₂ SO ₄ + 10 ⁻⁶ N NaCl	49.02	1930.0	nil	nil
	10N H ₂ SO ₄ + 10 ⁻³ N NaCl	28.58	1125.0	nil	nil
	10N H ₂ SO ₄ + 10 ⁻¹ N NaCl	1.96	77.0	0.01	0.2
	10N H ₂ SO ₄ + 0.5N NaCl	2.87	113.0***	0.04	1.6

* nil = less than 0.00254 mm/y (<0.1 mpy)

** specimen remained passive during corrosion test

*** specimens exposed to this environment cracked without anodic protection

10. Stress-Corrosion Cracking

Stress-corrosion cracking of austenitic stainless steels in chloride contaminated sulfuric acid is more of a laboratory curiosity than a problem in industry. Chlorides in sufficient quantity to cause stress-corrosion cracking are not present in plants manufacturing sulfuric acid nor in the acid produced. Where chloride contamination exists in processes utilizing sulfuric acid, it is rarely, if ever, present in quantities sufficient to cause stress-corrosion cracking.

There are very few environments that will produce stress-corrosion cracking at room temperature and so, when it was discovered that austenitic stainless steels would crack at this low temperature in sulfuric acid contaminated with large amounts of chloride (0.1- 1.0 N NaCl has been used in laboratory investigations), considerable research effort was expended investigating the phenomena.^{20, 21, 41-45} The investigators usually utilized 25-50 percent sulfuric acid but there are no data to suggest that stress-corrosion cracking is not possible in other concentrations. Both transgranular and intergranular cracking have been reported, although more recent work has indicated that the intergranular cracking was caused by selective grain boundary corrosion (in 304L stainless steel).⁴⁶ Understanding of stress-corrosion cracking was advanced by the referenced investigations as it was shown that the cracking occurred in the active potential region and could be prevented by the use of anodic protection to maintain the potential in the passive region.²⁰

Sedriks, working with conventional U-bend specimens in 50 percent sulfuric acid plus 3 percent sodium chloride and a number of other chloride environments, has shown that an increase in nickel content of the alloy is beneficial in regard to resistance to stress-corrosion cracking, as shown in Table IX.⁴⁷

In situations where the use of austenitic stainless steels may be questionable because of the presence of chlorides, one of the alloys with higher nickel content discussed subsequently should be considered.

11. Summary

Austenitic stainless steels are generally utilized in either dilute or concentrated sulfuric acid. The range of their application is usually extended by the presence of oxidizing agents such as air, nitric acid, ferric or cupric ion in the sulfuric acid, or restricted by the presence of chlorides and reducing agents in the sulfuric acid. Anodic protection has also been used to advantage to extend the range of application.

A word of caution is needed for anyone who seeks absolute corrosion rates for austenitic stainless steels in sulfuric acid environments. The test results reported have been determined with commendable precision. But, this precision applies to the particular test conditions and extrapolation to other conditions may lead to erroneous conclusions. Such a warning is applicable to corrosion data in general, but it is particularly appropriate for stainless steels in sulfuric acid because these alloys may exhibit either activity or passivity, and the difference in corrosion rates between active and pas-

TABLE IX
Stress-Corrosion Cracking in 50% H₂SO₄
Plus 3% NaCl at 30°C (86°F)

Alloy	Nickel Content (Wt. %)	Average Time To Failure (days)
Type 304 stainless steel	8.89	1
Type 310 stainless steel	21.59	NF*
INCOLOY alloy 800	31.90	NF
INCOLOY alloy 600	76 (nominal)	NF

* NF—No failure of the U-bend specimen during the 30 day test period

sive corrosion can be several orders of magnitude. If there is any doubt as to the applicability of an austenitic stainless steel in a sulfuric acid environment, it would be prudent to perform a corrosion test under the actual exposure conditions.

C. CAST STAINLESS STEELS

Unlike the fully austenitic, wrought 300 series stainless steels, their cast counterparts usually contain some second phase ferrite in the microstructure which is desirable so as to obtain sound castings free of cracks. It has been shown by several investigators that either the ferrite or the austenite in a duplex structured stainless steel is subject to a certain degree of selective attack in sulfuric acid solutions.⁴⁸⁻⁴⁹ Since these investigators usually worked with only one sulfuric acid concentration, they would report selective attack of either the ferrite or the austenite. Forbes-Jones and Kain working with several cast stainless steels, and also some high nickel alloys, showed that cast materials exhibited some degree of selective attack of different phases in the microstructure.⁵⁰ The degree of attack was related to the amount and morphology of the susceptible phase. However, the same phase was not always susceptible. For instance, in 25 percent sulfuric acid at 80°C (176°F), austenite was susceptible (in CF-8M and CD4-MCu) but the ferrite was more susceptible to attack in 93 percent

sulfuric acid at 80°C (176°F). In general, the cast alloys with the more homogeneous microstructure and the more uniform distribution of phases were more resistant to corrosion. Their corrosion test results are shown in Table X. Other test results for cast stainless steels are shown in Tables I, XI, XVIII, LIII, LIV and LVII. Based upon the foregoing, annealed and quenched castings should be employed for sulfuric acid service so as to obtain solution of carbides and homogenize the microstructure. With this precaution, the cast stainless steels will yield corrosion resistance approximately equivalent and sometimes superior to their wrought counterparts. As with the wrought versions, low carbon or stabilized grades should be selected if weld repair is anticipated.

Cast ACI CD-4MCu, which includes DURCOMET alloy 100 and ELCOMET alloy 48, is a duplex (i.e. austenitic-ferritic) stainless steel that does not have a close wrought counterpart except for the proprietary alloy FERRALIUM. (See Part II, Section D1). This alloy contains the same alloying elements as CN-7M but generally in lower amounts and its corrosion resistance lies between CN-7M and less highly alloyed CF-8M. Figure 22 is an isocorrosion chart for this alloy. The mechanical properties and erosion resistance are higher than the other cast stainless steels discussed in this section.

ILLIUM alloy PD is a duplex cast stainless steel with mechanical properties, corrosion and erosion resistance superior to CF-8M. Although similar to CD-4MCu, it differs from that alloy because it contains cobalt in an amount not found in CD-4MCu and it does not contain copper. The absence of copper leads to a slightly lower corrosion resistance in sulfuric acid in comparison to CD-4MCu, as shown by Figure 23.

The effect of velocity on the corrosion of several cast stainless steels is shown by Figures 24 and 25 which were obtained by testing in reagent grade acid in accordance with NACE Standard TM-02-70. Comparison with Figures 15 and 16 generally indicates the cast stainless steels to be superior to their wrought counterparts. As with the wrought stainless steels, extrapolation of these data to plant process conditions does not appear to be warranted because of differences in the impurity content of the acids and differences between the flow of acid in a pump or valve and the test method.

The erosion-corrosion resistance of cast stainless steels has been determined by weight loss studies utilizing disc speci-

TABLE X
Average Corrosion Rates* For Various Cast
Alloys in Sulfuric Acid at 80°C (176°F)

ACI Alloy	Nearest Comparable Wrought Alloy	Corrosion Rate in Acid Concentration Shown									
		10%		25%		50%		78%		93%	
		mm/y	mpy	mm/y	mpy	mm/y	mpy	mm/y	mpy	mm/y	mpy
CW 12M-2	HASTELLOY alloy C	0.02	0.8	0.04	1.5	0.17	6.7	0.92	36.3	0.07	2.9
IN-862	AL-6X	0.94	37.2	4.1	162	>182.5	>7185	3.7	145	3.94	155
CN-7M	CARPENTER 20	0.51	20.1	0.57	22.5	0.32	12.6	1.62	63.6	0.83	32.7
CF-8M	Type 316 stainless steel	1.32	52	84.7	3334	>942	>37100	8.7	342	6.1	240
CD4-MCu	FERRALIUM	0.002	0.1	1.23	48.6	>612	>24100	4.6	180	1.47	58

* Averaged corrosion rates of up to five 24-hour test periods in non-aerated solutions at 80°C (176°F)



A copper plant vat leaching area in which all of the pumps and valves are fabricated from cast ACI CF-8M and CF-3M and wrought Types 316 and 316L stainless steel to handle the dilute sulfuric acid leach liquor.

FIGURE 22

ISOCORROSION CHART FOR ACI CD-4MCu IN SULFURIC ACID

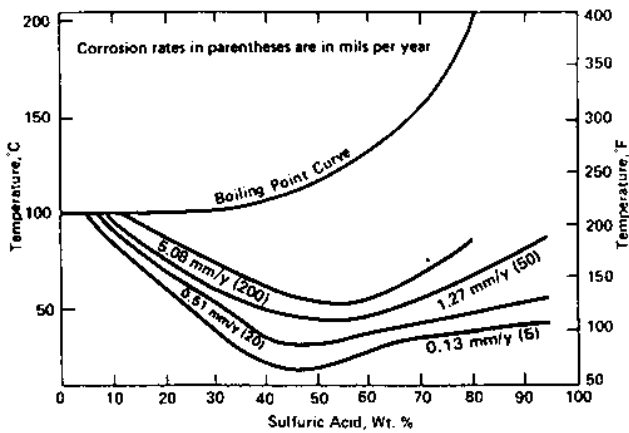


FIGURE 23

ISOCORROSION CHART FOR ILLIUM ALLOY PD IN SULFURIC ACID

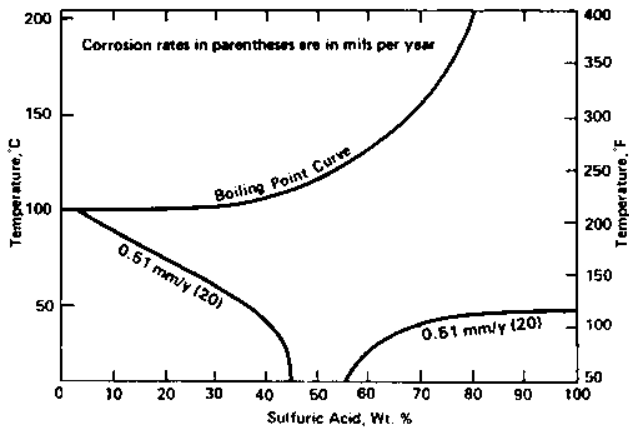


FIGURE 24

EFFECT OF VELOCITY ON CORROSION OF CAST ALLOYS IN 95% H₂SO₄ AT 49°C (120°F)

Average of duplicate specimens for 3 twenty-four hour test periods. (Tested in accordance with NACE Standard TM-02-70)

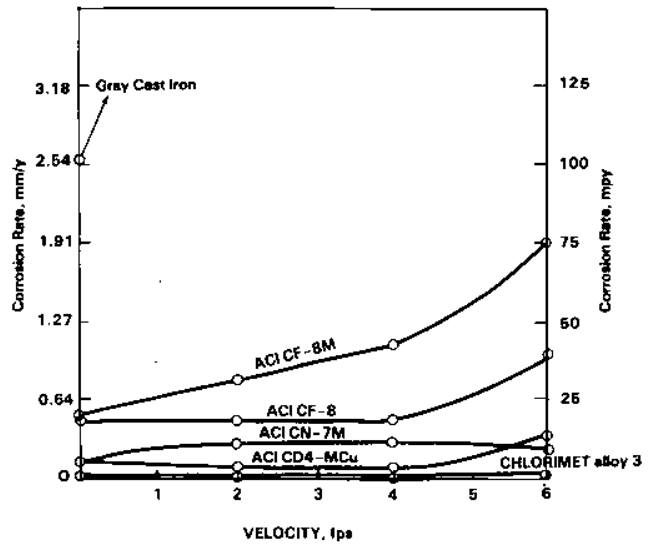
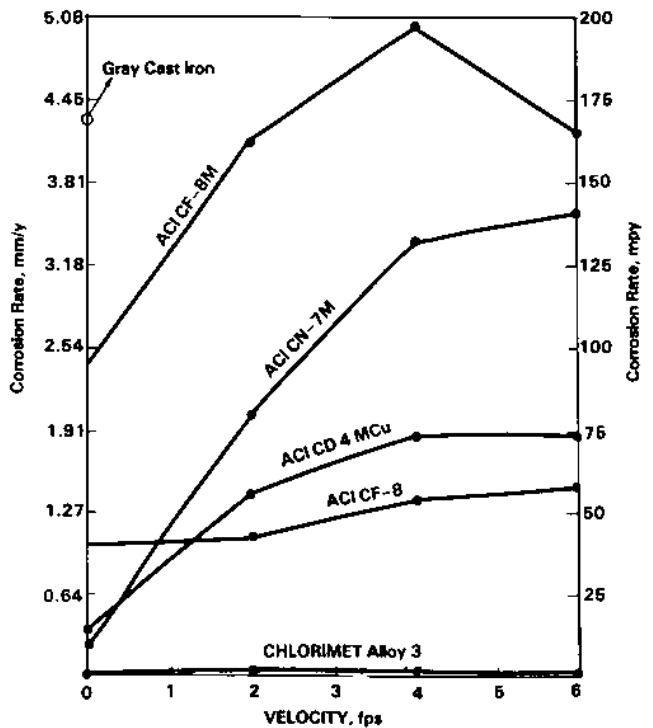


FIGURE 25

EFFECT OF VELOCITY ON CORROSION OF CAST ALLOYS IN 95% H₂SO₄ AT 71°C (160°F)

(Average of duplicate specimens for 3 twenty-four hour test periods. Tested in accordance with NACE Standard TM-02-70)

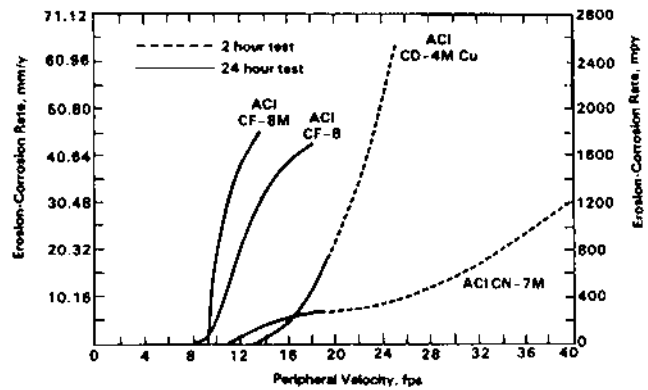


mens that were rotated in a 96 percent sulfuric acid - 20 volume percent alumina slurry at room temperature for either 24 hour periods (at peripheral velocities up to 20 fps) or 2 hour periods (at peripheral velocities of 20-40 fps).⁵¹ The alumina used was reagent grade with a particle size of 53-74 microns.

Negligible attack was measured for virtually all alloys at peripheral velocities up to 8 fps, but significant differences were observed among the alloys at higher velocities as shown by Figure 26.⁵² ACI CF-8M at several different ferrite levels exhibited a dramatic increase in attack above 9 fps. ACI CF-8 was slightly better than CF-8M but the best resistance was exhibited by the duplex austenite-ferrite CD-4MCu and fully austenitic CN-7M alloys. (Corrosion of CN-7M is discussed in greater detail in Part II, Section E). However, the authors' caution that these data should only be used as a general guide regarding the relative erosion-corrosion resistance of various cast alloys.

There are a few proprietary precipitation hardening cast stainless steels that do not have ACI designations. Little corrosion data exist for these alloys but some data are available for COOPER alloys PH-55A, PH-55B and PH-55C compared to Type 316 stainless steel as shown in Table XI from the work of Motts.⁵³ The corrosion resistance of precipitation hardening alloys is dependent upon their metallurgical condition and hence heat treatment. The heat treatment given the test pieces was not stated but is believed to be a solution anneal.

FIGURE 26
EROSION-CORROSION OF CAST ALLOYS IN ROOM TEMPERATURE SLURRIES OF 96% H₂SO₄ PLUS 20 V/O Al₂O₃



CF-8M Included specimens containing 0, 15, and 38% Ferrite
 CF-8 Included specimens containing 0 and 16% Ferrite

TABLE XI
Static Corrosion Rates of Cast PH-56 Alloys Versus ACI CF-8M

Sulfuric Acid Concentration		Temperature		Corrosion Rate							
				PH-55A		PH-55B		PH-55C		ACI CF-8M Stainless Steel	
(%)		°C	°F	mm/y	mpy	mm/y	mpy	mm/y	mpy	mm/y	mpy
50	(Ambient)	21	70	0.47	18.7	0.02	0.8	0.01	0.4	34.44	1356
65	"	21	70	0.46	18.2	0.03	1.1	0.05	2.0	7.87	310
78	"	21	70	0.09	3.7	0.02	0.6	0.01	0.2	2.08	82
10	"	80	176	0.59	23.2	0.02	0.6	0.003	0.1	2.54	100
20	"	80	176	11.31	445.2	2.81	110.6	0.01	0.5	12.19	480
30	"	80	176	-	-	-	-	3.80	149.6	-	-
78	"	80	176	3.47	136.8	3.34	131.4	0.15	6.1	38.1	1500
93	"	80	176	1.14	44.8	0.30	11.8	0.02	0.6	6.60	260
1	(Boiling)	100	212	0.03	1.3	0.21	8.3	0.01	0.4	1.39	55
2	"	100	212	1.34	52.8	1.72	67.6	0.03	1.2	3.81	150
5	"	100	213	6.89	271.3	7.39	291.1	1.12	44.2	6.71	264

Note: Corrosion coupons believed to be in solution annealed condition

D. SPECIAL WROUGHT STAINLESS STEELS

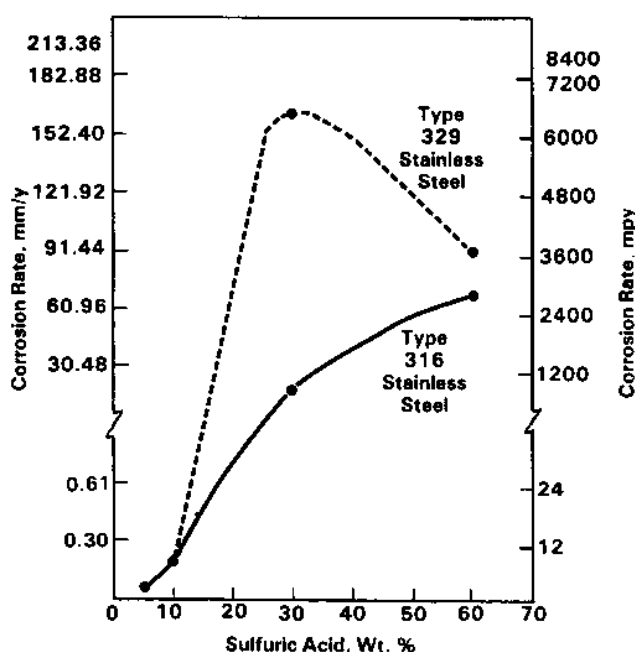
1. Duplex (Austenitic-Ferritic) Stainless Steels

AISI Type 329 stainless steel (which includes CARPENTER alloy 7 Mo) is available in a hardenable grade and a non-hardenable grade. The non-hardenable grade is generally more corrosion resistant and can be weld fabricated, whereas with the hardenable grade in the aged condition some corrosion resistance is lost and welding is not recommended. Lula, et al. have indicated that Type 329 stainless steel is satisfactorily resistant in sulfuric acid up to 10 percent concentration at 38°C (100°F) but is rapidly attacked at elevated temperatures except in extremely dilute concentrations.⁵⁴ Figure 27 shows corrosion rates at 38°C (100°F).

FERRALIUM is a duplex stainless steel available in wrought form but similar in composition to cast CD-4MCu. This alloy can be age-hardened to strengthen mechanical properties and erosion resistance but when this is done, weldability is sacrificed and corrosion resistance is reduced. For instance, solution annealed FERRALIUM corroded at 1.17 mm/y (46 mpy) and at 2.62 mm/y (103 mpy) in the aged condition [4 hrs. at 510°C (950°F)] in boiling five percent reagent grade sulfuric acid. Corrosion data for this wrought alloy in sulfuric acid is very sparse, but, based upon its composition, it would be expected to have corrosion resistance between Type 316 stainless steel and cast CD-4MCu.

FIGURE 27

SULFURIC ACID CORROSION RATES AT 38°C (100°F)



2. Precipitation Hardening Stainless Steels

The corrosion resistance of precipitation hardening stainless steels depends upon their structure (and hence heat treatment) and their chemical composition. Aging can cause chromium carbide precipitation and loss of some of the corrosion resistance. There are a number of alloys in this classification with various tradenames.

Corrosion data for the precipitation hardening stainless steels are generally sparse. The greatest amount of data is available for AISI/UNS S17400, S17700 and S15700 because of the work of Halbig and Ellis.⁵⁵ These precipitation hardening alloys are better known by their tradenames which include ARMCO 17-4 PH, 17-7 PH and 15-7 Mo; REPUBLIC 17-4 PH, 17-7 PH and 15-7 Mo; CRUCIBLE 17 Cr-4 Ni; and CARPENTER Custom 630. Corrosion rates in dilute sulfuric acid after various thermal treatments for several precipitation hardening stainless steels in comparison to Type 304 stainless steel are shown in Table XII. Because end grain and side grain attack occurred to a much greater extent on the bar stock than on the sheet specimens, the corrosion rates on the bar specimens were sometimes much higher than on the sheet specimens.

A meager amount of short term corrosion data in dilute sulfuric acid is shown in Table XIII for S35000 and S45000 in comparison to several other alloys. Their corrosion resistance is generally superior to Type 304 stainless steel in sulfuric acid under these test conditions.

3. Chromium-Nickel-Manganese Stainless Steels

Manganese and nitrogen have austenite stabilizers and, in periods of short nickel supply, these elements have been substituted for a portion of the nickel in some austenitic stainless steels. In general, the corrosion resistance of low nickel Type 216 and 216L stainless steels is equal to or, in some instances, superior to Type 316 and 316L stainless steels. However, in dilute sulfuric acid, nickel is an important alloying element and the corrosion resistance of Type 216 is slightly inferior to Type 316 stainless steel, as shown in Table XIV.

In addition to stabilizing austenite, manganese and nitrogen strengthen austenitic stainless steels and improve resistance to abrasion and galling. Armco Inc. has taken advantage of these attributes and markets a series of proprietary alloys with the tradename NITRONIC.

The most highly alloyed of this series of alloys, NITRONIC alloy 50, is also the most corrosion resistant in sulfuric acid. The corrosion resistance of NITRONIC alloy 50 is superior to Type 316 stainless steel in sulfuric acid as shown by Table XV. When weld fabrication is employed with this alloy, consideration should be given to a subsequent anneal at 1121°C (2050°F) to minimize the possibility of intergranular corrosion in heat affected zones.

NITRONIC alloy 60 is a galling and wear resistant alloy with corrosion resistance in dilute sulfuric acid that lies between Types 304 and 316 stainless steels as shown in Table XVI. This alloy should be utilized in the annealed condition as supplied by the manufacturer; if weld fabrication is employed, it should be given a subsequent anneal at 1066°C (1950°F) for maximum corrosion resistance.

TABLE XII
Corrosion Rates of Precipitation Hardening
Stainless Steels in Dilute Sulfuric Acid

			Corrosion Rate**									
			H ₂ SO ₄ @ 36°C (95°F)				H ₂ SO ₄ @ 80°C (176°F)					
Alloy (AISI/UNS)	Form	Heat Treatment *	1%		2%		5%		1%		2%	
			mm/y	mpy	mm/y	mpy	mm/y	mpy	mm/y	mpy	mm/y	mpy
S17400	Bar	H469°C(875°F)	0.00	0.0	0.00	0.0	0.04	1.7	0.03	1.1	0.27	10.8
	"	H496°C(925°F)	0.00	0.0	0.00	0.0	0.04	1.4	0.03	1.3	0.19	7.4
	"	H552°C(1025°F)	0.00	0.0	0.00	0.0	0.02	0.7	0.00	0.0	0.25	10.0
	"	H600°C(1075°F)	0.00	0.0	0.00	0.0	0.29	11.3	0.02	0.9	0.32	12.5
	"	H621°C(1150°F)	0.03	1.2	0.01	0.5	0.03	1.0	0.08	3.0	0.60	23.7
S517400	Bar	H496°C(925°F)	0.00	0.0	0.00	0.0	0.19	7.6	0.04	1.4	0.26	10.3
	"	H552°C(1025°F)	0.03	1.0	0.02	0.9	0.29	11.6	0.07	2.8	0.17	6.8
	"	H621°C(1150°F)	0.01	0.3	0.02	0.7	0.32	12.6	0.02	0.7	0.32	12.5
S17400	Bar	H496°C(925°F)	0.01	0.3	0.02	0.7	0.08	3.2	0.02	0.7	0.13	5.2
	"	H552°C(1025°F)	0.00	0.0	0.00	0.0	0.20	7.7	0.02	0.7	0.25	9.9
	"	H621°C(1150°F)	0.00	0.0	0.00	0.0	0.34	13.3	0.02	0.7	0.36	14.0
S17700	Bar	TH454°C(850°F)	13.72	540	7.57	298	30.23	1190	33.53 ³	1320 ³	61.47 ³	2420 ³
	"	TH510°C(950°F)	7.19	283	17.78 ³	700 ³	53.59 ²	2110 ²	34.54 ³	1360 ³	63.25 ³	2490 ³
	"	TH566°C(1050°F)	0.10	4.1	1.35	53	7.19	283	7.21	284	17.93	706
	"	TH621°C(1150°F)	0.12	4.9	0.20	7.7	3.94	155	3.12	123	11.20	441
	"	RH510°C(950°F)	1.01	39.9	3.40	134	14.07	554	15.98 ³	629 ³	4.29 ³	169 ³
S17700	Sheet	TH454°C(850°F)	0.01	0.5	0.20	0.8	21.08 ²	830 ²	19.20 ¹	756 ¹	47.24 ¹	1860 ¹
	"	TH510°C(950°F)	3.38	133	9.35	368	40.39 ¹	1590 ¹	20.80 ²	819 ²	48.01 ¹	1890 ¹
	"	TH566°C(1050°F)	0.02	0.6	0.04	1.4	5.74	226	6.55	258	15.32	603
	"	TH593°C(1100°F)	0.01	0.4	0.02	0.6	1.17	46	0.70	27.7	10.54	415
	"	TH621°C(1150°F)	0.02	0.6	0.02	0.8	4.95	195	0.82	32.4	12.70	500
	"	RH510°C(950°F)	0.01	0.3	0.02	0.9	3.63	143	6.73	265	19.02 ²	749 ²
	"	RH566°C(1050°F)	0.20	7.8	1.52	60	19.89	783 ³	10.39	409	26.16 ²	1030 ²
S17700	Sheet	TH454°C(850°F)	0.01	0.4	0.01	0.2	11.86	467	14.73	580 ¹	35.31 ¹	1390 ¹
	"	TH510°C(950°F)	0.84	33	2.95	116	21.67 ²	853 ²	13.03 ³	513 ³	37.59 ¹	1480 ¹
	"	TH566°C(1050°F)	0.01	0.4	0.01	0.4	0.56	22	0.05	1.8	3.68	145
	"	TH593°C(1100°F)	0.01	0.2	0.01	0.5	0.41	16	0.04	1.6,	0.91	36
	"	TH621°C(1150°F)	0.01	0.2	0.02	0.6	1.73	68	0.02	0.8	4.34	171
	"	RH510°C(950°F)	0.00	0.0	0.01	0.5	3.20	126	8.36	329	21.32 ²	839 ²
S15700	Sheet	TH510°C(950°F)	0.00	0.0	0.68	26.7	6.60	260	19.30 ²	760 ²	35.56 ¹	1400 ¹
	"	TH566°C(1050°F)	6.93	273	1.98	78	11.51	453	14.22 ³	560 ³	33.02 ²	1300 ²
	"	RH510°C(950°F)	0.01	0.5	0.02	0.7	12.24	482	17.53 ²	690 ²	36.58 ¹	1440 ¹
Type 304	Bar	A	0.71	28	1.45	57	6.10	240	8.89	350	12.19	480
Type 304	Sheet	A	0.01	0.4	0.01	0.4	0.03	1.2	0.03	1.2	1.70	67
	"	A	0.01	0.4	0.06	2.3	0.36	14.3	1.10	43.3	1.57	62

* A = Annealed at 1066°C (1950°F) and quenched
H = Hardened at indicated temperature
T = Conditioned at 760°C (1400°F)
R = Refrigeration at -73°C (-100°F)

** Rates were determined by immersion for five 48-hour periods, except where followed by a number in parentheses. The number in the parentheses indicates the number of 48-hour periods before the test was terminated, specimens were "activated" before last three periods. Where rates of replicates varied, highest rate is given.

Note: All alloys tested were produced by Armco Steel Corporation.

TABLE XIII
Corrosion Rates of S35000 and S45000 in Dilute Sulfuric Acid

AISI Type	Heat Treatment ¹ or Hardness	Corrosion Rate			
		1% H ₂ SO ₄ @ 38°C (100°F) ²		5% H ₂ SO ₄ @ 24°C (75°F) ³	
		mm/y	mpy	mm/y	mpy
S35000 (ALLEGHENY AM 350)	SCT	0.03	1.3	–	–
“	DA	2.36	93	–	–
S45000 (CARPENTER CUSTOM 450)	SA	–	–	0.03	1
“	H482°C (900°F)	–	–	0.03	1
“	H538°C (1000°F)	–	–	0.08	3
“	H621°C (1150°F)	–	–	0.23	9
304	R _B 80	1.46	57.6	0.28	11
S17400	H510°C (950°F)	–	–	0.05	2
410	R _C 45	–	–	44	1732 ⁴
431	R _C 45	–	–	36	1402 ⁴

¹ Heat Treatment

SCT = Annealed 982°C (1800°F) ½ hr., air cooled, cooled to –73°C (–100°F) 1 hr., tempered for 2 hrs. at 400°C (750°F)

DA = Annealed 982°C (1800°F) ½ hr., air cooled, intermediate aged for 1 hr. at 732°C (1350°F) and final aged for 1 hr. at 454°C (850°F)

SA = Solution annealed 1038°C (1900°F) 1 hr. and quenched

H = Hardened at indicated temperature

R_B = Rockwell B Hardness

R_C = Rockwell C Hardness

² Two hour test

³ Average of five 48-hour test periods except those with ⁴

⁴ First 48 hour test period. Several or all of those subsequent 48 hour test periods showed nil rate

TABLE XIV
Comparison of Types 216 and 316 Stainless Steel In Sulfuric Acid

Alloy	Corrosion Rate											
	Sulfuric Acid Concentration											
	1%		2%		3%		4%		5%		10%*	
	mm/y	mpy	mm/y	mpy	mm/y	mpy	mm/y	mpy	mm/y	mpy	mm/y	mpy
Type 216 stainless steel	0.08	3.2	0.06	2.3	0.04	1.4	0.09	3.5	2.01	79	0.05	1.9
Type 316 stainless steel	nil	nil	nil	nil	nil	nil	0.04	1.4	0.91	36	0.24	9.6

Notes: ¹ Tests in 1%-5% H₂SO₄ conducted at 66°C (150°F)

* Test in 10% H₂SO₄ conducted at 38°C (100°F)

² All specimens were activated in warm 1:1 hydrochloric acid prior to exposure

³ Average of five 48-hr. exposure periods

TABLE XV
Comparison of Nitronic Alloy 50 and Type 316 Stainless Steel in Sulfuric Acid

Alloy	Corrosion Rate ¹											
	Sulfuric Acid Concentration											
	Temperature		1%		2%		5%		10%		20%*	
	°C	°F	mm/y	mpy	mm/y	mpy	mm/y	mpy	mm/y	mpy	mm/y	mpy
NITRONIC alloy 50 ²	80	176	<0.03	<1	<0.03	<1	<0.03	<1	0.72	28.2	3.38	133
Type 316 stainless steel ³	80	176	0.05	2	0.28	11	1.52	80	2.54	100	12.2	480
NITRONIC alloy 50 ²	Boiling		0.68	26.9	1.64	64.4	3.33	131	9.04	356	41.66	1640
Type 316 stainless steel ³	Boiling		–	–	3.05	120	6.60	260	18.54	730	55.88	2200

Notes: ¹ Average of five 48-hour periods. Specimens were activated for third, fourth and fifth periods. Where specimens exhibited both active and passive behavior, only the motive rates are shown,

² Corrosion test on bars annealed at 1121°C (2050°F)

³ Corrosion test on annealed bars

TABLE XVI
Comparison Of Nitronic Alloy 60 With
Types 304 And 316 Stainless Steels
In 2% H₂SO₄ @ 80°C (176°F)

	Corrosion Rate*	
	mm/y	mpy
NITRONIC alloy 60	1.14	45
Type 304 Stainless Steel	6.17	243
Type 316 Stainless Steel	0.28	11

*Based on duplicate tests

NITRONIC alloy 32, available as bar and wire, and NITRONIC alloy 33, available as sheet and plate, find use in applications requiring galling, erosion and wear resistance. However, these alloys have very limited resistance in sulfuric acid. The manufacturer indicates that in mild acids the corrosion resistance of these alloys approach Type 304 stainless steel and in more severe environments their corrosion resistance is somewhat less than Type 304 stainless steel. For maximum corrosion resistance, the alloys should be in the annealed condition and annealing would probably also be required after welding.

4. Iron-Base Nickel-Chromium-Molybdenum Alloys

There are several proprietary alloys available that contain approximately 25 Ni - 20 Cr - 4.5 Mo, sometimes copper and sometimes titanium or columbium stabilizing elements.

Alloys in this category which do not include copper are generally more corrosion resistant than Type 316 stainless steel and include HASTELLOY alloy M-532* and JESSOP alloy JS-700. The greatest amount of corrosion data exists for HASTELLOY alloy M-532; Figure 28 shows an isocorrosion chart for this alloy. Note that the temperature and concentration range of useful corrosion resistance has been extended beyond that for Type 316 stainless steel as a result of its increased alloy content.

Corrosion data for JESSOP alloy JS-700 in sulfuric acid is very limited, although some data are given in Table XVII and also Tables LI, LIV, LVII, LIX, LX and LXXXII. However, the composition of this alloy is very similar to HASTELLOY alloy M-532 and the corrosion resistance would be expected to be similar. It should be noted that the range of useful behavior for these alloys can be extended still further by all the methods that are applicable for less highly alloyed stainless steels such as the addition of oxidizing agents to the sulfuric acid or the application of anodic protection.

The copper-bearing alloys in this class of stainless steel are more corrosion-resistant in sulfuric acid than the copper-free alloys. Figure 29 is an isocorrosion chart for a 25 Ni - 20 Cr - 4.5 Mo - 1.5 Cu alloy such as Alloy 904L.⁵⁶

*Originally this alloy was called HAYNES alloy 20 Mod

TABLE XVII
Corrosion Tests of Jessop JS-700 and JS-777
In Boiling Sulfuric Acid Solutions

Alloy	Corrosion Rate*							
	30% H ₂ SO ₄		50% H ₂ SO ₄		50% H ₂ SO ₄ + 1/2% HCl		70% H ₂ SO ₄	
	mm/y	mpy	mm/y	mpy	mm/y	mpy	mm/y	mpy
JS-777	0.91	36	2.59	102	7.56	298	701	27600
JS-700	3.81	150	6.27	247	22.35	880	1463	57600

* 48 hour laboratory test in reagent grade acids at the boiling point

FIGURE 28

ISOCORROSION CHART FOR HASTELLOY ALLOY M-532 IN SULFURIC ACID

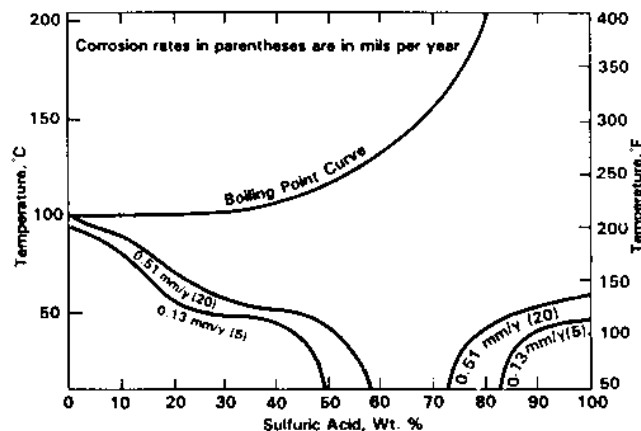
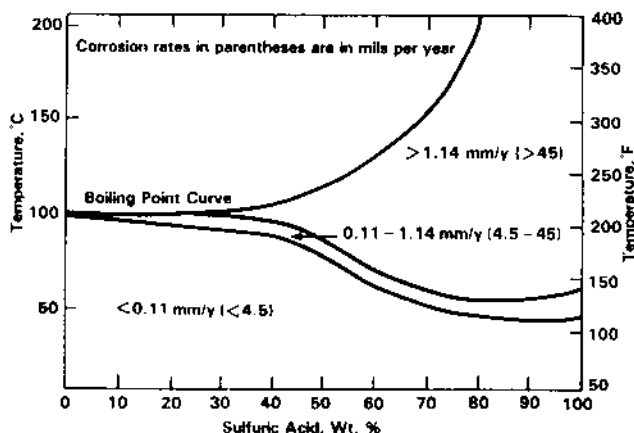


FIGURE 29

ISOCORROSION CHART FOR ALLOY 904L IN SULFURIC ACID



JESSOP alloy JS-777 is similar in composition to Alloy 904L although there are small differences in composition such as a slightly higher nominal copper content. Corrosion data for this alloy are shown in Table XVII. Because the tests were run in boiling solutions, the practical limits of use for the alloy were not defined. For estimating purposes, Figure 29 can be used but, as with the general admonitions for other stainless steels in preceding sections of this bulletin, a corrosion test under actual service conditions is desirable.

E. IRON-BASE NICKEL-CHROMIUM-COPPER-MOLYBDENUM (20 TYPE) ALLOYS

The first group of alloys usually considered when a sulfuric acid environment is too corrosive for the use of steel or cast iron, are the "20 type" alloys. Cast alloys of this type were originally developed by Fontana, specifically for sulfuric acid resistance. It is understood that the 20 in the designation of many alloys in this group resulted from the fact that the cast ACI CN-7M composition, typical of these alloys, was the twentieth modification tested by Dr. Fontana.

This group contains both cast and wrought alloys which are roughly equivalent in corrosion resistance, although some differences may be noticed in specific environments.

1. Cast ACI CN-7M

Figure 30 shows an isocorrosion chart for cast ACI CN-7M. One-half mm/y or 20 mpy is considered to be a high but sometimes a tolerable corrosion rate for a valve or pump body in a commercial application involving sulfuric acid. However, a lower limit such as 0.13 mm/y (5 mpy) is desirable, if not necessary, for critical components, such as stems and seats of valves or impellers of pumps. Some alloys that conform to this specification are better known by their tradenames such as DURIMET alloy 20 and ALOYCO alloy 20.

Corrosion rate curves reported for DURIMET alloy 20 in aerated sulfuric acid solutions at 80°C (176°F) are shown in

FIGURE 30
ISOCORROSION CHART FOR ACI CN-7M
IN SULFURIC ACID

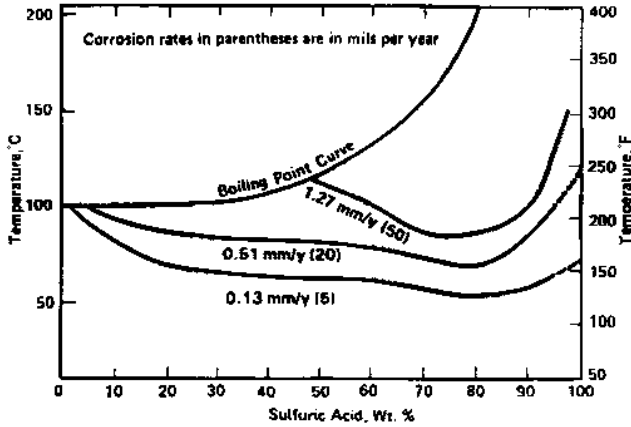


Figure 31. Corrosion rates in boiling sulfuric acid solutions are shown in Figure 32. The points on these curves show the results of individual corrosion tests under similar conditions. Each point represents the results of a 240 hour laboratory test in which air was bubbled through the sulfuric acid solution by means of a porous plug located at the bottom of the test flask. The bubbling agitated the solution.

Luce has indicated that the cast "20 type" alloys are generally acceptable to 80°C (176°F) up to 50 percent sulfuric acid concentration and above this good resistance can usually be expected to 65°C (150°F).⁵⁷

In general, the cast "20 type" alloys are much more resistant to sulfuric acid and less affected by contaminants than the austenitic stainless steels. However, the presence of oxidizing agents is usually helpful in preventing corrosive attack and chlorides in the acid can be detrimental.

FIGURE 31
CORROSION OF DURIMET ALLOY 20 IN AERATED
SULFURIC ACID AT 80°C (176°F)

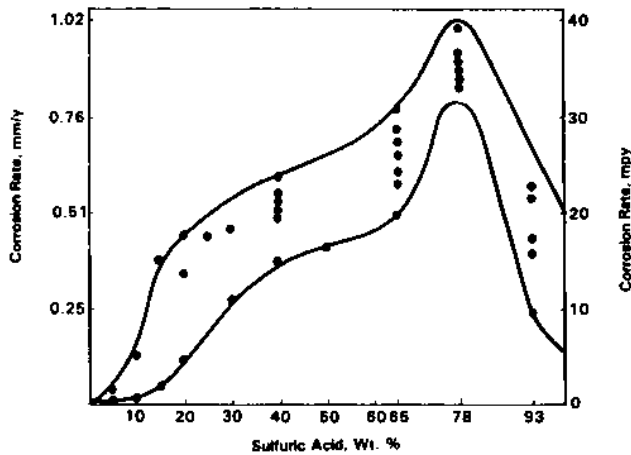


TABLE XVIII
Corrosion Test Data

Metal	Penetration Rate			
	Exposure No. 1		Exposure No. 2	
	mm/y	mpy	mm/y	mpy
ALOYCO-316 (CF-8M)	3.81	150.0	0	0
ALOYCO-20	0.90	35.5	0	0

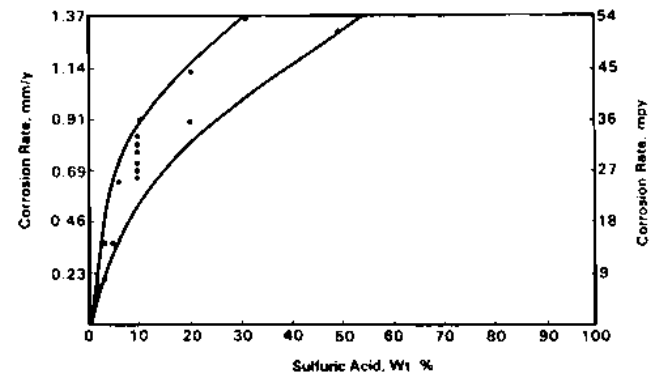
- Exposure. 1. 10% Sulfuric acid, no impurities (Laboratory Test)
2. 10% Sulfuric acid, plus nickel sulfide impurities (Field Test)
- Temperature: 1. 107°C (225°F)
2. 93°C (200°F)
- Exposure Hours. 1. 240 (Five 48-hour exposures. New solution after each exposure)
2. 672 (Continuous)

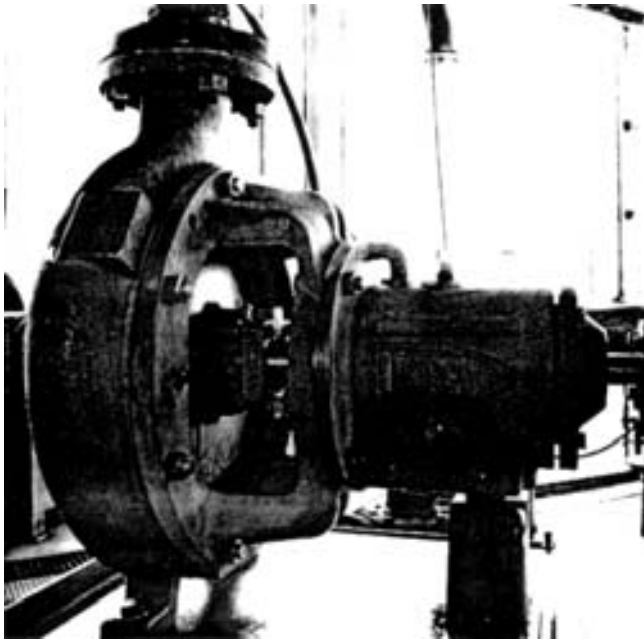
The beneficial effect of an oxidizing agent, in this case nickel in its higher valence state, in inhibiting corrosion with ALOYCO alloy 20 in 10 percent sulfuric acid is shown in Table XVIII.⁵⁸ Exposure 1 was a laboratory test whereas exposure 2 was a field test. It was unfortunate that the temperatures were not the same, but temperature alone cannot account for the very low corrosion rates in the field test. These data also indicate the value of a test under actual operating conditions.

The cast CN-7M compositions are subject to sensitization as described for the wrought austenitic stainless steels. Solution annealing of castings in accordance with ASTM A-744 for Grade CN-7M is required for maximum corrosion resistance.

Because these alloys are subject to intergranular corrosion if improperly heat treated, failures of the "20 type" alloys tend to be attributed to this cause. However, Klodt and Minick have shown that many of the failures attributed to intergranular corrosion were actually caused by erosion-corrosion.⁵⁹ Erosion-corrosion data for the CN-7M alloy are shown in Figure 26.

FIGURE 32
CORROSION OF DURIMET ALLOY 20
IN BOILING SULFURIC ACID





A DURIMET alloy 20 pump in service handling 93 percent H_2SO_4 at ambient temperature.

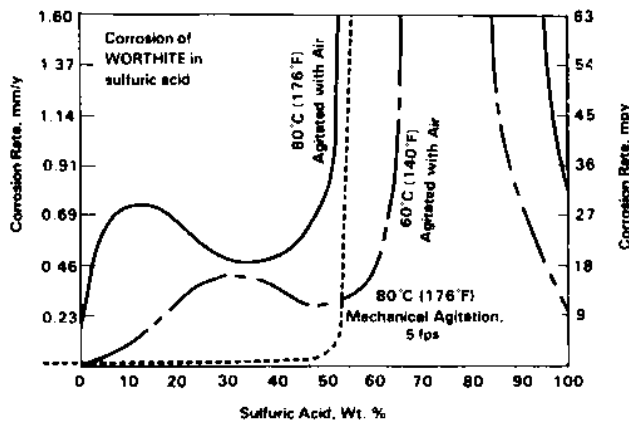
(Photograph courtesy of The Duriron Company, Inc.)

2. WORTHITE

The composition of WORTHITE is slightly outside the specifications for CN-7M but its corrosion resistance is quite similar. Corrosion rate curves as reported for WORTHITE in sulfuric acid solutions at 50°C (140°F) and 80°C (176°F) are shown in Figure 33. The air-agitated curves were derived from tests in which the test specimens were suspended in the acid bath equipped with reflux condenser and agitated by a stream of air bubbles emitting from a submerged tube orifice and held at constant temperature. Tests were of 24 and 48-hour duration

FIGURE 33

CORROSION OF WORTHITE IN SULFURIC ACID



following previous pickling of the specimens. It was reported that service life of pumps and valves is not always indicated properly by these air agitated tests. Consequently, a mechanically-agitated test was devised in which the specimens were hung on suitable hooks, projecting from the periphery of a horizontally positioned disc of non-metallic material which, by means of a variable speed motor, could be rotated at peripheral speeds of 0.24 to 13.7 m/sec. (0.8 to 45 fps). Glass baffles were attached to the walls of the glass container to prevent rotation and vortexing of the solution. Despite these precautions, the results suggest some air-entrapment in the acid. The published curve resulting from a series of such mechanically agitated tests at 80°C (176°F) and velocity of 1.5 m/sec. (5 fps) is also shown in Figure 33.

The test results would indicate that WORTHITE is suitable for use at 80°C (176°F) with sulfuric acid concentrations up to 50 percent. At 60°C (140°F) it may be useful with acid concentrations up to about 65 percent. In the concentration range from 65 to 85 percent, the limiting temperature probably is in the neighborhood of 50°C (122°F).

The results of laboratory corrosion tests of annealed WORTHITE in boiling 10 percent sulfuric acid with and without the addition of oxidizing agents are shown in Table XIX.⁶¹

3. CARPENTER alloy 20Cb-3

A wrought counterpart to cast ACI CN-7M developed about 1947 was known as CARPENTER 20. This alloy has undergone several improvements since then; in 1948, columbium was added for stabilization against chromium carbide precipitation; in 1963, the nickel content was raised to about 33-35 percent primarily to give greater resistance to stress-corrosion cracking and improved resistance to boiling sulfuric acid under heat-transfer conditions. Minor processing changes have been made subsequently to give even greater resistance to intergranular corrosion.

Figure 34 shows an isocorrosion chart for CARPENTER alloy 20Cb-3. The resistance of this alloy to boiling sulfuric acid is shown in Figure 35. This curve was generated by boiling the acid prior to immersion of the samples, so as to purge oxygen from the solution, and then obtaining the average of many samples over five 48-hour periods.

TABLE XIX
Laboratory Tests Of Worthite In 10 Percent Sulfuric Acid With Added Oxidizing Salts

Test Conditions	Corrosion Rate	
	mm/y	mpy
10% Sulfuric Acid		
10% Sulfuric Acid plus 0.5% $Fe_2(SO_4)_3$		
10% Sulfuric Acid plus 0.5% $Fe_2(SO_4)_3$		
10% Sulfuric Acid plus 0.1% Na_2CrO_4		

Temperature 100°C (212°F) Reflux condenser used Duration of tests, 31 days.

A peak in CARPENTER alloy 20Cb-3 corrosion rate occurs between 65 and 74 percent sulfuric acid concentration at 80°C (176°F) as shown in Figure 36. The cause of this peak has not been explained although Scharfstein has suggested it may be due to selective attack of certain phases present in the alloy.⁶²

In evaporators and heating coils, the wall temperature of the alloy is hotter than the bulk temperature of the solution being heated. Figure 37 shows the superior resistance of CARPENTER alloy 20Cb-3 to the older 20Cb composition in sulfuric acid solutions under heat transfer conditions. These curves were obtained by utilizing a soldering iron to heat the exterior of the alloy samples and cause boiling of the chemi-

cally pure sulfuric acid solutions in contact with the interior surface, a technique developed by Groves.⁶³ The beneficial effect of the six percent higher nickel content is very striking. Even if the effects of heat transfer are taken into account, it may still be necessary to consider other factors as well, such as impurities in the acid.

Oxidizing agents in sulfuric acid are generally beneficial in promoting passivity with CARPENTER alloy 20Cb-3. For instance, this alloy corroded at 1.02 mm/y (40 mpy) in pure 8

FIGURE 34
ISOCORROSION CHART FOR CARPENTER ALLOY 20Cb-3 IN SULFURIC ACID

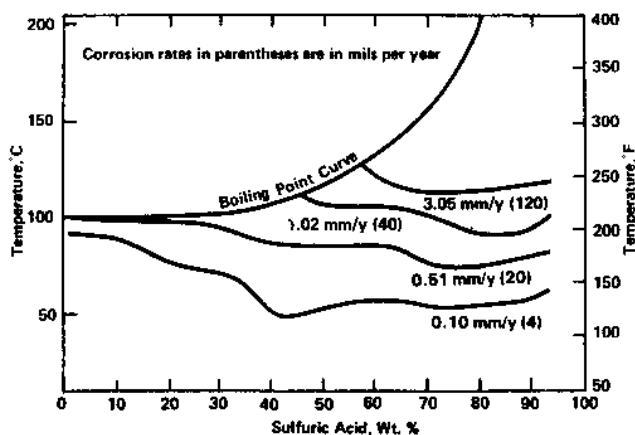


FIGURE 35
CORROSION RATE OF CARPENTER ALLOY 20Cb-3 IN BOILING SULFURIC ACID

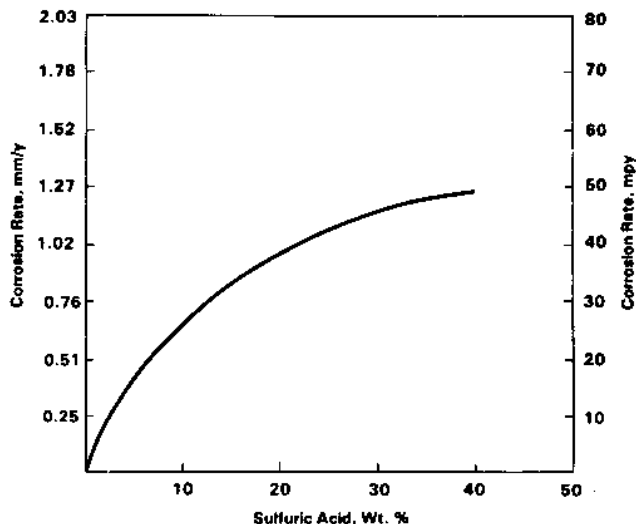


FIGURE 36
CORROSION RATE OF CARPENTER ALLOY 20Cb-3 IN NONAERATED SULFURIC ACID AT 80°C (176°F)

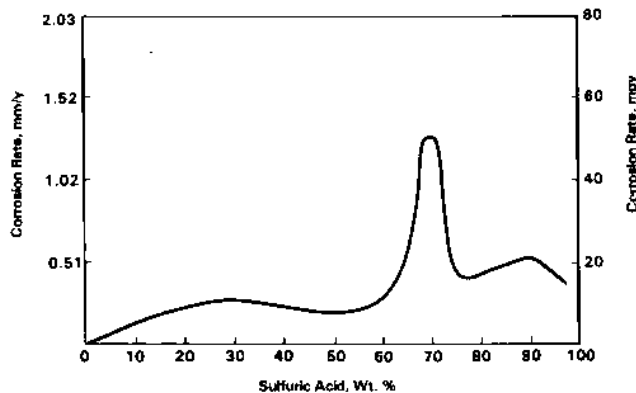
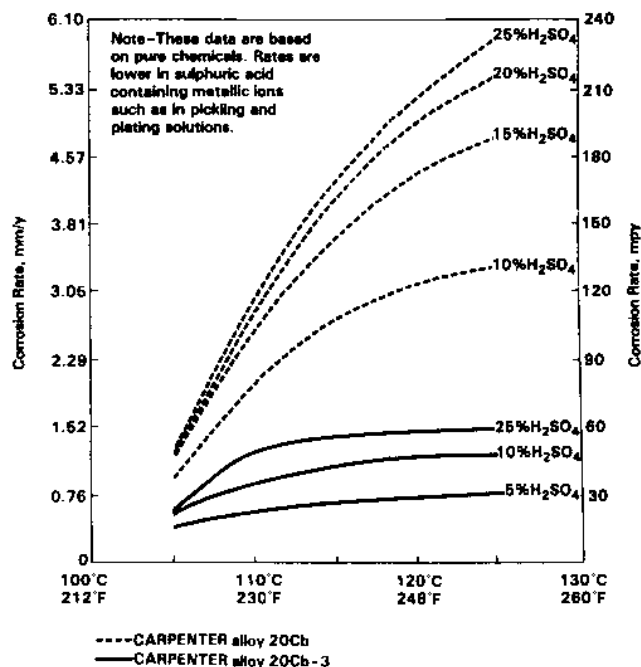


FIGURE 37
THE CORROSION OF CARPENTER ALLOY 20Cb AND IMPROVED CARPENTER ALLOY 20Cb-3 UNDER HEAT TRANSFER CONDITIONS TO CAUSE BOILING OF THE SULFURIC ACID AT THE INDICATED METAL TEMPERATURES



percent H_2SO_4 under heat transfer conditions in the laboratory where the bulk acid temperature was $100^\circ C$ ($212^\circ F$) and the metal temperature $150^\circ C$ ($302^\circ F$). Under the same conditions, except for the addition of 0.5 percent ferric sulfate to the acid, the corrosion rate of CARPENTER alloy 20Cb-3 was nil.⁶² Thus, the alloy was found suitable as heat exchanger tubing in an 8 percent sulfuric acid pickling solution.

The effect of chloride ion concentration in boiling 5-20 percent sulfuric acid on CARPENTER alloy 20Cb-3 from < 1 ppm to 1,000 ppm (0.1 percent HC 1) was determined. No effect was observed for these chloride concentrations in 5 and 10 percent sulfuric acid under boiling heat transfer conditions. However, an increase of approximately 50 percent in corrosion rate was observed for the solution containing 1,000 ppm Cl^- in 20 percent sulfuric acid boiling under heat transfer conditions.⁶² Thus, this alloy has much greater tolerance for chloride ion contamination than the 300 series austenitic stainless steels. In a similar manner, an application involving cooling in which the metal temperature is lower than the bulk temperature of the sulfuric acid solution would be expected to yield lower corrosion rates than those obtained isothermally. One of the most consistent errors made in alloy selection is consideration of the bulk temperature alone and improper use of an isocorrosion chart to determine applicability, rather than also considering metal temperature and impurities (either beneficial or harmful) in the acid.

The hygroscopic nature of concentrated sulfuric acid may cause the concentration to vary through absorption of moisture; it is common practice in concentrated acid service to use CARPENTER alloy 20Cb-3 for valve stems or pumps shafts that have to go through packing, and utilize the cast "20 type" alloys for the valve bodies and pump casings.

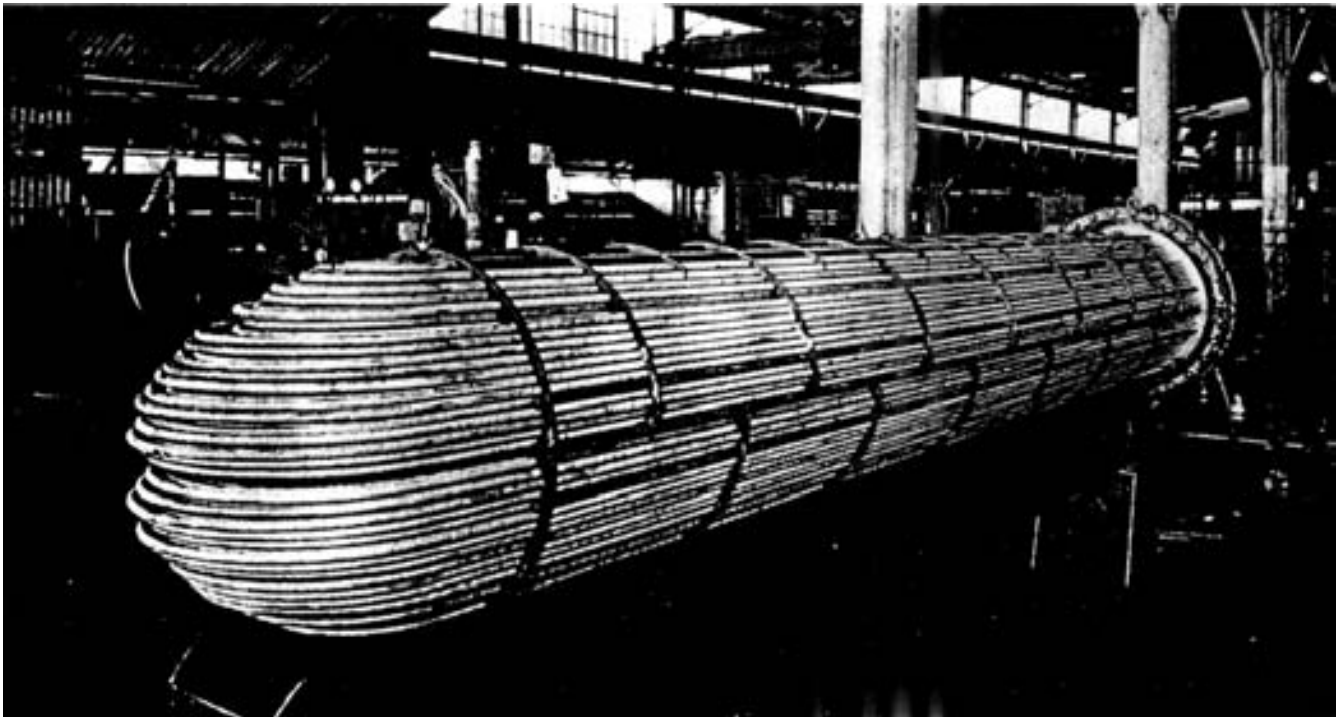
The "20 type" alloys are more easily passivated by anodic protection than the austenitic stainless steels because they generally have lower critical current densities in the same sulfuric acid environment. Because of the inherent corrosion resistance of these alloys in sulfuric acid solutions, however, they are rarely anodically protected. Anodic protection has been used to advantage in some instances with these alloys³¹ and might be seriously considered as a means of extending useful service life.

F. NICKEL-BASE IRON-CHROMIUM-MOLYBDENUM-COPPER ALLOYS

1. INCOLOY alloy 825

INCOLOY alloy 825 has excellent resistance to sulfuric acid, especially in the concentration range up to 40 percent and in concentrated acid, as shown by its isocorrosion chart, Figure 38. Based upon test results and service experience, INCOLOY alloy 825 should have useful resistance to corrosion in sulfuric acid solutions in concentrations up to 40 percent at the atmospheric boiling point, up to 78 percent concentration at $80^\circ C$ ($176^\circ F$) and in all concentrations of the acid up to $65^\circ C$ ($150^\circ F$). This alloy is stabilized against carbide precipitation by a titanium addition so that it can be used in the as-welded condition.

Additional corrosion data for higher temperatures are given in Figure 39 which shows the results of a series of laboratory tests in reagent grade (C.P.) acid. The tests were run in acid



Tube bundle of CARPENTER alloy 20Cb-3 is used by a large oil refiner to handle concentrated acid at temperatures from: $80-90^\circ C$ ($175-184^\circ F$).

(Photograph courtesy of Carpenter Technology Corporation)

concentrations in increments of 5 percent concentration by weight up to 95 percent acid. Each point through which the curves are drawn represents the average of five test periods of 48 hours each in fresh sulfuric acid solutions.

Another series of tests- were made in C.P. sulfuric acid solutions of 40, 50, 60 and 80 percent concentration at temperatures of 50°C (122°F), 100°C (212°F) and at boiling temperatures. The results of these tests are shown in Table XX.

FIGURE 38

ISOCORROSION CHART FOR INCOLOY ALLOY 825 IN SULFURIC ACID

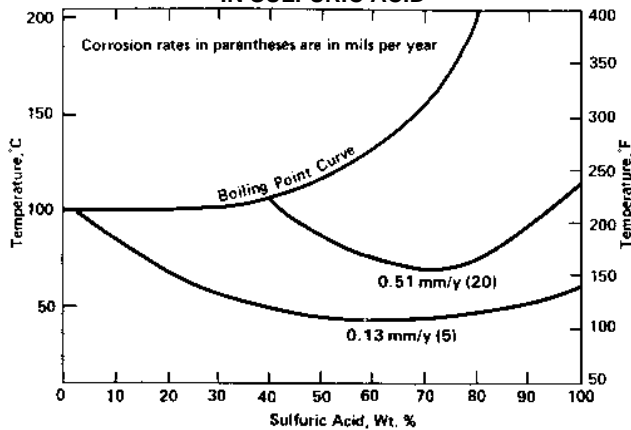
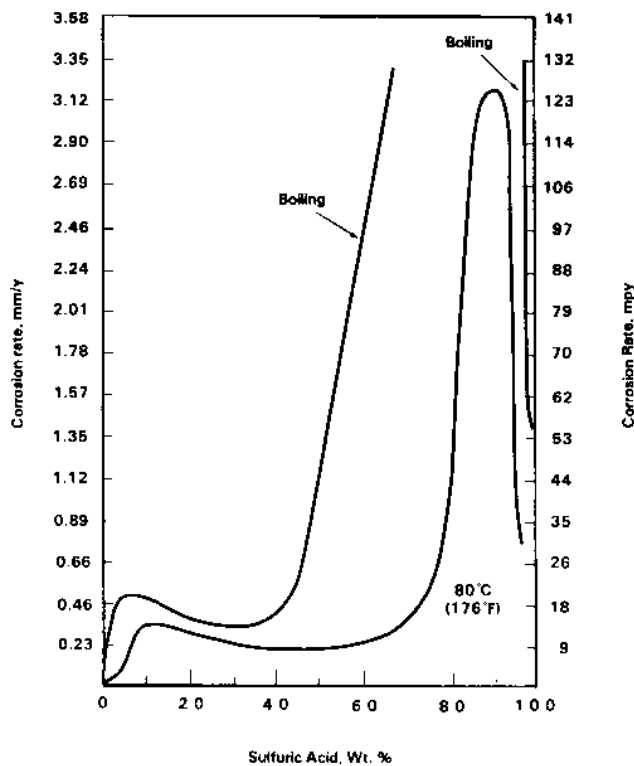


FIGURE 39

LABORATORY CORROSION TESTS OF INCOLOY ALLOY 825 IN C.P. SULFURIC ACID SOLUTIONS

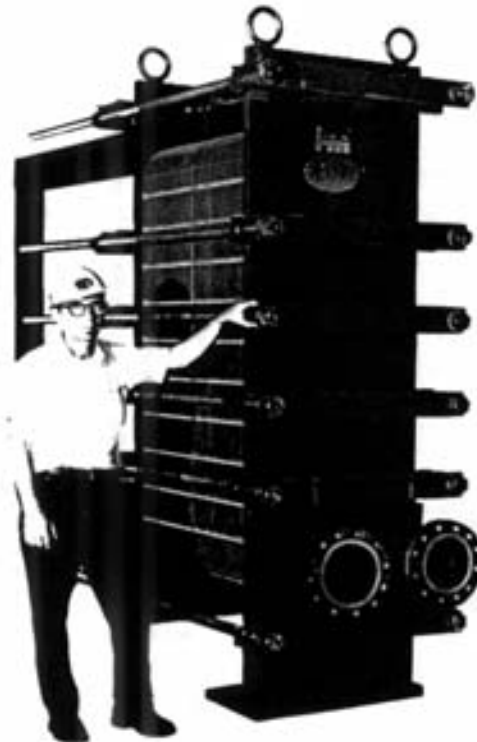


A number of laboratory tests were run at the Brookhaven National Laboratory evaluating INCOLOY alloy 825 as a material of construction for the Sulfex process dissolver vessel.⁶⁴ In the Sulfex process, which never became commercial, the stainless steel cladding of a nuclear power reactor fuel element is first dissolved in a hot, dilute sulfuric acid solution and then the uranium-dioxide core is subsequently dissolved in nitric acid. The results indicated that INCOLOY alloy 825

TABLE XX
Laboratory Corrosion Tests of Incoloy Alloy 825 In C.P. Sulfuric Acid

Sulfuric Acid Concentration	Corrosion Rate-Temperature					
	50°C (122°F) ¹		100°C (212°F) ¹		Boiling ²	
	mm/y	mpy	mm/y	mpy	mm/y	mpy
40	0.01	0.5	0.36	14	0.28	11
50	0.03	1.0	0.36	14	0.51	20
60	0.10	4.0	0.51	20	3.05	120
80	0.13	5.0	0.51	20	34.54	1360

¹ Test duration 168 hrs.
² Test duration 48 hrs.



This large [2.8m (9 ft.) high] heat exchanger utilizes plates of INCOLOY ally 825 to provide 455 m² (4,900 ft.²) of heat transfer surface for handling dilute sulfuric acid copper ore leaching solution. The acid enters the exchanger at 52°C (125°F) and leaves at 27°C (81°F). The flow rate is 233.5 liters/sec. (3,700 gallons/minute). A highly corrosion resistant alloy is required for the relatively thin plates.

(Photograph courtesy of American Heat Reclaiming Corporation)

was a satisfactory material of construction for dissolution of the stainless steels, such as Type 304, in 4 molar (31.8 percent) sulfuric acid solution. Data from several of the tests are shown in Tables XXI - XXIV and show that:

- The corrosion rate of INCOLOY alloy 825 is independent of either the particular heat of the alloy or whether the corrosion tests were run in technical grade or C.P. acid (see Table XXI). For this reason, subsequent tests were run in technical grade acid.

- The corrosion rate was dependent upon the type of condenser used for the test apparatus. Tests run using a Liebig condenser (a straight updraft condenser open to the atmosphere) gave the same results in the boiling 31.8 percent solution regardless of whether the acid was merely boiling or was sparged with air, whereas higher rates were obtained in the same concentration of acid when a cold finger condenser was used (see Table XXII).

- Metal ions present in the acid from dissolution of the stainless steel act as oxidizing agents and lower the corrosion rate by a factor of about 10 as shown by Table XXII. This inhibition was independent of the concentration of dissolved stainless steel within the range of 5 to 50 g/l of dissolved stainless steel. This effect was much greater than that obtained by bubbling air in the solution, probably because of the limited solubility of oxygen in the boiling acid solution. This also indicates that inhibition could also be achieved by anodic protection.

- Corrosion rates were approximately the same in both the liquid and the vapor on specimens of one-quarter inch thick plate welded by the Tungsten inert-gas process using INCOLOY filler metal 65, as shown in Table XXIII.

- Since the surfaces of heating coils would be at some temperature above the boiling point of the sulfuric acid, heat transfer tests were run, with the results shown in Table XXIV. Although heat transfer increased the corrosion rate somewhat, the corrosion rate was lowered by the presence of dissolved stainless steel, as a result of the oxidizing power of ferric and other metal ions.

2. HASTELLOY alloys G and G-3

HASTELLOY alloy G is a modification of obsolete HASTELLOY alloy F with improved resistance to sulfuric acid. It is a low-carbon, nickel-base alloy containing significant amounts of chromium, molybdenum and copper and is stabilized against carbide precipitation with columbium so that it can be used in the as-welded condition. In hot or cold sulfuric acid service, it will withstand the effects of both oxidizing and reducing media.⁶⁵ The extent of its resistance to sulfuric acid is shown in the isocorrosion chart given in Figure 40.

HASTELLOY alloy G has several attributes that make it a preferred material of construction for certain sulfuric acid environments. These attributes include excellent resistance to chloride stress-corrosion cracking and outstanding resistance to the halide contaminants found in wet process phosphoric acid production. (See Part IV-B). Solution heat-treated and stressed samples of this alloy were free of cracks after 1,000 hours of exposure in boiling 45% magnesium chloride. The effect of 200 ppm chloride ions in sulfuric acid solutions is shown in Figure 41.

TABLE XXI
Corrosion Rates of Incoloy Alloy 825
In Boiling 31.8 Percent (4M) H₂SO₄

Heat	Corrosion Rate			
	Technical Grade		C.P. Grade	
	mm/y	mpy	mm/y	mpy
1	0.58	22.9	0.60	23.5
2	0.57	22.5	0.72	28.5
3	0.65	25.5	0.41	16.2
Average	0.60	23.6	0.58	22.7

Note: Corrosion rates are the average of single specimens for five 48-hour exposure periods in pyrex glass equipment using Liebig condensers, 200 ml/in² solution volume to metal surface area ratio.

TABLE XXII
Corrosion Rates Of Incoloy Alloy 825
In Boiling Technical Grade Sulfuric Acid Solutions

Solution	Corrosion Rate	
	mm/y	mpy
Boiling 31.8% H ₂ SO ₄ using cold finger condenser	1.08	42.6
Boiling 31.8% H ₂ SO ₄ using Liebig condenser with a constant air sparge of .9 - 1.5 l/minute	0.59	23.1
Boiling 31.8% H ₂ SO ₄ plus 5 g/l dissolved Type 348 stainless steel, Liebig condenser	0.05	2.0
Boiling 31.8% H ₂ SO ₄ plus 25 g/l dissolved Type 348 stainless steel, Liebig condenser	0.15	5.8
Boiling 31.8% H ₂ SO ₄ plus 50 g/l dissolved Type 348 stainless steel, Liebig condenser	0.06	2.3
Boiling 31.8% H ₂ SO ₄ plus 25 g/l dissolved Type 304 stainless steel, Liebig condenser	0.02	0.8

Note: Corrosion rates are the average of duplicate specimens for five 48-hour exposure periods in pyrex glass equipment, 200 ml/in² solution volume to metal surface ratio.

TABLE XXIII
Corrosion Of Incoloy Alloy 825
Welded With Incoloy Filler Metal 65 In Boiling
31.8 Percent (4M) Technical Grade
Sulfuric Acid Solution

Phase	Corrosion Rate	
	mm/y	mpy
Liquid	0.53	21.0
Vapor	0.59	23.3

Note: Corrosion rates are the average of duplicate specimens for five 48-hour exposure periods in pyrex glass equipment using Liebig condensers, 200 ml/in² solution volume to metal surface area ratio.

TABLE XXIV
Corrosion of Incoloy Alloy 825 In Boiling
31.8 Percent (4M) Technical Grade Sulfuric Acid
Under Heat Transfer Condition

Metal Temperature		Corrosion Rate		Comment
°C	°F	mm/y	mpy	
127	260	0.76	30.0	
138	280	0.93	36.8	
149	300	0.86	34.0	
149	300	0.50	19.6	25 g/l dissolved stainless steel in the 4M H ₂ SO ₄

Note: Corrosion rates are the results of a single 260-hour test in apparatus similar to that developed by Groves.⁶³

HASTELLOY alloy G-3 is a modified version of HASTELLOY alloy G that has the same general corrosion resistance as HASTELLOY alloy G. It was developed so as to be resistant to the formation of grain boundary precipitates during prolonged heating, such as might occur during stress-relief of a carbon steel vessel clad with the alloy. A comparison of the corrosion resistance of the two alloys is given in Tables XXV

and XXVI. In table XXVI, the alloys are compared after several aging treatments by means of ASTM standard A-262-Practice B; a corrosion test for detecting susceptibility to intergranular corrosion. (It should be noted that Alloy G is resistant to intergranular corrosion in the heat-affected zones after normal welding operations, which heat the alloy for relatively short time periods).

FIGURE 40

ISOCORROSION CHART FOR HASTELLOY ALLOY G IN SULFURIC ACID

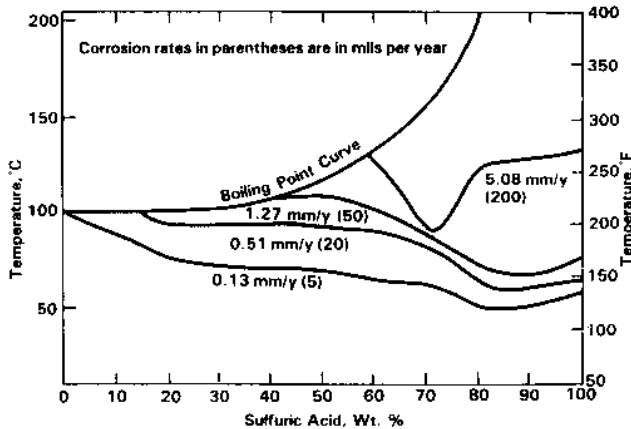


FIGURE 41

ISOCORROSION CHART FOR HASTELLOY ALLOY G IN SULFURIC ACID SOLUTIONS CONTAMINATED WITH CHLORIDE IONS

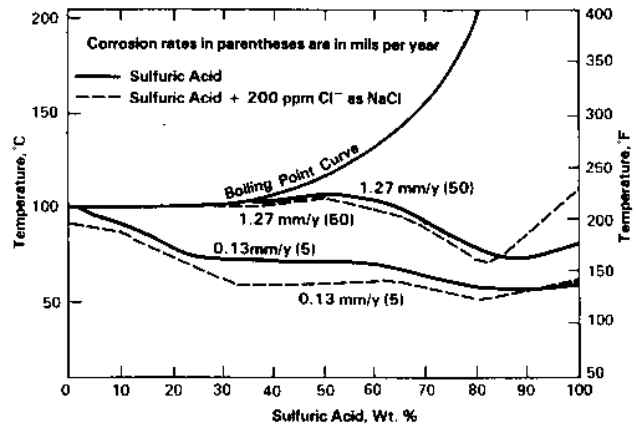


TABLE XXV
Comparison of Hastelloy Alloys G and G-3
In Sulfuric Acid Environments

Environment	Corrosion Rate					
	Temperature		Alloy G		Alloy G-3	
	°C	°F	mm/y	mpy	mm/y	mpy
5% H ₂ SO ₄	Boiling		0.28	11	0.30	12
10% H ₂ SO ₄	Boiling		0.36	14	0.48	19
20% H ₂ SO ₄	Boiling		-	-	0.81	32
50% H ₂ SO ₄	Boiling		2.7	108	3.6	143
7% H ₂ SO ₄ + 3% HCl + 1% CuCl ₂ + 1% FeCl ₃	21	70	-	-	nil*	nil*
7% H ₂ SO ₄ + 3% HCl + 1% CuCl ₂ + 1% FeCl ₃	21	70	-	-	.03**	1**
7% H ₂ SO ₄ + 3% HCl + 1% CuCl ₂ + 1% FeCl ₃	70	158	30.5	1200	11.6	455
7% H ₂ SO ₄ + 3% HCl + 1% CuCl ₂ + 1% FeCl ₃	70	158	8.6**	339**	11.3**	445**
7% H ₂ SO ₄ + 3% HCl + 1% CuCl ₂ + 1% FeCl ₃	Boiling		61	2400	48.8	1920
7% H ₂ SO ₄ + 3% HCl + 1% CuCl ₂ + 1% FeCl ₃	Boiling		-	-	34.5**	1360**
50% H ₂ SO ₄ + 42 g/l Fe ₂ (SO ₄) ₃	Boiling		-	-	0.30	12

* Nil = <.03 mm/y (<1 mpy)

** With crevice

TABLE XXVI
Comparison of Hastelloy Alloys G and G-3
In Ferric Sulfate-Sulfuric Acid Test
For Detecting Susceptibility to
Intergranular Attack (ASTM G-28)

Aging Temperature		Corrosion Rate Aging Time											
		1 hour		2 hours				4 hours					
		Alloy G		Alloy G-3		Alloy G		Alloy G-3		Alloy G		Alloy G-3	
C	F	mm/y	mpy	mm/y	mpy	mm/y	mpy	mm/y	mpy	mm/y	mpy	mm/y	mpy
649	1200	0.33	13	0.30	12	0.38	15	0.33	13	0.41	16	0.30	12
760	1400	2.2	86	0.94	37	6.9	270	2.7	105	11.2	442	4.7	184
871	1600	8.9	351	2.7	105	15.9	625	4.0	159	18	708	6.5	254
982	1800	3.1	122	0.30	12	4.5	177	0.30	12	4.1	160	0.36	14

G. NICKEL-COPPER ALLOYS

MONEL Alloy 400 is widely used for handling sulfuric acid under reducing conditions. Thus, this alloy offers an alternative to stainless steels, and other alloys of similar behavior, when the sulfuric acid solutions are not strongly oxidizing. By reference to Figures 42-44, MONEL alloy 400 exhibits reasonably low corrosion rates in air-free sulfuric acid up to 85 percent concentration at 30°C (86°F) and up to 60 percent concentration at 95°C (203°F). At the boiling point, Alloy 400 has good resistance to about 20 percent sulfuric acid concentration as shown by Table XXVII.

FIGURE 42

CORROSION OF MONEL ALLOY 400 AT 30°C (86°F) AND VELOCITY OF 5.18 m/minute (17 fpm)

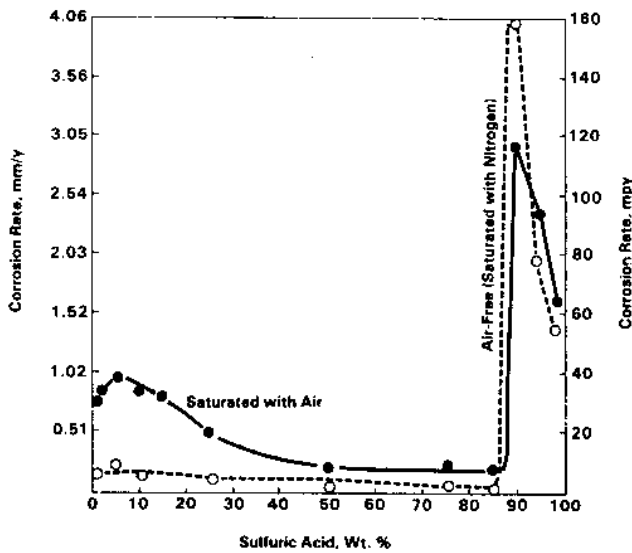


FIGURE 43

CORROSION OF MONEL ALLOY 400 AT 60°C (140°F) AND VELOCITY OF 5.03 m/minute (16.5 fpm)

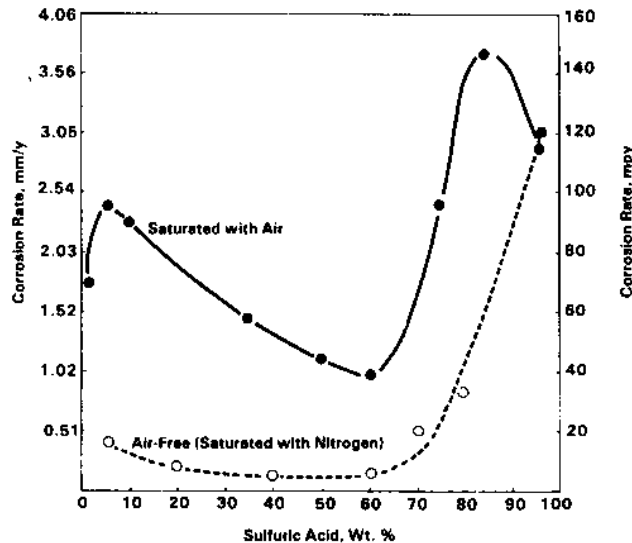


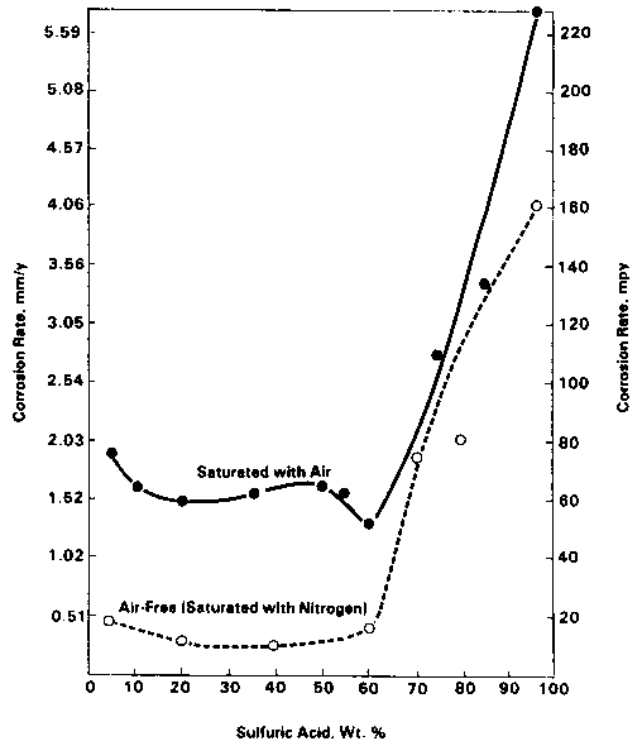
TABLE XXVII

Corrosion Of Monel Alloy 400
By Boiling Sulfuric Acid Solutions

Sulfuric Acid Concentration	Boiling Temperature		Duration of Test	Corrosion Rate	
	°C	°F		mm/y	mpy
5	101	214	23	0.086	3.4
10	102	216	23	0.061	2.4
19	104	219	23	0.19	7.5
50	123	253	20	16.5	650
75	182	360	20	58.4	2300
96	293	560	3	83.8	3300

FIGURE 44

CORROSION OF MONEL ALLOY 400 AT 95°C (203°F) AND VELOCITY OF 5.03 m/minute (16.5 fpm)



tending to remove it from solution and may also aid in the formation of a more protective film on the alloy surface.

Figure 45 shows the effects of increasing temperature upon the corrosion rates of MONEL alloy 400 in air-free and air-saturated five percent sulfuric acid. In air-free acid of 5-6% concentration, temperature has little effect; however, in air-saturated acid, increasing temperature has a considerable accelerating effect. The maximum corrosion rate in air saturated solutions occurs about 82°C (180°F). At higher temperatures the rate decreases until the boiling point is reached, when the corrosion rate is the same as in air-free acid.

Because of the drastic increase in corrosion rate at high concentrations of H₂SO₄, a margin of safety may be prudent. In practice, Alloy 400 has shown satisfactory resistance in the storage of 80 percent sulfuric acid at room temperature but should not be used continuously at higher concentrations without proper testing. Similarly, Alloy 400 has shown suitable resistance to boiling sulfuric acid solutions up to about 15 percent concentration.

Oxidizing salts such as cupric and ferric salts, when dissolved in significant amounts in sulfuric acid solutions will increase considerably the corrosiveness of the solutions toward Alloy 400. To illustrate the corrosive effect of ferric ion, laboratory corrosion tests were made with MONEL alloy 400 in dilute, air-saturated sulfuric acid solutions at 30°C (86°F) with and without the addition of various amounts of ferric sulfate. The tests were made with continuous movement of the specimens. The results are shown in Table XXVIII. Changes in concentration of ferric sulfate are seen to have affected the rate of corrosion more than changes in acid concentration.

A 6 percent sulfuric acid solution containing 0.5 percent copper sulfate and agitated at 82°C (180°F) corroded MONEL alloy 400 at the rate of 9.14 mm/y (360 mpy). Other oxidizing salts, such as chromates, dichromates, nitrates, nitrites, and peroxides when added in significant amounts to sulfuric acid solutions also may make them corrosive to Alloy 400.

Ferrous and cuprous salts in solution usually do not increase the corrosion rate of Alloy 400 but it is important in handling such solutions to avoid oxidation which would tend to convert these salts to the higher valence form. In practice, it

has been found that certain contaminants will also inhibit corrosion. Organic materials such as milk albumen have already been mentioned and amines, ketones and mercaptans also inhibit corrosion to some extent.

Increasing the velocity of sulfuric acid usually increases the corrosion rate. It brings fresh acid and oxygen, if present, to the metal surface, removes spent acid, and thins the diffusion film through which soluble reacting substances and corrosion products must pass. If movement is relatively swift, it may prevent the retention of what otherwise might be protective films. In the case of MONEL alloy 400, the effect of high velocities is most pronounced in aerated acid solutions as shown in Figure 46.

In the case of tubular heaters or of heat jacketed vessels, it should be kept in mind that the film of acid adjacent to the tube or vessel wall will probably be at a higher temperature than the

FIGURE 45
EFFECT OF TEMPERATURE ON CORROSION OF MONEL ALLOY 400 IN 5-6% SULFURIC ACID WITH AND VELOCITY OF 4.72-5.03 m/minute (15.5-16.5 fpm)

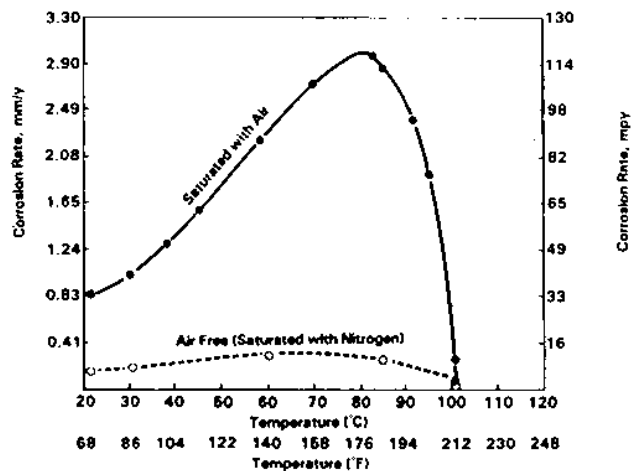


FIGURE 46
EFFECT OF VELOCITY ON THE CORROSION OF MONEL ALLOY 400 IN AIR-SATURATED 5 PERCENT H₂SO₄ AT ROOM TEMPERATURE

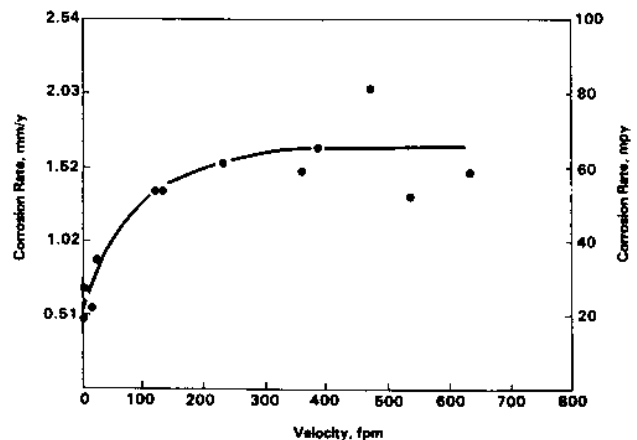


TABLE XXVIII
Corrosion of Monel Alloy 400
In Air-Saturated Sulfuric Acid
Containing Ferric Sulfate at 30°C (86°F)

Total Acidity, % H ₂ SO ₄	Iron, % *	Corrosion Rate		Ratio of Corrosion to that in Pure H ₂ SO ₄
		mm/y	mpy	
2.02	Nil	0.70	27.7	—
2.44	1.0	>25.4	>1000	41.1
1.60	Nil	0.58	22.8	—
1.66	0.05	5.02	197.7	8.7
0.532	Nil	0.47	18.7	—
0.604	0.05	6.17	242.9	13.0
0.710	0.10	10.7	423	23.1
0.0635	Nil	0.31	12.4	—
0.0650	0.005	1.0	39.5	32
0.0857	0.010	1.74	68.5	5.5

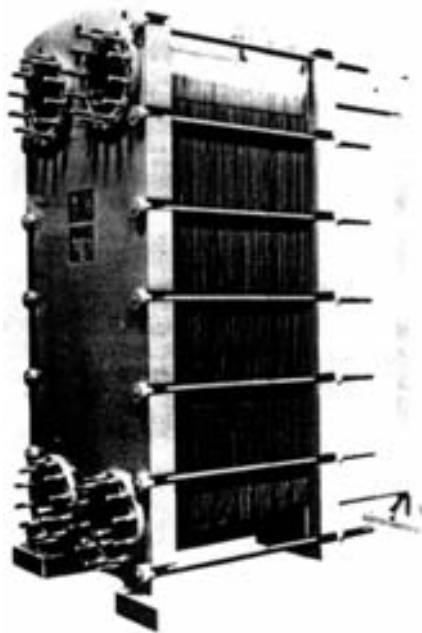
* Added as ferric sulfate

main body of the solution and that corrosion rates may be governed by the wall or "skin" temperature. To prolong equipment life, the use of steam or heating fluid at temperatures which are higher than necessary should be avoided. Similarly, cooling coils may show considerably lower corrosion rates than would be expected in the bulk solution under isothermal conditions.²⁵

In sulfuric acid solutions, Alloy 400 is either cathodic (protected) or is substantially neutral when in contact with most of the other common materials of construction, with the exception of lead, silver-brazing alloys of high silver content, and in some cases carbon. The galvanic protection afforded to Alloy 400 by contact with steel accounts for the very long life obtained from Alloy 400 baskets and crates used in the pickling of steel products in hot sulfuric acid solutions.

Experience indicates Alloy 400 is not susceptible to stress-corrosion cracking in sulfuric acid solutions, except those containing mercury salts or a considerable amount of hydrofluoric or fluosilicic acid. In these cases the possibility of stress-corrosion cracking can be avoided by giving the fabricated Alloy 400 equipment a stress-relieving heat treatment [540-650°C (1000-1200°F) for 1 hr. and slow cooling] before placing it in service.

Alloy K-500 has substantially similar corrosion resistance in sulfuric acid as Alloy 400. In some plant tests Alloy K-500 had slightly better corrosion resistance, as for example in organic sulfonations at temperatures to 177°C (350°F), and in tests in sulfuric acid treatment of petroleum distillates [66°C (150°F) max.]. Typical applications for Alloy K-500 are pump shafts and impellers, springs, valve trim, etc.



The plates of this heat exchanger were fabricated from HASTELLOY alloy C-276. This unit went into a phosphoric acid plant cooling dilute sulfuric acid on one side of the plates with seawater on the other side. HASTELLOY alloy C-276 is one of the few alloys with sufficient corrosion resistance in both environments to allow its use for the thin plates in this application.

H. NICKEL-BASE MOLYBDENUM-CHROMIUM-IRON ALLOYS

1. HASTELLOY alloys C-276 and C-4

HASTELLOY alloy C-276 has wide application in sulfuric acid environments as shown by its isocorrosion chart, Figure 47. At room temperature, the corrosion rate in all concentrations of reagent grade H₂SO₄ is less than 4 mils/year. Because of its chromium and other alloy content, it is considerably more resistant to acid solutions containing oxidizing salts than alloys such as Alloy 400 or HASTELLOY alloy B-2. Chlorides in solution slightly increase the corrosiveness of sulfuric acid to the alloy as shown in Figure 48.

This alloy has replaced an older alloy known as HASTELLOY alloy C because a solution annealing heat treatment was necessary after welding the former alloy to eliminate precipitates in the heat affected zones of welds that lowered corrosion resistance. As a result of this metallurgical instability, the composition was altered to produce HASTELLOY alloy C-276 which exhibits stability during welding.

FIGURE 47

ISOCORROSION CHART FOR HASTELLOY ALLOY C-276 IN SULFURIC ACID

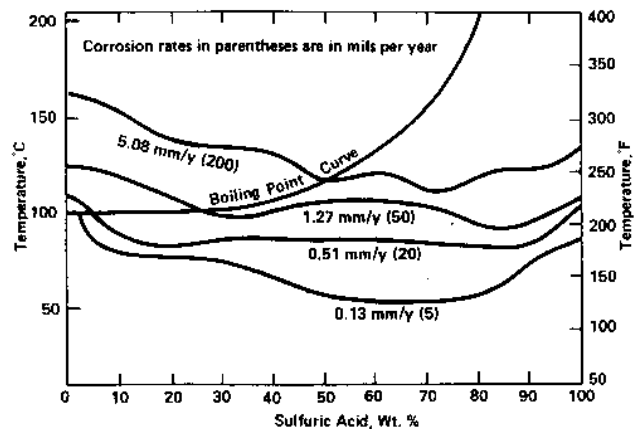
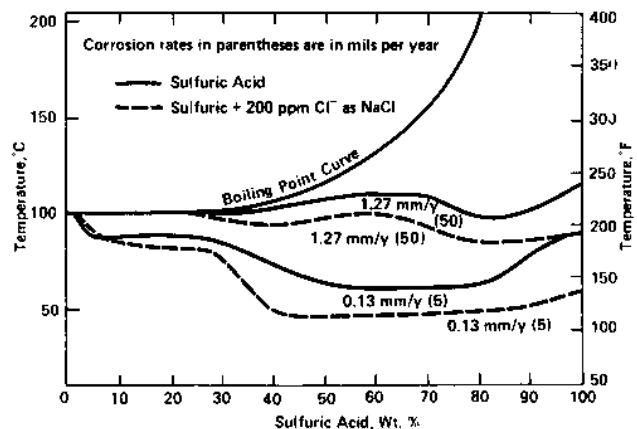


FIGURE 48

ISOCORROSION CHART FOR HASTELLOY ALLOY C-276 IN SULFURIC ACID AND SULFURIC ACID PLUS CHLORIDES



Hodge⁶⁶ investigated phases present in HASTELLOY alloy C-276 after various heat treatments. It was shown that HASTELLOY alloy C-276 exhibits a minimum amount of heat affected zone precipitation and a reduced rate of intermetallic phase precipitation within the grains. For almost all fabrication procedures involving welding, HASTELLOY alloy C-276 has sufficient resistance to sensitization in the heat-affected zones of welds to allow its use in the as-welded condition. However, grain boundary carbide and intermetallic phases precipitate when the alloy is aged for longer periods in the temperature range of 650-1090°C (1200-2000°F), reducing the corrosion resistance of the alloy. The nature of the intermetallic precipitate in HASTELLOY alloy C-276 was determined as an intermetallic Mu phase.

The identification of the intermetallic precipitate as a topologically close packed phase suggested that further improvements could be effected in this alloy system by control of the substitutional alloying elements. HASTELLOY alloy C-4, developed as a result of this investigation, does not precipitate an intermetallic Mu phase upon aging. Carbide precipitation has been further reduced as a result of both improved melting control and titanium stabilization.

Figures 49 and 50 show that HASTELLOY alloy C-4 is very similar in corrosion resistance to HASTELLOY alloy C-276. Thus, HASTELLOY alloy C-4 has a substantially reduced aging response which allows it to be used for some applications not possible with Alloy C-276.⁶⁶ Uses for HASTELLOY alloy C-4 include the cladding of steel equipment or where it is attached to steel requiring stress-relief for long periods of time.

2. Wrought and Cast Alloy 625

Wrought INCONEL alloy 625 exhibits good resistance to low and medium concentrations of sulfuric acid at 80°C (176°F) as shown by Table XXIX. Its corrosion rate in 15 percent sulfuric acid at 80°C (176°F) is compared with its cast counterpart and INCOLOY alloy 825 in Table XXX. Under

these conditions, aeration inhibits corrosion of the Alloy 625 but increases the corrosion of Alloy 825. Although Alloy 625 appears to be equivalent or slightly superior to INCOLOY alloy 825 in this test, this relationship is not maintained at higher sulfuric acid concentrations and temperatures. The corrosion resistance of Alloy 625 at the boiling point has been poor in all concentrations studied.

Corrosion data for the cast Alloy 625 in sulfuric acid are very sparse. The laboratory test data shown in Table XXX indicate that the cast Alloy 625 is approximately equivalent to its wrought counterpart in corrosion resistance. Because of the similarity in composition between the wrought and cast versions, it seems reasonable to assume that cast Alloy 625 will exhibit similar corrosion resistance to the wrought alloy in other sulfuric acid solutions.

TABLE XXIX
Laboratory Corrosion Tests Of
Inconel Alloy 625 In 80°C
(176°F) Sulfuric Acid

Acid Concentration	Corrosion Rate	
	mm/y	mpy
15	0.19	7.4
50	0.43	17
60	0.71	28
70	1.6	64
80	2.3	90

TABLE XXX
Laboratory Corrosion Tests In
15% Sulfuric Acid At 80°C (176°F)

Alloy	Corrosion Rate			
	Solution saturated with			
	Air		Nitrogen	
	mm/y	mpy	mm/y	mpy
INCONEL alloy 625	0.02	0.7	0.11	4.5
Cast Alloy 625	0.02	0.7	0.22	8.6
INCOLOY alloy 025	0.49	19.4	0.11	4.5

FIGURE 49

ISOCORROSION CHART FOR HASTELLOY ALLOY C-4 IN SULFURIC ACID

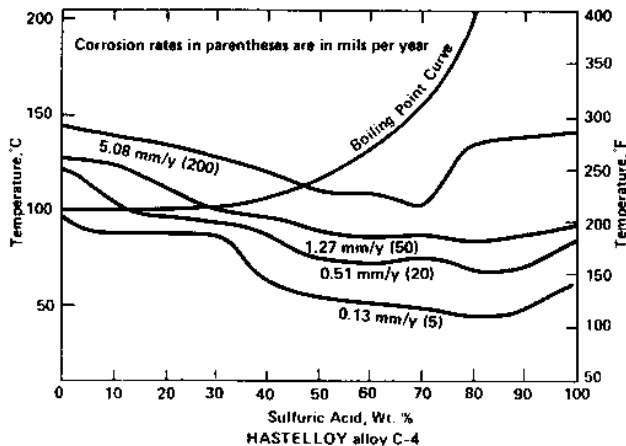
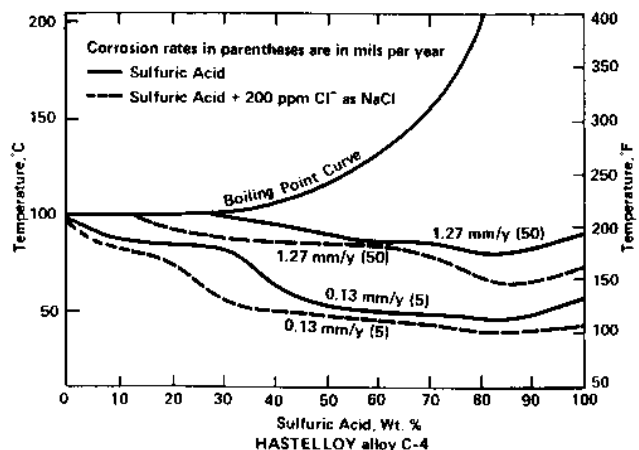


FIGURE 50

ISOCORROSION CHART FOR HASTELLOY ALLOY C-4 IN SULFURIC ACID AND SULFURIC ACID PLUS CHLORIDES



3. Cast ACI CW-12M-1

There are several proprietary cast alloys that conform to ASTM A-494 Grade CW-12M-1. The most well known, cast HASTELLOY alloy C, is no longer made by Cabot Corporation although they still supply remelt stock to foundries for the production of cast Alloy C. Other foundries cast alloys conforming to this specification with tradenames such as ILLIUM alloy W-1, ALOYCO alloy N3, LABOUR alloy Y-17, ELCOMET alloy Y-17, etc. All of these alloys exhibit corrosion resistance similar to wrought HASTELLOY alloy C.

4. Cast ACI CW-12M-2

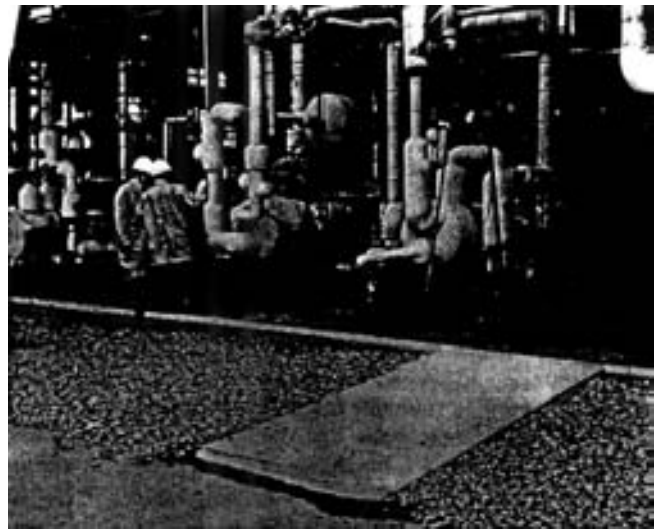
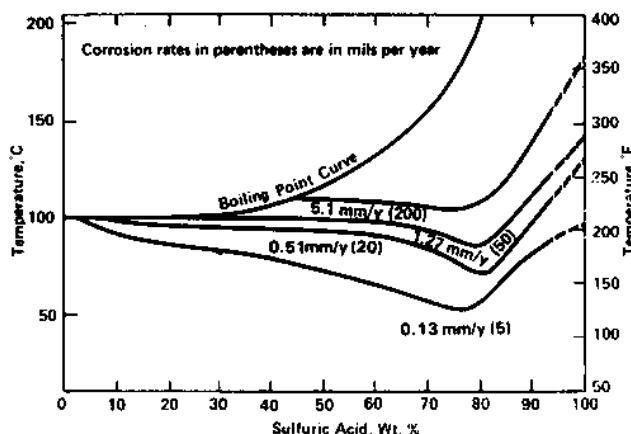
CHLORIMET alloy 3 conforms to ASTM A-494 Grade CW-12M-2 specifications. CHLORIMET alloy 3 exhibits excellent resistance to corrosion in all concentrations of sulfuric acid up to 66°C (150°F) and has good resistance to all concentrations of the acid, except 60-85%, to 93°C (200°F) as shown in Figure 51. In the 60-85% range, the good resistance is limited to about 74°C (165°F). Table XXXI gives corrosion test results for CHLORIMET alloy 3 at 80°C (176°F) for various acid concentrations.

ILLIUM alloy W-2 also conforms to the specifications for CW-12M-2 and should be similar in its resistance to sulfuric acid solutions.

TABLE XXXI
Corrosion Of Chlorimet Alloy 3
In Sulfuric Acid Solutions At 80°C (176°F)

Acid Concentration	Corrosion Rate	
	Wt. %	mm/y mpy
10	0.02	0.6
25	0.10	4
50	0.33	13
78	1.1	44
93	0.10	4

FIGURE 51
ISOCORROSION CHART FOR CHLORIMET ALLOY 3
IN SULFURIC ACID



HASTELLOY alloy B-2 heat exchangers used in a plant producing methyl methacrylate. This alloy is utilized because of its resistance to hot 98 percent sulfuric acid used in the process.

(Photograph courtesy of the High Technology Division of Cabot Corporation)

I. NICKEL-BASE MOLYBDENUM ALLOYS

1. HASTELLOY alloy B-2

HASTELLOY alloy B-2 has replaced HASTELLOY alloy B. The corrosion resistance of HASTELLOY alloy B-2 is slightly superior to the former alloy in sulfuric acid but even more important is the fact that it is a metallurgically stable alloy that does not require a solution heat treatment after welding.

HASTELLOY alloy B-2 has excellent corrosion resistance in sulfuric acid over a wide range of temperatures and concentrations, as shown in Figure 52. It can be used in the as-welded condition in boiling solutions of pure sulfuric acid up to a concentration of 70 percent (see Table XXXII). Chlorides in solution will increase corrosion rates somewhat, as shown in Figure 53. Oxidizing agents in solution, such as ferric ion, will considerably increase corrosion rates as indicated by Figure 54. If other alloys containing iron or copper utilized in the same system corrode and contribute ferric or cupric ion to the solution, it could cause premature failure of the HASTELLOY alloy B-2 components.

2. Cast ACI N-12M-1

Alloys similar in corrosion resistance to wrought HASTELLOY alloy B are available in cast form, as covered by ASTM A-494 Grade N-12M-1. Foundry remelt stock for Alloy B may be obtained from Cabot Corporation. Other foundries cast alloys conforming to this specification with tradenames such as ILLIUM alloy M-1, ALOYCO alloy N2, LABOUR alloy Y30, ELCOMET alloy Y30 etc. All of these alloys exhibit corrosion resistance similar to wrought HASTELLOY alloy B.

FIGURE 52

ISOCORROSION CHART FOR HASTELLOY ALLOY B-2 IN SULFURIC ACID

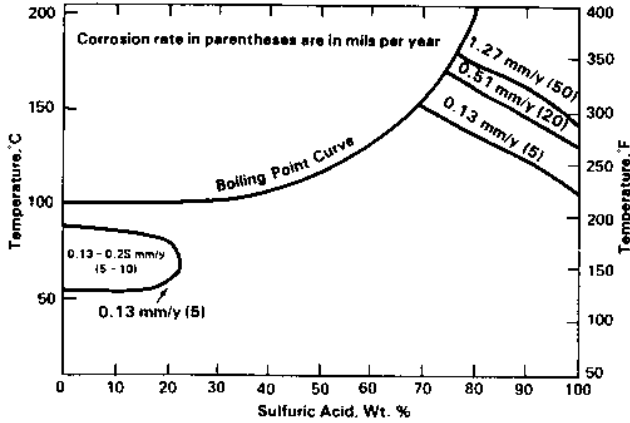


FIGURE 53

ISOCORROSION CHART FOR HASTELLOY ALLOY B-2 IN SULFURIC ACID SOLUTIONS CONTAMINATED WITH CHLORIDES

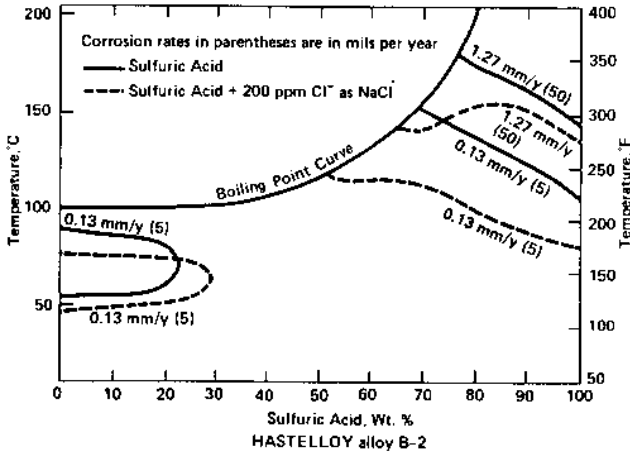


TABLE XXXII

Corrosion Rate Of Hastelloy Alloy B-2 In Boiling Sulfuric Acid

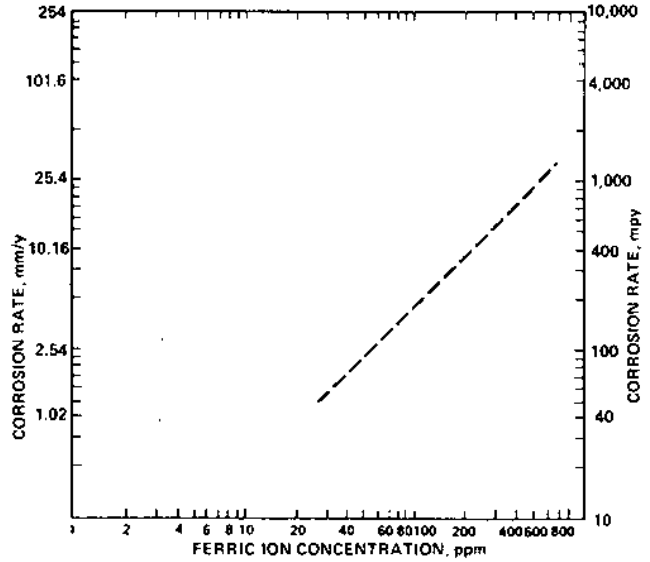
Acid Concentration	Corrosion Rate	
	wt. %	mm/y
2	0.013	0.5
5	0.076	3
10	0.051	2
20	0.018	0.7
30	0.018	0.7
40	0.023	0.9
50	0.025	1
50	0.051*	2*
50	0.025**	1**
60	0.051	2
70	0.23	9

* As gas tungsten arc welded
 **Aged 48 hours at 538°C (1000°F)

Laboratory Test: 120 hrs.
 All test specimens were heat-treated at 1066°C (1950°F) and water quenched unless otherwise noted.

FIGURE 54

EFFECT OF FERRIC ION CONCENTRATION ON CORROSION RATE OF HASTELLOY ALLOY B-2 IN BOILING 30% H₂SO₄



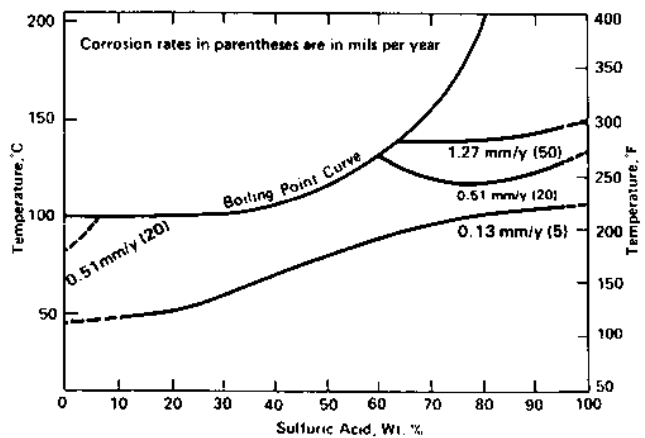
3. Cast ACI N-12M-2

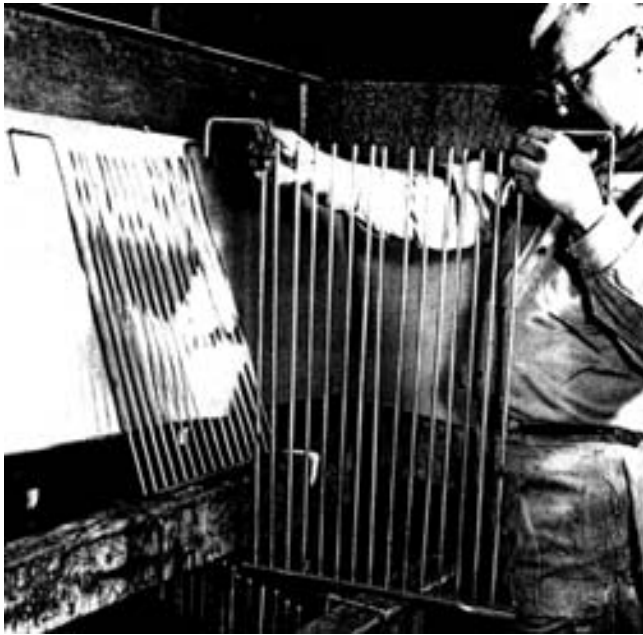
CHLORIMET alloy 2 conforms to ASTM A-494 N-12M-2 specifications. This alloy has excellent resistance to all concentrations of sulfuric acid up to 65°C (150°F) and good resistance up to the boiling point in the 10-60 percent concentration range as shown in Figure 55. At concentrations above 60% sulfuric acid, the maximum temperature should not exceed 120°C (250°F).

ILLIUM alloy M-2, besides having a similar composition and mechanical properties, has similar corrosion resistance. Oxidizing agents in solution will increase the corrosion rates of these alloys considerably.

FIGURE 55

ISOCORROSION CHART FOR CHLORIDET ALLOY 2 IN SULFURIC ACID





HASTELLOY alloy B tubing was utilized in this installation to heat 50 percent sulfuric acid to 93°C (200°F). Steam passes through the tubing while acid is in direct contact with the outside surface.

(Photograph courtesy of the High Technology Materials Division of Cabot Corporation)

J. NICKEL-BASE CHROMIUM-MOLYBDENUM-COPPER ALLOYS

1. ILLIUM alloy G

ILLIUM alloy G is a cast alloy which was originally developed to resist mixtures of sulfuric and nitric acids as encountered in the Chamber Process manufacture of sulfuric acid and in nitrating operations.

It resists H_2SO_4 at all concentrations to 71°C (160°F) and is satisfactory at all temperatures from dilute to 40% acid. Other areas exist where satisfactory performance occurs and these are shown in Figure 56. The alloy is also used in handling mixtures of H_2SO_4 and H_2S in viscose rayon and cellophane coagulation baths. It is a highly useful, machinable and weldable casting alloy for pumps and valves which must resist attack by a great variety of solutions containing H_2SO_4 along with other chemicals. It is most corrosion resistant in its annealed state where the carbon and chromium are held in solution.

2. ILLIUM alloy 98

ILLIUM alloy 98 is a weldable, machinable cast alloy that was originally designed to withstand hot, 98% percent sulfuric acid. However, it can be used over a wide range of concentrations and temperatures as indicated in Figure 57. ILLIUM alloy 98 is a preferred material for the very corrosive mid H_2SO_4 concentration range as shown in Figures 58 and 59. Note the superiority of ILLIUM alloy 98 over cast ACI CN-7M. Maximum corrosion resistance with this alloy is obtained after a solution anneal followed by water quenching.

FIGURE 56
ISOCORROSION CHART FOR ILLIUM ALLOY G
IN SULFURIC ACID

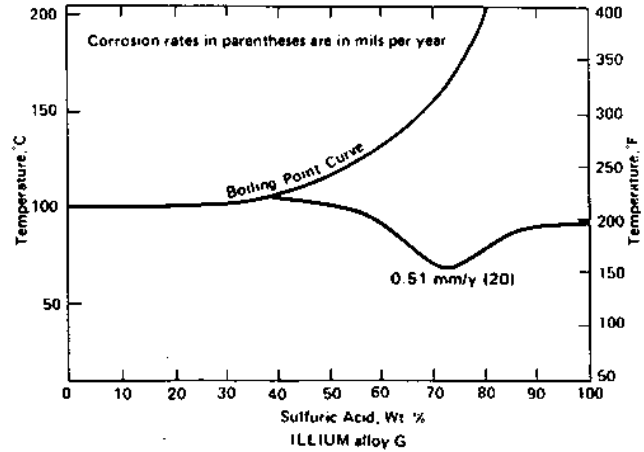


FIGURE 57
ISOCORROSION CHART FOR ILLIUM ALLOY 98
IN SULFURIC ACID

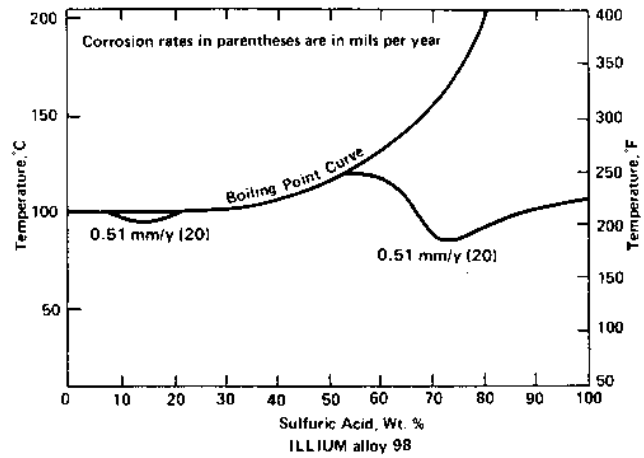


FIGURE 58
CORROSION RATES OF CAST ALLOYS IN 80°C (176°F)
SULFURIC ACID SOLUTIONS

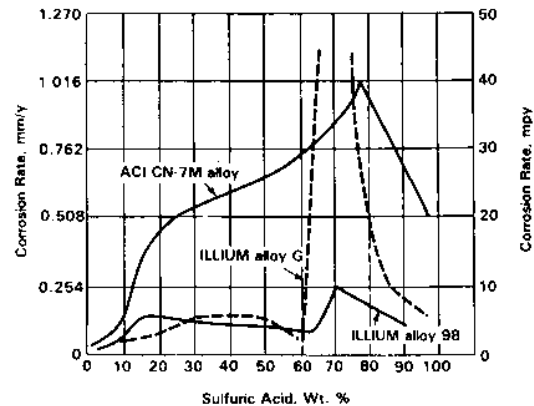
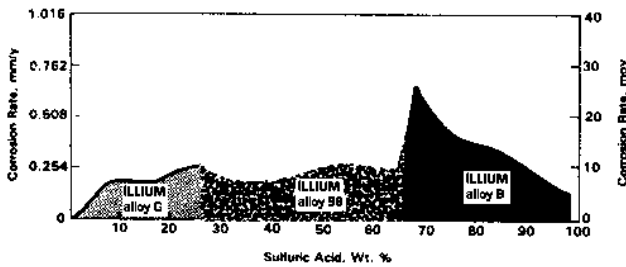


FIGURE 59
CORROSION RATES OF ILLIUM ALLOYS IN
SULFURIC ACID AT 100°C (212°F)



3. ILLIUM alloy B

ILLIUM alloy B, another cast alloy, is a modification of ILLIUM alloy 98 which extends the useful service range in 98% sulfuric acid to higher temperatures, as shown in Figure 60. Note that aeration of the sulfuric acid enhances the corrosion resistance of the ILLIUM alloys under these conditions. Although aeration has been shown to be beneficial in reducing

FIGURE 60
CORROSION OF ILLIUM ALLOYS IN 96-98%
SULFURIC ACID SOLUTIONS

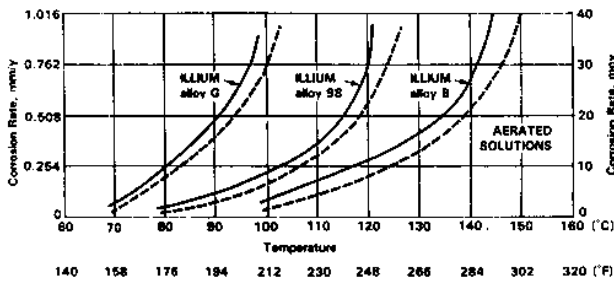
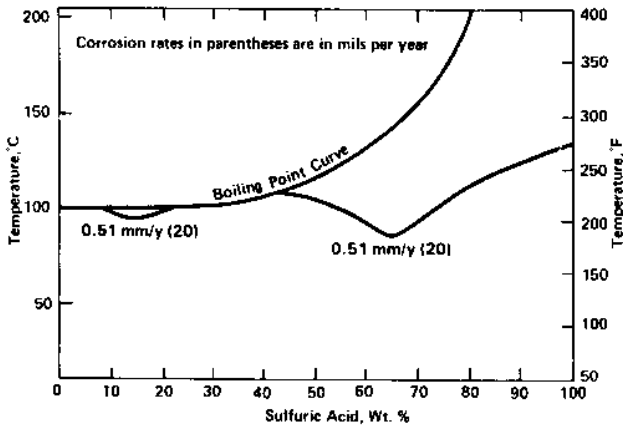


FIGURE 61
ISOCORROSION CHART FOR ILLIUM ALLOY B IN
SULFURIC ACID



corrosion with ILLIUM alloy B in 96-98% H₂SO₄, the alloy is not recommended where strongly oxidizing conditions are present.

An isocorrosion chart for ILLIUM alloy B, Figure 61, shows the excellent corrosion resistance of this alloy over the entire concentration range, although its outstanding resistance at the higher sulfuric acid concentrations makes it the alloy of choice in that region (see Figure 59). In addition, ILLIUM alloy B is hardenable for maximum wear and galling resistance. However, welding operations should be completed before hardening.

K. NICKEL-BASE CHROMIUM-IRON-MOLYBDENUM-COPPER ALLOY AND NICKEL-BASE CHROMIUM-IRON-COPPER ALLOY

1. LEWMET alloy 55

LEWMET alloy 55 is a cast, nickel-base alloy specifically designed for hot, concentrated sulfuric acid service. Isocorrosion curves for acid concentrations from 77 through 99.4% H₂SO₄, where the alloy finds greatest application, are shown in Figure 62. The effect of temperature on corrosion of LEWMET alloy 55 in 98 percent sulfuric acid, as determined in laboratory tests, is shown in Figure 63.

This alloy is age-hardenable from about 225 BHN up to 500 BHN. In the hardened condition, equivalent corrosion resistance with the unhardened alloy is claimed but with greater resistance to abrasion, galling and siezing. However, any necessary welding has to be performed prior to hardening. LEWMET alloy 55 has been used in the soft condition for pump impellers, orifice plates, etc. and in the hardened condition as pump-impeller-wear-rings, bearings, etc.

FIGURE 62
ISOCORROSION CURVES FOR LEWMET ALLOY 55 IN
SULFURIC ACID

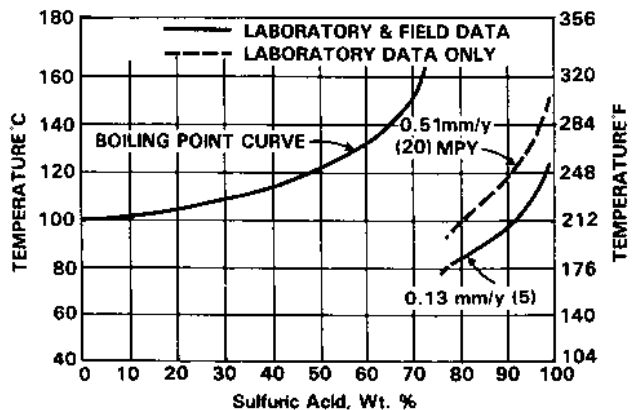
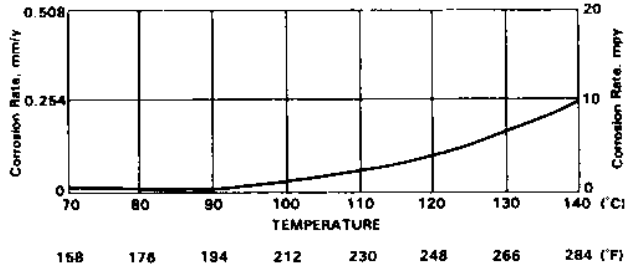


FIGURE 63
**CORROSION OF LEWMET ALLOY 55 IN 98%
 SULFURIC ACID**



2. LEWMET alloy 66

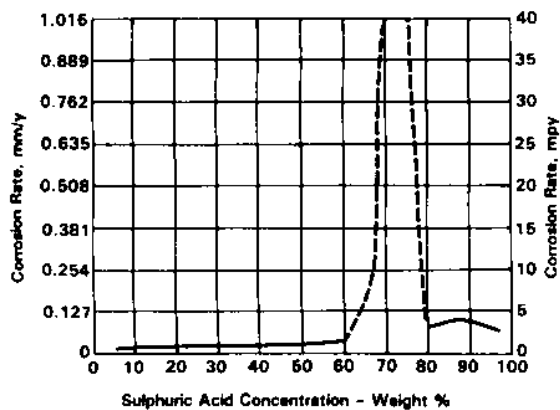
LEWMET alloy 66 is a ductile, cast, nickel-base alloy that can also be made in wrought form. Both the cast and wrought versions exhibit excellent corrosion resistance in the 0-60% and 80-98% sulfuric acid concentration range, as shown in Figure 64. Corrosion rates tend to be erratic and are sometimes high in the range of 60-80% sulfuric acid.

Because of the excellent resistance of LEWMET alloy 66 in dilute sulfuric acid, it has been used for dilution pipes and spray nozzles. It has also been used for sulfuric acid concentrations above 80% where its ductility in combination with corrosion resistance was required.

L. NICKEL

Nickel 200, commercially pure wrought nickel, can be used with sulfuric acid solutions at low or moderate temperatures. Nickel is not generally chosen for sulfuric acid service because it is usually less resistant than Alloy 400. However,

FIGURE 64
**CORROSION RATES OF LEWMET ALLOY 66 IN
 SULFURIC ACID SOLUTIONS AT 100C (212F)**



there are occasions when Nickel 200 or electroplated nickel components are included in equipment and this information is supplied so that a judgment can be made as to the suitability of such components for sulfuric acid service.

Nickel shows an active-passive transition in sulfuric acid solutions.^{67, 68} The large critical current density which nickel displays at a relatively noble potential indicates that passivity is not usually achieved in weakly or moderately oxidizing media, although anodic protection is a possible means of reducing the corrosion rate and extending the range of utilization.⁶⁷ Without anodic protection or the presence of an inhibitor, the principal applications of Nickel 200 are in ambient temperature, un-aerated sulfuric acid solutions.

The results of a number of laboratory corrosion tests of Nickel 200 in acid solutions at atmospheric temperatures are shown in Table XXXIII. It will be noted that, in dilute solutions, the corrosion rate of Nickel 200 is increased by a high degree of aeration to an even greater extent than that of MONEL alloy 400. In aerated concentrated acid, however, the combination of aeration and oxidizing power of the acid itself appear to be sufficient to have a passivating effect on



A LEWIS vertical pump for sulfuric acid service featuring LEWMET alloys 55 and 66 for impeller, wear rings, journals and bearings.

(Photograph courtesy of Charles S. Lewis & Co., Inc.)

nickel so that its corrosion rate is considerably lower than in air-free acid. In view of the uncertainty of maintaining aerated conditions in plant practice, and the availability of other resistant materials, it is not customary to use Nickel 200 in handling pure concentrated acid.

Corrosion of Nickel 200 is increased by elevated temperatures, even in unaerated sulfuric acid solutions, as indicated by the laboratory test results given in Table XXXIV. In

aerated hot solutions, corrosion rates usually are high except in very low concentrations.

The addition of oxidizing agents such as ferric or cupric ion to sulfuric acid solutions usually increases corrosion of Nickel 200. Occasionally, a passivating effect will be observed at lower temperatures, but this method of achieving passivation cannot be counted on unless demonstrated by continued service experience.

TABLE XXXIII
Laboratory Corrosion Tests Of Nickel 200 In Sulfuric Acid Solutions At Atmospheric Temperatures

Acid Concentration	Temperature		Duration of Test	Velocity		Corrosion Rate			
						Unaerated		Air-Saturated	
% H ₂ SO ₄ by Wt.	°C	°F	Hrs.	m/sec.	ft./sec.	mm/y	mpy	mm/y	mpy
1	30	86	120	0.08	0.26	—	—	1.24	49.0
2	21	70	5	None	None	0.05	2.0	—	—
5	19	65	100	None	None	0.06	2.2	—	—
5	30	86	24	0.08	0.26	0.23	9.0	1.55	61.0
10	21	70	96	None	None	0.04	1.7	—	—
20	21	70	5	None	None	0.10	4.0	—	—
50	30	86	24	0.08	0.26	—	—	.41	16.0
93	30	86	24	0.08	0.26	—	—	.25	10.0
95	21	70	20	None	None	1.8	71.0	—	—

TABLE XXXIV
Laboratory Corrosion Tests Of Nickel 200 In Sulfuric Acid Solutions At Elevated Temperatures

Acid Concentration	Temperature		Duration of Test	Velocity		Corrosion Rate			
						Unaerated		Air-Saturated	
% H ₂ SO ₄ by Wt.	°C	°F	Hrs.	m/sec.	ft./sec.	mm/y	mpy	mm/y	mpy
1	78	172	20	0.08	0.26	—	—	2.79	110
5	60	140	100	None	None	0.25	10	—	—
5	60	140	20	0.08	0.26	—	—	2.24	88
5	71	160	18	0.08	0.26	—	—	2.62	103
5	77	170	120	None	None	0.53	21	—	—
5	78	172	20	0.08	0.26	0.76	30	5.08	200
5	101*	214*	23	None	None	0.86	34	—	—
10	60	140	20	0.08	0.26	—	—	2.26	89
10	77	170	120	None	None	0.30	12	—	—
10	80	176	6	None	None	—	—	3.05	120
10	102*	216*	23	None	None	3.05	120	—	—
19	104*	219*	23	None	None	2.79	110	—	—
25	82	180	20	0.13	0.43	—	—	2.11	83
48	70	158	—	None	None	0.46	18	—	—
50	122*	252*	20	None	None	86.4	3400	—	—
70	38	100	24	0.08	0.26	0.74	29	—	—
75	182*	360*	20	None	None	23.1	910	—	—
93	65	149	—	None	None	3.71	146	—	—
96	294*	561*	3	None	None	58.4	2300	—	—

* Boiling

M. IRON-BASE NICKEL-CHROMIUM ALLOY

INCOLOY alloy 800 has been used as tubing in coolers handling concentrated (98%) acid in sulfuric acid manufacture although it is not known as a sulfuric acid resistant alloy and its usefulness is usually restricted to either dilute or concentrated acid solutions. Under the particular plant conditions of acid concentration, temperature, impurity content and flow velocity, existing in the coolers, INCOLOY alloy 800 corroded at a lower rate than Types 304 and 316 stainless steels. It has already been shown in Figure 16 that this type of behavior is possible. Under conditions of heat transfer where the Alloy 800 surface is cooler than the bulk sulfuric acid temperature and in a plant acid stream containing inhibiting impurities, corrosion rates would be considerably lower than those indicated in Figure 16. In addition, the higher nickel content of Alloy 800 results in increased resistance to chloride stress-corrosion cracking from the water side of the heat exchanger tubing. Corrosion tests under plant conditions are suggested to determine applicable alloys. Plant acids should be employed if laboratory tests are utilized, so that impurities which may increase or decrease corrosion rates are present.

Very little corrosion data exist for Alloy 800 in sulfuric acid. Laboratory tests in five percent H_2SO_4 at 50°C (122°F) show rates of 0.51 mm/y (20 mpy) in unaerated acid and an increase to 1.27 mm/y (50 mpy) when the solution is aerated. In aerated 75 percent acid at 60°C (140°F) the rate is still higher, 4.57 mm/y (180 mpy). Laboratory test results in reagent grade 95 percent sulfuric acid are shown in Table XXXV. The apparent anomaly in which the corrosion rate for INCOLOY alloy 800 is lower at 70°C (158°F) than 50°C (122°F) suggests an unstable condition in which the corrosion potential is oscillating between the active region and passive region as discussed in Part II-B-1 and illustrated by Figures 3 and 4.

N. NICKEL-BASE CHROMIUM ALLOYS

Chromium additions to nickel result in a reduction in critical current density, passivity over a wider potential range and generally a reduction in passive current density in sulfuric acid solutions in comparison to pure nickel.⁶⁹ The reduction in critical current density is illustrated in Figure 65 which was taken from the work of Bond and Uhlig.⁷⁰

1. Alloy 600

Alloy 600 is the wrought nickel-chromium alloy most widely employed in the chemical and process industries. It may be used in unaerated sulfuric acid solutions up to about 60 percent concentration and again at concentrations above 90 percent at room temperature. Aeration, except in concentrated acid, or an increase in temperature at all acid concentrations increases the corrosion rates considerably as shown by corrosion test results for INCONEL alloy 600 (see Tables XXXVI and XXXVII).

Strong oxidizing agents such as nitric acid, ferric or cupric ions frequently will inhibit corrosion of Alloy 600 at low or moderate temperatures. However, the oxidizing effect of dissolved air alone is not sufficient to maintain passivity except in

TABLE XXXV
Laboratory Test Of Alloys In 95 Percent
Reagent Grade Sulfuric Acid

Alloy	Corrosion Rate*			
	50°C (122°F)		70°C (158°F)	
	mm/y	mpy	mm/y	mpy
CARPENTER alloy 20Cb-3	0.26	10.1	0.42	16.4
Type 316 stainless steel	0.41	16.1	2.42	95.2
Type 304 stainless steel	0.74	29.0	0.92	36.4
INCOLOY alloy 800	1.12	44.1	0.99	38.9
Carbon Steel (1020)	1.59	62.7	3.25	128.0

* Average corrosion rates for duplicate specimens exposed for three 24-hour periods. Fresh acid used for each period with a 60 ml/cm² volume to surface area ratio. (No flow or heat transfer).

FIGURE 65
CRITICAL CURRENT DENSITIES FOR PASSIVITY OF
NICKEL-CHROMIUM ALLOYS IN N_2 -SATURATED 1.1N
 H_2SO_4 AT 25°C (77°F)

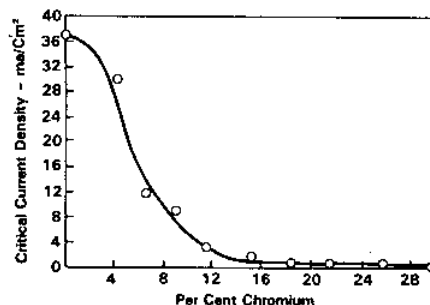


TABLE XXXVI
Corrosion Rate of Inconel Alloy 600
In Sulfuric Acid Solutions

Acid Concentration, %	Room Temperature		Boiling Temperature	
	Corrosion Rate*			
	mm/y	mpy	mm/y	mpy
10	0.08	3.2	3.43	135
20	0.05	2.0	4.72	186
30	0.06	2.5	5.49	216
40	0.05	1.8	17.8	700
50	0.04	1.6	—	—
60	0.05	1.9	—	—
70	0.06	2.3	—	—
80	0.57	22.3	—	—
90	0.01	0.5	—	—
98	0.19	7.4	—	—

* Average of two tests

concentrated acid.

Corrosion rates of Alloy 600 in boiling sulfuric acid are high except in very dilute concentrations or where boiling temperatures are considerably reduced by the use of vacuum, as in rayon spinning bath evaporators.

2. Cast Alloy CY-40

ACI CY-40 is the cast counterpart of wrought Alloy 600 but corrosion data for this alloy in sulfuric acid are scarce. Lacking other data, the information just given for Alloy 600 may be used as a guide to its possible usefulness.

3. Other Nickel - Chromium Alloys

There are a number of alloys available containing from 60 to 80 per cent nickel and from 13 to 20 per cent chromium, with the remainder mostly iron. The two most common alloys in this group are one containing about 80 per cent nickel and 20 per cent chromium, and a second alloy of about 65 per cent nickel, 15 per cent chromium, balance iron. These alloys are used principally for electric resistance and heat resisting purposes. They are somewhat similar in corrosion resistance to alloy 600, the data for which may be used as a guide to their possible usefulness. The results of several laboratory corrosion tests of these nickel-chromium alloys in pure sulfuric acid solutions are given in Table XXXVIII. The data for 10 percent solutions were taken from Rohn.⁷¹

TABLE XXXVII
Laboratory Tests of Inconel Alloy 600
In Sulfuric Acid Solutions

Acid Concentration	Temperature	Test	Corrosion Rate						
			Velocity		Unaerated		Air-Saturated		
			(Hrs.)	m/sec.	ft/sec.	mm/y	mpy	mm/y	mpy
0.16	100	212	—	—	—	0.09	3.7	—	—
1	30	86	120	0.08	0.26	—	—	1.24	49
1	78	172	22	0.08	0.26	—	—	2.79	110
5	19	65	100	None	None	0.06	2.4	—	—
5	30	86	20	0.08	0.26	0.23	9	—	—
5	30	86	23	0.08	0.26	—	—	2.0	78
5	60	140	100	None	None	0.25	10	—	—
5	80	176	20	0.08	0.26	0.76	30	3.81	150
10	Room	Room	24	None	None	0.11	4.2	—	—
70	30	86	20	0.08	0.26	1.2	46	—	—
93	30	86	20	0.08	0.26	6.86	270	0.25	10

TABLE XXXVIII
Laboratory Test Of Nickel-Chromium Alloys
In Sulfuric Acid Solutions
(Ambient Temperature)

Nominal Alloy Composition				Acid Concentration	Test	Corrosion Rate	
Ni	Cr	Fe	Mn	% By Wt.	(Hrs.)	mm/y	mpy
88	11	—	1	10	24	0.11	4.2
84	15	—	1	10	24	0.17	6.7
79	20	—	1	10	24	0.04	1.7
69	20	10	1	10	24	0.33	13
65	15	20	—	10	24	0.02	0.7
65	15	20	—	10	24	2.1	82
80	20	—	—	31	—	2.5	82
80	20	—	—	31	—	2.5	100
80	20	—	—	60	45	2.2	87
61	16	23	—	60	45	32.3	1270

(Ambient Temperature)

O. COPPER-NICKEL ALLOYS

Copper-nickel alloys provide good resistance to air free hot and cold dilute sulfuric acid as well as to cold concentrated acid. The corrosion rate of C71500 (70-30 copper-nickel) is usually less than 0.15 mm/y (6 mpy) at all concentrations of air-free sulfuric acid up to 80 percent at room temperature. In air saturated acid at room temperature up to 80 percent concentration, the maximum corrosion rate of about 1 mm/y (40 mpy) occurs at approximately 5 percent concentration. C71500 is used with air-free sulfuric acid up to 60°C (140°F) in solutions up to 60 percent concentration and in boiling acid up to 10 percent.⁷²

Little difference is noted in the sulfuric acid corrosion behavior of the lower nickel content C71000 and C70600 alloys (80-20 and 90-10 copper nickels) in comparison to C71500. In sulfuric acid, at ambient temperature and concentrations from one to five percent, the corrosion rates for all alloys in the range of 70 to 90% copper (balance nickel) are 0.07-0.13 mm/y (3-5 mpy).⁷³

Above room temperature, concentrated sulfuric acid may be corrosive to all copper base alloys because of a breakdown of the acid with the formation of metallic sulfides and sulfur dioxide gas causing localized corrosion attack.⁷⁴

Corrosion rates for the wrought alloys may be used as a guide for the cast counterparts of these copper-nickel alloys (C96200, C96300 and C96400) since specific corrosion data for them are not available.

P. AUSTENITIC CAST IRONS (NI-RESISTS)

The Ni-Resist alloys consist of a family of cast irons to which sufficient nickel has been added to produce an austenitic structure. Several types of Ni-Resist are produced by varying the nickel as well as the copper and chromium content. Ni-Resist Types 1 and 1b have copper additions for added corrosion resistance in many environments. (Only those alloys without copper can be made in a ductile grade).

There has been considerable practical application of the Ni-Resist alloys in dilute and concentrated, un-aerated sulfuric acid at low temperatures. Ni-Resist Type 1, which contains 5.5-7.5% copper, is preferred for sulfuric acid applications and shows marked superiority over gray cast iron in un-aerated dilute acid.

An isocorrosion chart for Ni-Resist Type I in air-free acid originally published by Fontana⁷⁵ is given in Figure 66. Agitation and/or aeration as well as an increase in temperature can increase the corrosion rate many times.

Advantage can be taken of the combination of the low temperature corrosion resistance of the Ni-Resists in sulfuric acid and their non-galling characteristics for acid transfer gear pumps.

PART III - CORROSION IN SULFUR DIOXIDE, SULFUR TRIOXIDE AND OLEUM

A. SULFUR DIOXIDE

Although the scaling rates of iron-base alloys are higher in dry sulfur dioxide than in air, carbon steel can be utilized at temperatures up to 400°C (750°F) or even 538°C (1000°F), according to how conservative the designer wishes to be. (Where corrosion products cause pluggage problems in the catalyst beds of converters, unprotected steel is often limited to the lower end of this temperature range). However, if moisture is present in a sulfur dioxide gas stream, sulfurous acid can form below the dewpoint with almost catastrophic results. Carbon steel may corrode at a rate as high as 15 mm/y (600 mpy) in sulfurous acid at 25°C (77°F).⁷⁶ Type 316L stainless steel is resistant to corrosion under these conditions.

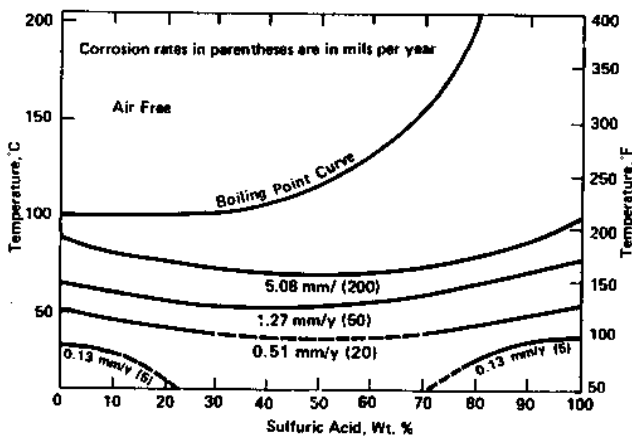
When sulfur or sulfur bearing compounds are burned in the presence of excess oxygen, some of the sulfur dioxide is oxidized to sulfur trioxide. However, the reaction proceeds slowly and the commercial production of the trioxide requires catalysts. Many metal oxides are catalysts for this reaction, including the iron corrosion products on steel. Usually less than 2% of the SO₂ is converted to SO₃ when sulfur bearing compounds are burned, but the burning of Bunker C oil may yield 15-20% conversion of the contained sulfur values to SO₃ because of the catalytic action of vanadium oxide in the ash. Thus, in practice, sulfur dioxide gas streams very often contain other gases such as oxygen, nitrogen, sulfur trioxide and water vapor. If this type of mixed gas is cooled below the dewpoint, sulfuric acid condenses on the metal. All sulfuric acid condensates are considerably enriched in sulfuric acid concentration as indicated by the equilibrium diagram, Figure 67.

Corrosion rates for a number of alloys in commercial sulfur dioxide gas streams are shown in Table XXXIX. The temperature of the gas streams increases as one reads from left to right.

Corrosion rates for the austenitic chromium-nickel stainless steels are low enough to consider them as materials of construction in all cases, except for Exposure 4 where temperature fluctuations were apparently both above and below the dewpoint and sulfuric acid is believed to have condensed (and

FIGURE 66

ISOCORROSION CHART FOR TYPE 1 NI-RESIST IN AIR-FREE SULFURIC ACID



may have boiled and concentrated still further as the temperature was raised). Indeed, in dry sulfur dioxide the austenitic stainless steels are much more resistant than carbon steel and are generally considered to have acceptable resistance up to 800°C (1472°F).⁷⁸

Although nickel is more resistant to sulfur dioxide than to sulfur or hydrogen sulfide, it is subject to sulfidation in these environments at elevated temperatures. Nickel is reasonably resistant in dry sulfur dioxide up to 370°C (700°F)⁷⁹ but in commercial streams containing contaminants it may suffer serious corrosive attack at lower temperatures, as shown in Table XXXIX.

Chromium is the most important alloying element in high nickel alloys in conferring resistance to sulfur attack. Alloy 800 with a nominal composition of 46% Fe - 32.5% Ni - 21% Cr is among the most resistant of the high nickel alloys in dry sulfur dioxide environments. Note in Table XXXIX that nickel alloys without chromium such as MONEL alloy 400 and HASTELLOY alloy B tend to be severely attacked in sulfur dioxide environments. Alloy 600, nominally containing 76% Ni and 15.5% Cr, has been reported to be serviceable in dry sulfur dioxide up to 815°C (1500°F).⁸⁰ However, more recent work has shown that Alloy 600 goes through a maximum in sulfidation attack at about 700°C (1292°F) because of slagging (melting) of the sulfide corrosion products. Table XL shows

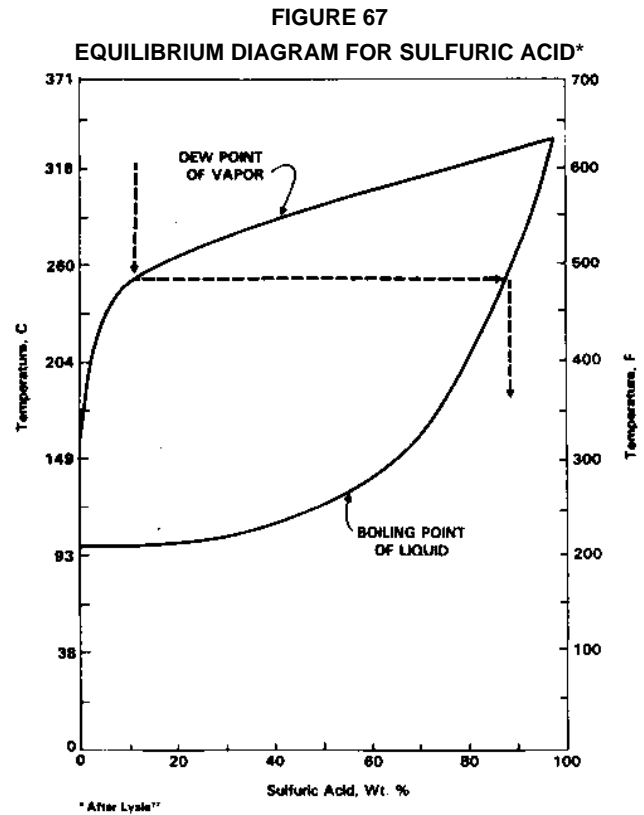


TABLE XXXIX
Corrosion of Alloys in Sulfur Dioxide Containing Environments

Alloy	Exposure*	Corrosion Rate								
		1		2		3		4		
		Temp. C-F	4-24	40-75	29-35	85-95	4-54	40-130	121-232	250-450
		mm/y	mpy	mm/y	mpy	mm/y	mpy	mm/y	mpy	
Type 304 stainless steel			Nil**	Nil	Nil	Nil	-	-	2.39	94
Type 309 stainless steel			-	-	-	-	Nil	Nil	-	-
Type 310 stainless steel			-	-	-	-	Nil	Nil	-	-
Type 316 stainless steel			0.01	0.3	Nil	Nil	Nil	Nil	1.30	51
Type 317 stainless steel			-	-	Nil	Nil	Nil	Nil	1.19	47
Type 347 stainless steel			Nil	Nil	-	-	0.30	12	-	-
Type 430 stainless steel			-	-	-	-	-	-	-	-
CARPENTER alloy 20			-	-	Nil	Nil	Nil	Nil	-	-
ILUUM alloy G			-	-	-	-	0.04	1.5	-	-
INCOLOY alloy 825			-	-	Nil	Nil	-	-	-	-
Nickel 200			-	-	-	-	>4.06***	>160***	1.85	52
MONEL alloy 400			-	-	0.56	22	1.85	73	0.84	33
INCONEL alloy 600			-	-	0.01	0.2	0.43	17	0.79	31
HASTELLOY alloy B			-	-	1.70	67	-	-	-	-
HASTELLOY alloy C			-	-	Nil	Nil	Nil	Nil	0.51	20
Chemical Lead			0.01	0.3	0.64	25	0.03	1.0	1.85	73
Mild Steel			-	-	-	-	-	-	-	-
Gray Cast Iron			-	-	-	-	-	-	-	-

* Exposure (Temperatures indicated above)
 ** Nil <0.00254 mm/y (<0.1 mpy)
 *** Corroded away during test

1. Water-saturated, scrubbed gas from a non-ferrous smelter containing 80% SO₂ and 20% N₂ feed to an adjacent sulfuric acid plant. Test duration 94 days.
2. In bottom tray of cooling section of scrubber handling water-saturated 10% SO₂ with excess air present. Some sulfuric acid reported to be in mist. Test duration 20 days.
3. Air saturated fumes from a metal calcining operation containing 5% SO₂, 8% CO₂, 11% O₂ and a small amount of SO₃ mist. Test duration 34 days.
4. Suspended in precipitator of process used for recovery of sulfur from pyrite. Gas contains an undetermined amount of SO₂, elemental sulfur mist plus minor amounts of oxygen, water vapor and sulfuric acid. Short duration test of 50 hours.

the results of a 1,000 hour test in air - 10% sulfur dioxide - 5% water vapor at 700°C (1292°F). Other tests were run in a similar environment but with either 2% or 50% sulfur dioxide and at 850 and 1000°C (1562 and 1832°F). Although the attack was somewhat more severe at the higher SO₂ level at 700°C (1292°F), sulfur dioxide did not appreciably influence the corrosion at 850 and 1000°C (1562 and 1832°F) and the alloys tested could be ranked according to oxidation resistance alone. It is interesting to note that INCONEL alloy 601 with lower nickel and higher chromium and iron contents was not subject to the melting and slagging of its corrosion product in the test shown in Table XL.

B. SULFUR TRIOXIDE

The austenitic stainless steels have excellent resistance and high nickel alloys have good to excellent resistance in anhydrous sulfur trioxide at room temperature. The results of a laboratory test in liquid sulfur trioxide at 99-113°C (210-235°F) are given in Table XLI. This would appear to be about the limiting temperature for MONEL alloy 400 and possibly Nickel 200.

The austenitic stainless steels and some, but not all of the

high nickel alloys, possess excellent resistance to mixed gas streams containing SO₃ such as are encountered in contact process sulfuric acid plants as shown in Table XLII. Austenitic stainless steels such as Types 304, 321 and 347 have useful corrosion resistance to at least 650°C (1200°F) in sulfur trioxide.⁸¹ This useful corrosion resistance may extend above 650°C (1200°F) but data to define the useful upper temperature limit are lacking.

C. OLEUM

Thick-walled (Schedule 80) carbon steel is usually used for handling oleums at moderate temperatures. However, there are little data to determine the limiting conditions for steel in oleum at higher temperatures. The use of gray cast iron in oleum should be avoided because it has been found that the free sulfur trioxide can combine with silicon in the cast iron, resulting in high internal stresses and cracking of the cast iron, sometimes with explosive violence.⁸² Note also that high Si iron such as DURIRON is not recommended for oleum or any service containing free SO₃.

Very little data have been published on corrosion in oleum and the following two summary paragraphs are mainly the result of personal communications.^{83, 84}

TABLE XXXIX (Continued)
Corrosion of Alloys in Sulfuric Dioxide Containing Environments

Corrosion Rate											
5		6		7		8		9		10	
204-500		204-500		204-232		400-450		260-371		500-700	
454		850		427-482		800-900					
mm/y	mpy	mm/y	mpy	mm/y	mpy	mm/y	mpy	mm/y	mpy	mm/y	mpy
0.15	6	0.03	1	0.05	2	-	-	0.01	0.3	0.01	0.3
-	-	-	-	-	-	-	-	-	-	nil	nil
-	-	-	-	-	-	-	-	-	-	nil	nil
0.13	5	0.03	1	0.05	2	0.01	0.2	-	-	nil	nil
-	-	-	-	-	-	0.01	0.3	-	-	-	-
-	-	-	-	-	-	-	-	-	-	-	-
0.20	8	0.03	1	-	-	-	-	0.03	1	0.01	0.2
-	-	-	-	-	-	0.01	0.2	-	-	-	-
-	-	-	-	-	-	-	-	-	-	-	-
0.10	4	0.03	1	0.03	1	nil	nil	-	-	-	-
-	-	-	-	0.46	18	-	-	-	-	0.02	0.7
-	-	-	-	1.73	68	-	-	-	-	-	-
0.51	20	0.03	1	0.15	6	-	-	-	-	0.05	2
-	-	-	-	-	-	-	-	-	-	-	-
0.08	3	0.01	0.5	-	-	-	-	-	-	nil	nil
-	-	-	-	-	-	-	-	-	-	-	-
0.69	27	-	-	0.36	14	0.03	1	0.18	7	-	-
-	-	0.10	4	0.38	15	0.03	1	-	-	0.28	11

5. Flue gas from nickel converter containing 5% SO₂. Test duration 39 days.

6. Flue gas from another nickel converter containing 5% SO₂. Test duration 39 days.

7. Effluent gas stream from a sulfur burner containing 5% SO₂, 1.25% SO₃, 6% H₂O and 8% O₂. Operated for 68 days of a 100 day exposure.

8. Effluent gas stream from a sulfur burner containing 18% SO₂ plus small amounts of SO₃, O₂ and H₂O. Although Type 316 stainless steel corroded at a low and acceptable rate in this test, a Type 316 stainless steel fan runner had suffered severe corrosion in this service and test was performed to select another material of construction. Test duration 90 days.

9. Suspended in precipitator downstream of a nickel ore roaster. Gas contained 10% SO₂. Test duration 73 days.

10. Gas stream in a sulfuric acid plant containing dry 7-8% SO₂ and 9-10% O₂. Test duration 487 days.

TABLE XL
Oxidation Of Alloys In Air—10% Sulfur Dioxide—5% Water Vapor For 1,000 Hours At 700°C (1292°F)

Alloy	Weight Loss		Maximum penetration	
	(mg/cm ²)	mm	mm	mils
Type 304 stainless steel	0.8	0.01	0.01	0.2
INCONEL alloy 601	1.05	0.01	0.01	0.4
HASTELLOY alloy X	16.8	0.02	0.02	0.6
INCOLOY alloy 800	1.8	0.02	0.02	0.9
INCONEL alloy 617	13.6	0.04	0.04	1.6
Type 310 stainless steel	1.5	0.05	0.05	2.0
INCONEL alloy 600	180	1.50	1.50	59.0

* Includes internal sulfidation

TABLE XLI
Plant Corrosion Test In Liquid Sulfur Trioxide

Alloy	Corrosion Rate	
	mm/y	mpy
Types 302 and 347 stainless steel	nil*	nil*
WORTHITE	nil	nil
DURIMET 20	nil	nil
INCONEL alloy 600	0.01	0.2
Mild steel	0.14	5.6
Nickel 200	0.23	9.0
MONEL alloy 400	0.43	17.0

* nil <0.00254 mm/y (<0.1 mpy)

Conditions: Immersed in liquid sulfur trioxide in pressure vessel under 120-160 lbs. per sq. in. pressure, temperature 99-113°C (210-235°F), duration of test 167 hours.

TABLE XLII
Corrosion Test In Dry Sulfur Trioxide Gas Stream From Contact Process Sulfuric Acid Plant

Alloy	Corrosion Rate	
	mm/y	mpy
HASTELLOY alloy C	0.02	0.9
HASTELLOY alloy X	0.02	0.9
Type 309 stainless steel	0.03	1.0
WORTHITE	0.03	1.3
Type 316 stainless steel	0.05	1.8
Type 304 stainless steel	0.05	2.0
INCOLOY alloy 800	0.08	3.0
Type 310 Stainless steel	0.08	3.0
Carbon steel	0.12	4.9
INCONEL alloy 600	>0.33*	>13*
Nickel 200	>0.48*	>19*

* Corroded away

Gas stream: 6-7% SO₃, 1-2% SO₂, 8-9% O₂, Balance N₂
 Temperature: 582°C (1080°F) Avg. Range 577-588°C (1070-1090°F)
 Flow Rate: Rapid

Type 304 stainless steel is the preferred material of construction for handling the lower concentrations (less than 20%) and higher temperature applications of oleum. Although the low carbon counterpart (Type 304L) can be utilized, it is not necessary, unless dilution of the acid is anticipated, because sensitized Type 304 stainless steel does not appear to be subject to intergranular corrosion in oleum. Type 316 stainless steel does not offer an advantage in oleum as it does in dilute sulfuric acid. In fact, Type 316 stainless steel is sometimes less resistant than Type 304 in hot, strong, oleum.

Service experience has indicated that oleum below about 20% is more aggressive than higher concentrations, especially at elevated temperatures. High velocities tend to activate corrosion of Type 304 stainless steel in hot [100-150°C (212-300°F)] oleum; flow rates are therefore controlled to 3-4 fps. Oleum below 14% concentration is often aggressive even at moderate [20-60°C (68-140°F)] temperatures and a high flow velocity will increase the attack.

The effect of temperature on a Russian IKh18N10T stainless steel in 19.1% oleum was investigated by Poluboyartseva et al. and their results are shown in Table XLIII.⁸⁵ There is no matching AISI standard stainless steel although it is so close in composition to Type 304 stainless steel that the corrosion resistance should be quite similar. These authors also assessed the effect of motion on the corrosion of this same stainless steel at 20°C (68°F) and 70°C (158°F) by means of rotating diskshaped samples. There was practically no effect on the corrosion rates under these conditions, when the rate of rotation was varied from 150 to 1720 rpm which was believed to be representative of flow rates from 1.8 - 11.5 m/sec. (5.9 - 37.7 fps). On the basis of these tests, the IKh18N10T stainless steel was determined to be suitable for tubular and spiral coolers for 20% oleum.

Tables XLIV - XLVII show the results of corrosion tests in various concentrations of oleum.

TABLE XUIII
Corrosion Of 1Kh18N10T Stainless Steel* In 19.1% Oleum

Corrosion Rate								
Temperature	Test Duration	Vapor	Liquid-Vapor Interface		Liquid			
			mm/y	mpy	mm/y	mpy		
C	F	(Hrs.)	mm/y	mpy	mm/y	mpy	mm/y	mpy
10-12.9	50-55	93.0	nil**	nil	nil	nil	nil	nil
9.6-16	49-61	98.0	0.01	0.03	0.01	0.4	0.01	0.3
19.5-21.3	67-70	98.5	nil	nil	0.01	0.3	nil	nil
30	86	95.0	nil	nil	0.01	0.2	nil	nil
45	113	116.5	nil	nil	nil	nil	nil	nil
75	167	240.0	nil	nil	0.01	0.4	nil	nil
75	167	523.0	nil	nil	0.01	0.2	0.01	0.4
95	203	95.0	0.01	0.3	0.02	0.7	0.06	2.5

* Composition: 18.04 Cr, 10.22 Ni, 0.06 C, Ti 0.53, Mn 1.31, Si 0.61, P 0.027

**Nil <.00254 mm/y (<0.1 mpy)

TABLE XLIV
Corrosion Rates In 100.5-101.5% H₂SO₄
(2-7% Oleum) At 149-163°C (300-325°F)

Alloy	Corrosion Rate	
	mm/y	mpy
Type 302 stainless steel	0.05	2
Type 304 stainless steel	0.15	6
Ductile Iron-Annealed	0.33	13
Ductile Iron-As Cast	0.53	21
Carbon Steel	0.58	23*
Gray Cast Iron	0.89	35
Ni-Resist Type 3	1.85	73
Ni-Resist Type 2	1.98	78
Ni-Resist Type D2	2.13	84

Immersed in open tank for 32 days.

* The corrosion rate of carbon steel in oleum concentrations below 2% is excessive.⁸⁴

TABLE XLV
Corrosion Rates in 101.35-102.02%
H₂SO₄ (6-9% Oleum) at 170°C (338°F)

Alloy	Corrosion Rate	
	mm/y	mpy
Type 309 stainless steel	0.09	3.5
Type 310 stainless steel	0.15	6
Type 304L stainless steel	0.20	8
Type 304H stainless steel	0.20	8

Installed in oleum line for 46 days.

TABLE XLVI
Corrosion Rates In Air-Free 25% Oleum At
10-32°C (50-90°F)

Alloy	Corrosion Rate	
	mm/y	mpy
HASTELLOY alloy C	nil	0.1
INCOLOY alloy 825	0.01	0.2
INCONEL alloy 600	0.01	0.2
Type 316 stainless steel	0.02	0.7
MONEL alloy 400	0.03	1.2
HASTELLOY alloy B	0.04	1.7
Ni-Resist Type 2B	0.07	2.6
9% Nickel Steel	0.17	6.7
Gray Cast Iron	1.12	44
Ductile Iron	2.06	81

Exposed in bottom of oleum tank for 55 days.

TABLE XLVII
Corrosion Rates In 40% Oleum At
32-54°C (90-130°F)*

Alloy	Corrosion Rate	
	mm/y	mpy
DURIMET alloy 20	nil**	nil
Type 309 stainless steel	nil	nil
Type 316 stainless steel	nil	nil
Type 317 stainless steel	nil	nil
Type 304 stainless steel	0.01	0.2
Type 321 stainless steel	0.01	0.2
Type 310 stainless steel	0.01	0.2
Type 347 stainless steel	0.01	0.2
HASTELLOY alloy C	0.01	0.2
Carbon Steel	0.12	4.9***
Carbon Steel coupled to Type 304 stainless steel	0.11	4.4
Type 304 stainless steel coupled to carbon steel	0.01	0.2

Immersed in pump tank for 109.5 days in plant producing 40% oleum.

* Oleum contained 4% Nitric Acid as antifreeze

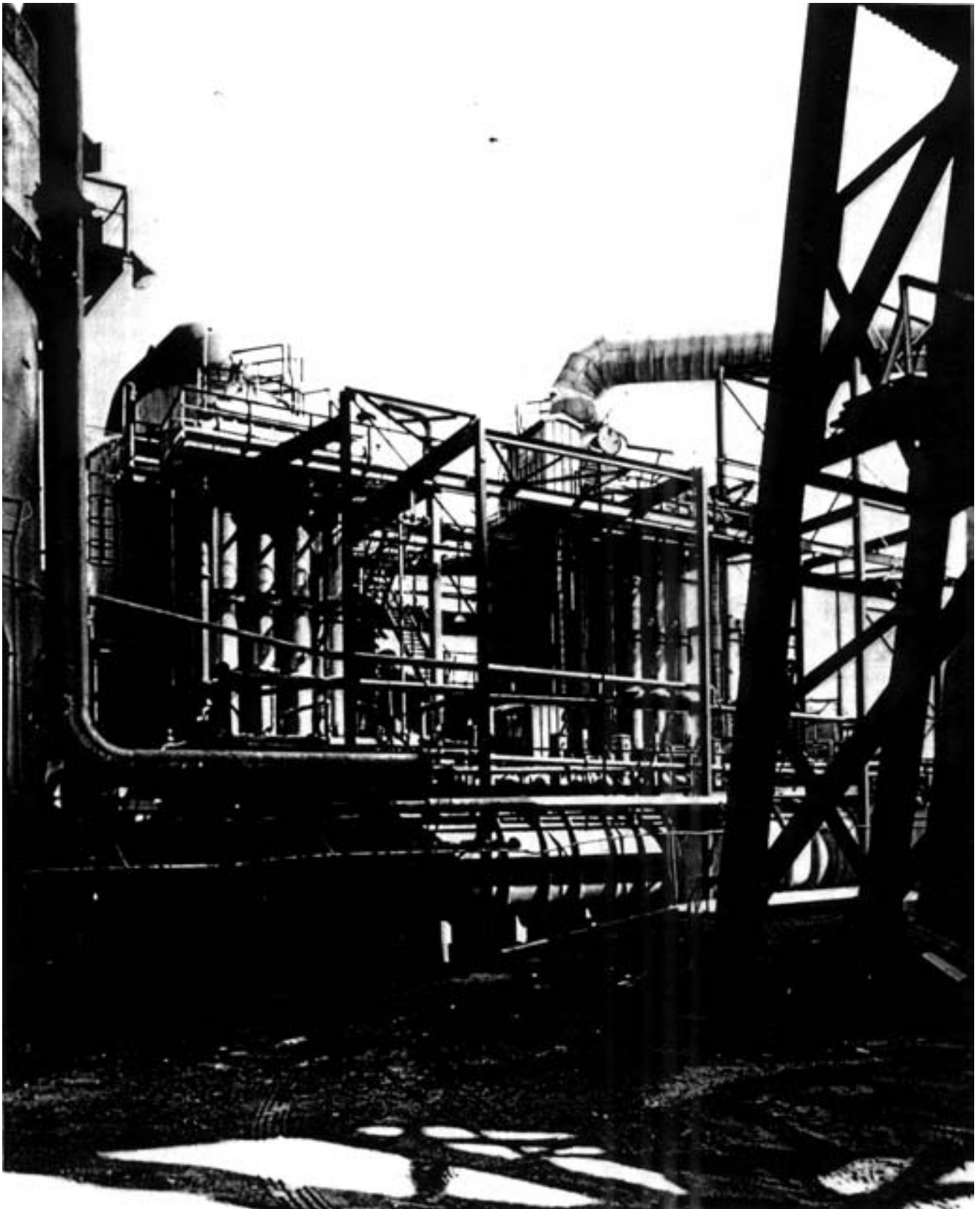
** Nil <0.00254 mm/y (<0.1 mpy)

*** Crevice corrosion to a maximum depth of 0.18 mm (7 mils)

ACI CN-7M castings have been used successfully for pumps and valves handling oleum and good service has been obtained at temperatures approaching 150°C (300°F).⁵⁷ Note the excellent corrosion resistance of DURIMET alloy 20 in 40% oleum, Table XLVII. In addition, more highly alloyed materials, such as ILLIUM alloys B and 98 or LEWMET alloy 55, have been used to advantage, especially in the more aggressive environments.

Among the wrought alloys, the superior corrosion resistance of Type 309 stainless steel, as indicated in Tables XLV and XLVII, suggests that it might offer an advantage over Type 304 stainless steel in some instances.

In practice, the performance of various alloys in oleum may be governed by the amount of water dilution which occurs as a result of the exposure conditions. One particular company has protected the shaft of submersible pumps from corrosion by dilute oleum by means of a heat-shrinkable fluorocarbon sleeve at the liquid-vapor interface and in the vapor region.



A portion of Inco's sulfuric acid complex at Sudbury, Ontario. The vertical shell and tube heat exchangers were the first Type 316L stainless steel anodically protected sulfuric acid coolers placed in service in 1970.

PART IV - INDUSTRIAL APPLICATIONS

A. SULFURIC ACID MANUFACTURE

The Contact Process, which accounts for practically all of the sulfuric acid manufactured today, had its origin in the filling of a patent in 1831 by Peregrine Phillips who found that, in the presence of a platinum catalyst, sulfur dioxide could be reacted directly with atmospheric oxygen to form sulfur trioxide. However, the process was not utilized to any extent for about 70 years because of rapid impairment of the platinum catalyst.

A large majority of sulfuric acid plants utilize elemental sulfur as a raw material and the rest of the plants make use of a number of sulfur sources including hydrogen sulfide, iron sulfide, sulfur dioxide from metal smelter gases, and waste spent and refinery sludge acids. The corrosion problems associated with plants utilizing these different sources of sulfur vary to some degree because of the impurities present and operating temperatures. However, because Contact sulfuric acid plants have been operating for such a long period, there have not been very many corrosion tests run recently; rather, the plant operators draw upon their long experience in selecting materials of construction. Therefore, a large proportion of the information contained in this section is based upon practical experience. Although "hard numbers" may be scarce, there is a lot of merit in actual experience.

Because of the predominance of sulfur-burning plants, they will be considered first. A simplified flow diagram for a typical double contact absorption sulfuric acid plant is shown in Figure 68. Usually sulfur is handled molten and can be quite corrosive depending upon temperature, purity and oxygen content, as shown in Tables XLVIII, XLIX, and L.

Carbon steel or cast iron is usually utilized to convey molten sulfur with frequent replacement often required. Fyfe and Brooks have indicated that sulfur, which has been allowed to solidify and is stored outside, absorbs moisture and forms sulfurous and sulfuric acids.⁸⁷ When remelted, the acid refluxes in the carbon steel melting vessel and causes heavy corrosion in the vessel and downstream carbon steel equipment handling the molten sulfur. Where maintenance costs are high in these systems, the possibility of substituting one of the stainless steels or a high nickel alloy such as Alloy 600 should be investigated.

Types 309 and 310 stainless steels have been successfully used for the burner nozzles of the sulfur burner and as tube inserts to protect the inlet portions of the waste heat boilers. The dry sulfur dioxide gas stream, downstream of the waste heat boiler, could be handled in carbon steel from the standpoint of corrosion alone but, from a practical standpoint, the flaky and friable corrosion products formed would soon plug the catalyst bed of the converter. Therefore, Type 304 stainless steel is often utilized for the hotter portions of the system and is preferred to aluminum coated steel which is another alternative. The excellent corrosion resistance of the austenitic stainless steels in sulfur dioxide and sulfur trioxide was discussed in the previous section of this bulletin. Fyfe and Brooks noted that in situations where flexing of the steel takes place, such as at expansion joints, there is a higher rate of metal loss.⁸⁷ Their experience indicated that the most severe

condition was in the duct out of the first catalyst mass of the converter, since the temperature of 604-613°C (1120-1135°F) is close to the melting point of aluminum used to metallize the duct, and that Type 304 stainless steel must be used for expansion joints in that duct. When the economy that can be realized from the standpoint of reduced maintenance costs and downtime for catalyst screenings, etc. is taken into account, austenitic stainless steels can be justified for this portion of the sulfuric acid plant.

Chemetics International Ltd. utilized Type 316L stainless steel to advantage for the catalyst "candles" of its radial flow converter. A candle consists of two perforated coaxial cylinders with vanadium pentoxide catalyst in the annulus. The conventional converter is responsible for up to one-half of the total pressure drop in a sulfuric acid plant and is thus the largest consumer of energy.⁸⁸ Additionally, the first catalyst pass is the one most subject to pluggage by corrosion products which requires downtime for screening of the catalyst. With a surface area about four times that of the conventional flat bed, the velocity is lower, reducing sensitivity to dust accumulation and extending the period between catalyst screenings. Another advantage is that the stainless steel candles can be removed and recharged using a crane which is a faster and more convenient method than removal and replacement of the catalyst in the conventional in-situ bed. But the main advantage with the design is energy savings which has gained in importance as power costs escalate.

Another energy efficient plant has been installed with the entire converter and hot gas piping constructed of austenitic stainless steel. Heat from the exothermic reaction is conserved in an austenitic stainless steel gas-to-gas heat exchanger located within the converter. This proprietary and novel design utilizes the hot SO₂ and SO₃ gases flowing between the first and second catalyst masses to reheat SO₂ being returned to the converter. Types 304, 321, 309 or 310 stainless steels may be selected for this service according to the specific

TABLE XLVIII
Laboratory Corrosion Tests of Type 304
Stainless Steel in Molten Sulfur

Temperature		Test Duration	Corrosion Rate	
C	F	days	mm/y	mpy
127	260	4	0.14	5.6
296	565	2.7	0.13	5.0
366	690	2.7	0.45	17.7
440	825	2	1.32	52

FIGURE 68
TYPICAL DOUBLE CONTACT ABSORPTION SULFURIC ACID PLANT

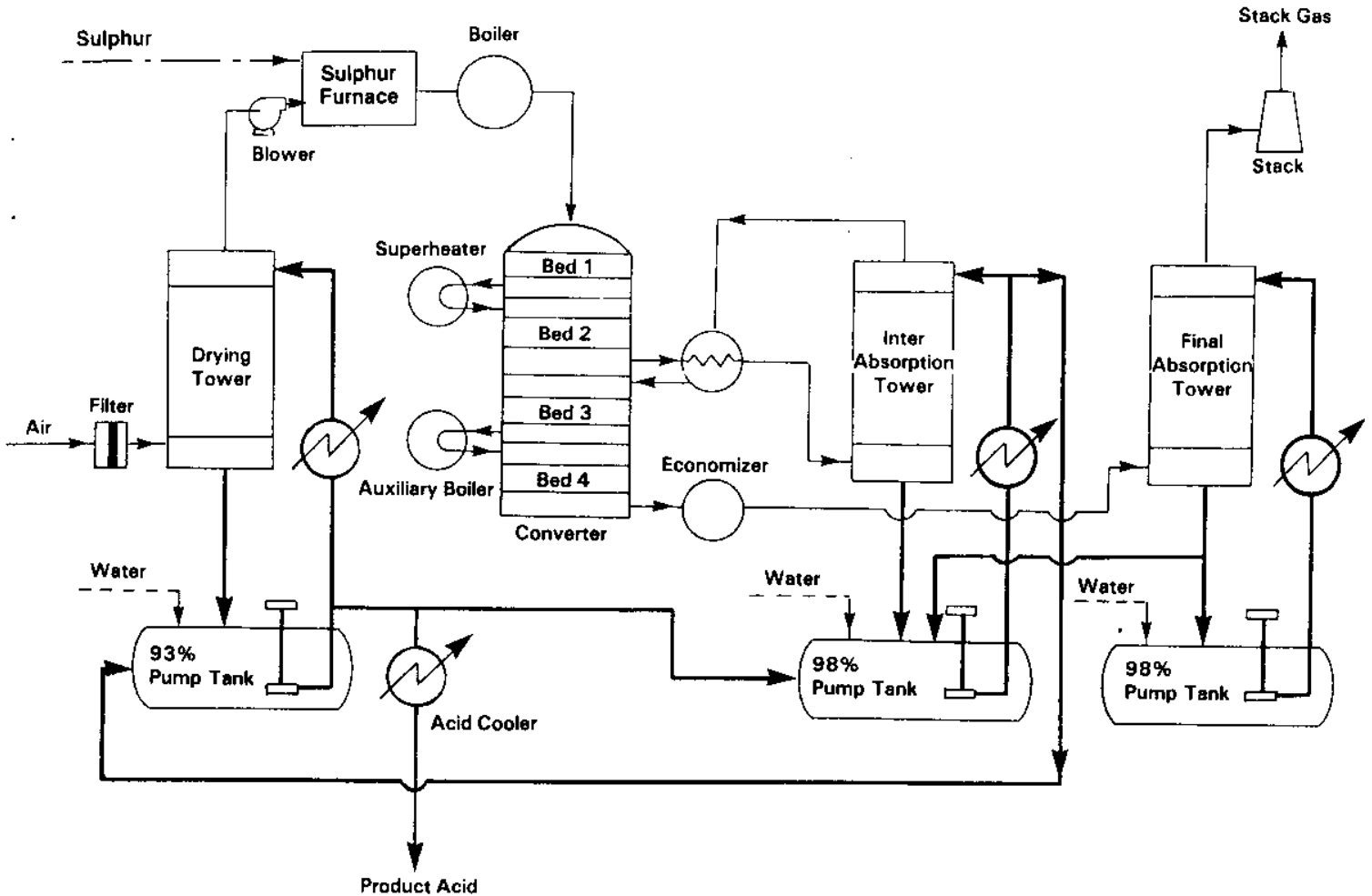


TABLE XLIX
Laboratory Corrosion Tests In Molten Sulfur
At 127°C (260°F)

Alloy	Partly Immersed For 20 Hours with Some Air Admitted*		Partly Immersed For 24 Hours with Air Freely Admitted*	
	mm/y	mpy	mm/y	mpy
Type 304 stainless steel	0.08	3.1	0.25	9.7
Carbon Steel	0.10	3.9	1.08	42.7
INCONEL alloy 600	0.10	4.0	0.27	10.6
Type 1 Ni-Resist	0.17	6.8	0.86	33.8
Gray Cast Iron	0.19	7.6	1.15	45.4
MONEL alloy 400	0.22	8.5	0.91	36.0
Nickel 200	0.35	13.9	0.78	30.8

* The exact amount of air is unknown

TABLE L
Field Test In Frasch Sulfur Mining
Pipeline Between Well And Gathering Station

Alloy	Corrosion Rate	
	mm/y	mpy
HASTELLOY alloy C	0.02	0.9
HASTELLOY alloy B	0.06	2.2
INCONEL alloy 600	0.18	7
Type 310 stainless steel	0.46	18
Type 317 stainless steel	0.48	19*
Type 316 stainless steel	0.53	21
Type 304 stainless steel	0.94	37
Gray Cast Iron	1.40	55**
Type 430 stainless steel	1.42	56
Carbon steel	1.98	78
Nickel 200	3.73	147

* pitted to a maximum depth of 11 mils.

** pitted to a maximum depth of 15 mils.

Test Duration: 11 days

Temperature: 150-157°C (300-315°F)

Aerated: Water with pH of 1.5 to 3.5 percent



A type 316L "candle" for a radial flow converter. The candle was loaded in a weatherproof loading area to keep both it and the catalyst free from moisture. Shown fully charged here, it is being lifted to the top of the converter for installation through the manway.

(Photography courtesy of Chemetics International, Ltd.)

conditions of the process. By utilizing a corrosion resistant nickel stainless steel, much lighter gauges may be utilized, with a resultant savings in weight and construction costs.

Absorption columns are usually constructed of brick-lined steel with a membrane and utilize ceramic packing. However, alloys are needed for certain internal hardware such as mist eliminators. Usually Type 316 stainless steel, CARPENTER alloy 20Cb-3 or INCOLOY alloy 825 will be satisfactory. For example, Brink et al.⁸⁹ have noted "Experience has shown that elements with structural parts of all 316 stainless steel have an economic life in the top of absorbing towers (98-99% H₂SO₄) at temperatures up to about 180°F. At temperatures in the 200°F range and higher, stainless steel Alloy 20 must be used, at least for some parts, for satisfactory life. Corrosion of the wires (about 1/8 inch in diameter) is accentuated by higher acid flows across them resulting from higher mist loadings. Therefore, where mist loadings and/or temperatures are high, Alloy 20 screens may be used in conjunction with other parts



The first of several Type 316L stainless steel catalyst "candles" are placed in position within a radial flow converter.

(Photograph courtesy of Chemetics International Ltd.)

made of 316 stainless steel to achieve a system of intermediate cost and satisfactory service life."

However, one sulfuric acid plant did not get entirely satisfactory service from these alloys and a corrosion test was run in the space above the packing but below the mist eliminator of the absorber, as shown in Table LI. Pitting occurred on many of the alloys suggesting that unreported chlorides may have contributed to the aggressiveness of the environment in this particular plant. It appears anomalous that Type 316 steel was pitted to a lesser depth than Type 317 stainless steel. However, the test duration was comparatively short and there were numerous pinpoint pits on the Type 316 stainless steel specimens, whereas there were a few random pits on the Type 317 stainless steel; and hence, the results are explainable on this basis. Of the wrought materials tested, only HASTELLOY alloy C-276 did not show pitting or non-uniform general corrosion and it was suggested as a possible material of construction in this particular plant.



Last stage of assembly of the first all-austenitic, nickel stainless steel converter for a 1200 ton-per-day, energy efficient sulfuric acid plant. Note the heat exchanger within the converter in this proprietary design.

(Photograph courtesy of Chemetics International Ltd.)

TABLE LI
Field Corrosion Test In Top
Of Absorbing Tower In Sulfur Burning
Sulfuric Acid Plant

Alloy	Corrosion Rate*		Maximum Pit Depth	
	mm/y	mpy	mm/y	mpy
Type 317 stainless steel	0.03	1.1	0.10	4
Type 316 stainless steel	0.05	2.1	incipient**	incipient**
HASTELLOY alloy C-276	0.11	4.4		
ILLIUM alloy 98	0.12	4.6		
JESSOP alloy JS-700	0.12	4.7	0.13	5
INCONEL alloy 625	0.17	6.7	0.41	16
HASTELLOY alloy G	0.19	7.6	0.05	2
INCOLOY alloy 825	0.21	8.1	0.20	8
CARPENTER alloy 20Cb-3	0.25	9.9		
HASTELLOY alloy B	1.01	30.8		

* General corrosion tended to be non-uniform

**Incipient = less than 0.0254 mm (<1 mil)

Exposure Time: 44 days

Temperature: 91-99°C (195-210°F)

Environment: 98% H₂SO₄ mist, 8% O₂, traces of SO₂, balance N₂

Conditions tend to be more aggressive in the drying tower where the acid strength is 93 to 94 percent. The Monsanto Company indicates that Type 316 stainless steel can be used for the structural parts of mist eliminators for temperatures up to about 43°C (110°F) but Alloy 20 type materials are preferred at higher temperatures.⁸⁹

Cast iron serpentine coolers with water cascaded down the outside used to be traditional for cooling both the drying column acid and product acid and they are still found in many of the older plants. Although accomplishing the required task, cast iron coolers have a number of disadvantages: they take up a large land area (an acre or more for a 1200 ton-per-day plant); water salts deposit on the tubes requiring periodic cleaning; corrosion of the cast iron contaminates the acid product, there are numerous flanged joints and leakage; occasional cracks, and acid losses cannot be avoided; ground pollution occurs and the dilute acid attacks both concrete and steel. In addition, the vapor plume in colder climates can freeze on roadways and other structures and create a hazard.

Modern plants make use of corrosion resistant nickel-containing alloys to overcome these difficulties. One well-known chemical company has successfully utilized INCOLOY alloy 800 tubing in shell and tube heat exchangers for their concentrated sulfuric acid coolers. The selection of Alloy 800 seems surprising at first glance; although the alloy has an excellent reputation as a high temperature alloy, it is not known for resistance to sulfuric acid nor is it stabilized to prevent intergranular corrosion in the heat affected zones of welds. (It does contain some titanium added for high temperature strength which would help but not completely stabilize the alloy). However, annealed, seamless tubing was selected and dynamic tests indicated it was quite corrosion resistant in the concentrated plant acid. (Oxidizing contaminants present in plant acid can cause passivity as discussed in Part II - B-3). It was chosen mainly because its 32.5% nickel content makes it highly resistant to chloride stress-corrosion cracking in the chloride contaminated water utilized for cooling. This same company has also used Type 304L stainless steel to advantage in 98% sulfuric acid with a flow velocity of six fps at 88°C (190°F).

Plate type coolers have utilized HASTELLOY alloy C-276 for cooling 98.5% product acid from 90 to 70°C (194 to 158°F) with seawater. In addition to resistance to sulfuric acid on the process side, HASTELLOY alloy C-276 possesses excellent resistance to seawater and resistance to crevice corrosion in chloride environments, which is necessary in this type of heat exchanger where an elastomer forms a tight crevice between the metal plates.

The most popular coolers which are being employed in most new sulfuric acid plants are anodically protected Type 316L stainless steel shell and tube heat exchangers, which can be oriented horizontally or vertically. These were originally introduced by Chemetics International Limited, which is a wholly-owned subsidiary of Canadian Industries Limited (CIL). CIL has considerable experience in sulfuric acid manufacture and is Canada's largest sulfuric acid marketer. The anodically protected coolers were tested and proven in CIL's sulfuric acid plants before introduction by Chemetics International Ltd. in 1970. Although it may take all of the current capacity of the anodic protection unit to drive the potential past the active critical current density peak, the current de-

nsity required to maintain the Type 316L stainless steel in the passive region is only 1 to 5 ma/ft² (usually 2-3 ma/ft²) which corresponds to a corrosion rate of less than 0.02 mm/y (<1 mpy).

The advantages of this type of cooler include:

- Reduced maintenance costs
- Reduced downtime
- Improved heat transfer because of higher temperature operation [120°C (250°F)] and a great reduction in water side scaling
- Waste heat from the acid cooling system can be utilized for a variety of end uses. (See reference 90 for a more thorough discussion of this means of reducing energy costs)
- Higher acid velocities can be used without suffering erosion-corrosion effects
- The more efficient heat transfer allows the use of smaller pumps and smaller diameter piping with consequent savings
- Higher purity product results because low corrosion rates mean less iron contamination
- Reduced space requirements
- Improved safety
- Less installation time
- No acid spills so that both acid loss and ground contamination are avoided
- No vapor plume is generated
- If for some reason the electric power to the passivation system fails, the alloys used have sufficient corrosion resistance to allow ample time for repairs to be made.

It is not surprising that with all these advantages, anodically protected coolers have become the standard for new construction and that other engineering firms are now offering competitive anodically protected units.

Although the process (shell) side of these coolers are anodically protected, the cooling water (tube) side is not. This poses no problem in locations where fresh cooling water is available and Type 316L stainless steel can be used. Inco's sulfuric acid plants* at Copper Cliff, Ontario have been operating with up to 1,000 ppm chlorides in the cooling water for 13 years with no evidence of pitting or chloride stress-corrosion cracking. The high water velocity in the tubes while operating has kept the tubes relatively clean and free of scale and the wall temperatures below the point where stress-corrosion cracking is a problem. In addition, the tube side is kept fully flooded so that the surfaces are not alternately wet and dry.

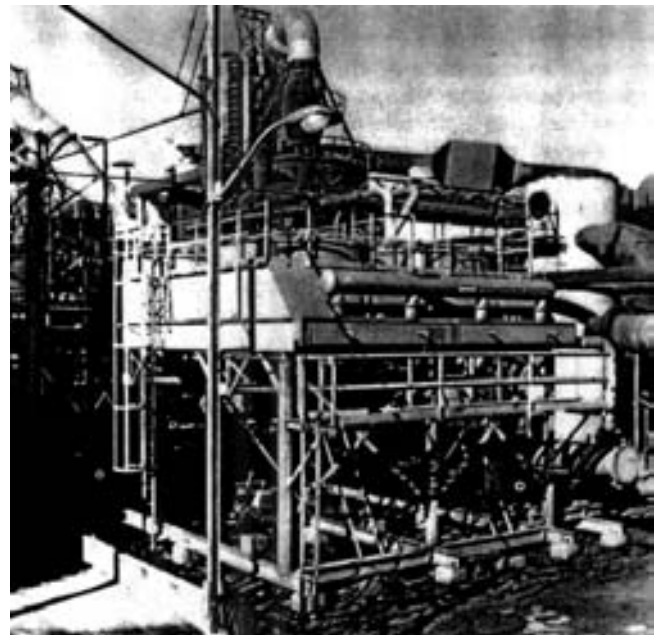
There are several alternatives when the available cooling water is high in chlorides or even brackish. An anodically protected Type 316L stainless steel air-cooler can be used (see illustration). Anodic protection of an air cooler presented Chemetics International Ltd. with a problem of throwing power to protect at least one-half the length of the tubes (cathodes are located in the channels at each end of the exchanger). The first anodically protected air cooler has run essentially trouble-free since 1972 at Inco's Copper Cliff works.

Another alternative with poor quality cooling water is to use a shell and tube cooler utilizing more corrosion resistant alloys

such as INCOLOY alloy 825, Alloy 904L, CARPENTER alloy 20Cb-3 and HASTELLOY alloy G. All of these alloys are currently being successfully used in anodically protected shell and tube heat exchangers utilizing brackish water. These alloys combine exceptional resistance to chloride stress-corrosion cracking with excellent resistance to the sulfuric acid. Fyfe et al. have indicated field service with these units and have also indicated some of the practical problems that have been overcome.³⁴

Figure 69 shows a typical alkylation sludge acid or hydrogen sulfide sulfuric acid plant. Sulfuric acid plants which utilize sludge burning to generate SO₂ have more corrosion problems with the carbon steel portions of their process than do plants utilizing elemental sulfur burning for SO₂ generation. The contents of waste spent and sludge acids typically range from 88-90% H₂SO₄ and 5-6% hydrocarbons through 55% H₂SO₄ and 1.2% hydrocarbons. Not only are waste acids dilute and consequently more corrosive, but they carry entrained carbon particles which can contribute to erosion-corrosion. To minimize the erosive effects of the particles, fluid velocities are kept below 1.5 m/sec (5 fps) and long radius elbows are used where possible.⁹¹ The residues burn at a higher temperature producing nitrogen oxides and more sulfur trioxide. Where the higher temperatures and undesirable contaminants cause corrosion difficulties with carbon steel, Type 304L stainless steel can be utilized successfully in most instances.⁹²

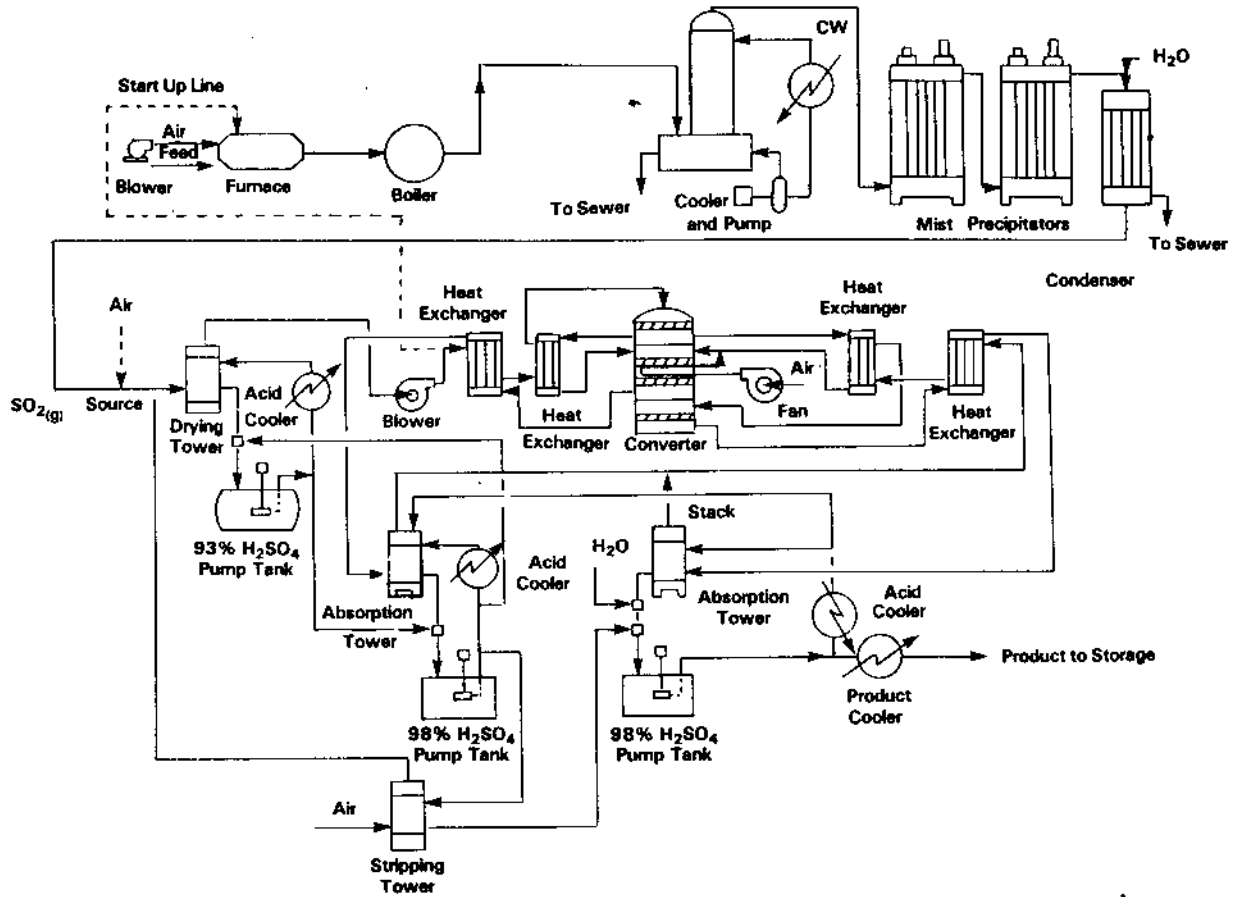
The sulfur dioxide gas streams from metallurgical plants contain entrained solids which have to be removed in cyclones and scrubbers prior to introduction into the converter. Acid-resistant, brick-lined Type 316 stainless steel



The world's first anodically protected Type 316L stainless steel air cooler at Inco's sulfuric acid complex at Copper Cliff, Ontario. An induced draft fan at the top of this 269m² (2,890 ft.²) exchanger cools 82 liters/sec. 1,300 gallons/minute) of 98 percent H₂SO₄ from 116°C (240°F) to 77°C (170°F). The electrical connections to the HASTELLOY alloy C-276 cathodes can be seen on the headerbox cover. Cathodes are located in both inlet and outlet boxes.

* These plants were formerly owned and operated by CIL utilizing sulfur dioxide from Inco's metallurgical operation close by.

FIGURE 69
TYPICAL ALKYLATION SLUDGE OR H₂S SULFURIC ACID PLANT



A bank of four anodically protected Type 316L stainless steel air coolers for 98 percent H₂SO₄, as seen from above. Anodic protection of these air coolers has allowed higher temperature operation 120°C (250°F) than conventional air coolers which are limited to about 85°C (185°F) to avoid corrosion difficulties. The result is a reduction in the number of fans, installed horsepower and hence higher operating efficiency.

(Photograph courtesy of Chemetics International Ltd.)

cyclones have been used to remove larger particles but the finer dust is still entrained in the gas. After cooling, the gas is often scrubbed with dilute (0.1-1.5%) sulfuric acid in alloy equipment. The concentration of the acid is a function of the sulfur trioxide content of the gas and the makeup water rate. The scrubber water may also contain about one percent (sometimes even higher) entrained abrasive solids. Crevice corrosion, intergranular corrosion in the heat affected zones of welds and erosion corrosion have been experienced in dilute acid scrubbers. Nolan has indicated precautions that can be taken to minimize these corrosive effects:⁹³

1. Minimize crevices
2. Utilize more corrosion resistant alloys. He ranked alloys* in order of increasing resistance to crevice corrosion as follows:

Type 430 stainless steel
 Type 304L stainless steel
 Type 316L stainless steel
 CARPENTER alloy 20Cb-3 and
 INCOLOY alloy 825
 Alloy 904L

* It should be noted that there are other alloys with excellent resistance to crevice corrosion in this environment such as INCONEL alloy 625, HASTELLOY alloys G and C-276.

3. Utilize low carbon stainless steels or a stabilized alloy. Also utilize proper weld techniques.
4. Maintain the flow rate at less than five fps where possible.
5. Utilize erosion resistant alloys such as ACI CD-4MCu for the scrubber feed pump.
6. Design the unit so as to minimize pump cavitation; an example would be to utilize a pump tank upstream of the pump to allow a short residence time (such as 10 seconds) and also eliminate a valve just upstream of the pump.

Entrained acid mist and any fine dust particles in the effluent gas from the scrubber have to be removed. This is usually accomplished by sending the gas first through a wet electrostatic precipitator followed by contact with 93% sulfuric acid in a drying column filled with ceramic packing. Type 316L stainless steel has been used to advantage as ducting between the scrubber and the electrostatic precipitator, for the wires of the precipitator and to replace corroded carbon steel tubes in these units.

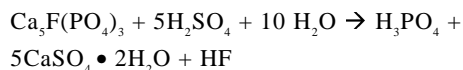
Downstream of the drying column, the sulfuric acid plant utilizing metallurgical stack gases as an SO₂ source is quite similar to a sulfur burning plant already described with similar materials of construction and corrosion problems.

Pumps and valves in all of these plants are commonly made of cast ACI CN-7M with wrought internals constructed of CARPENTER alloy 20Cb-3 or a similar alloy. Where abrasion is a factor, ACI CD-4MCu is often used. The very early practice of using carbon steel or cast iron pumps and valves gave way to the use of Alloy 20 type materials because of the considerable savings in maintenance costs that were realized. Now, with the higher sulfuric acid temperatures that have resulted because of the use of anodically protected coolers, LEWMET 55 has been used to advantage in both the soft and hardened conditions for concentrated acid at temperatures up to 132°C (270°F) for pumps and valves.

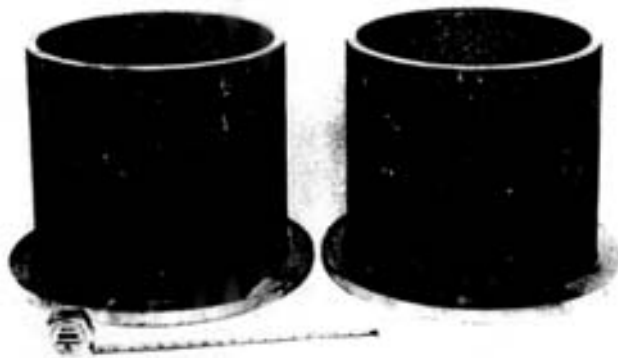
B. PHOSPHORIC ACID MANUFACTURE

Phosphoric acid is manufactured by either the wet process or the electric furnace process. (Flow sheets for both processes as well as corrosion data for numerous alloys are detailed in Inco's Corrosion Engineering Bulletin No. 4, "Corrosion Resistance of Nickel-Containing Alloys in Phosphoric Acid"; the reader is referred to that bulletin for further information on corrosion in phosphoric acid.)

The wet process of manufacture is of concern here because it utilizes the reaction of sulfuric acid with calcium phosphate rock followed by filtration to separate the product from calcium sulfate. The chemical reaction is:



Although pure phosphoric acid is less corrosive than the mineral acids such as sulfuric, hydrochloric and hydrochloric, the latter are found as impurities in phosphoric acid produced by



Cast LEWMET alloy 55 Product Acid outlet thimbles for a sulfuric acid plant. These thimbles will handle 98 percent H₂SO₄ at 110-120°C (230-250°F).

(Photograph courtesy of Charles S. Lewis & Co., Inc.)

the wet process and tend to increase corrosion rates. Other impurities, such as silica, may tend to complex the fluoride and thus reduce the corrosiveness of the phosphoric acid, so that the impurities have a profound influence on corrosivity and account for differences in corrosion rate at different locations utilizing different phosphate rock as a raw material.

Before acidulation of the phosphate rock, entering concentrated sulfuric acid may be mixed with recirculated phosphoric acid of intermediate concentration. A set of data obtained at this step is shown in Table LII. The reactors themselves (also called digesters, extractors, or attack vessels) are usually lined with rubber or brick or both, exposing metal only in the agitators where mechanical strength is the overriding requirement. Table LIII provides data in the slurry within such a reactor, though it may not fully reflect the effect of erosion.

Sulfuric acid resisting alloys such as CARPENTER alloy 20Cb-3, HASTELLOY alloy G and INCOLOY alloy 825 are used to advantage in the dilution and reaction steps. One of the most corrosion resistant alloys in wet process phosphoric acid is Alloy 625 and this has been utilized to advantage, especially in later evaporation steps.

A variant of the above described process, which produces 50% P₂O₅ directly, is the hemihydrate process in which the phosphate rock is reacted with concentrated sulfuric acid to produce phosphoric acid and calcium sulfate hemihydrate (rather than dihydrate) slurry. The temperature is higher in this process than in the dihydrate process (90-95°C instead of 75°C) and the acid concentration is higher leading to more stringent conditions as far as materials of construction are concerned. However, less energy is required for this process and it is favored for that reason. Table LIV shows the results of a test in the reactor of a hemihydrate process plant.

After the reaction between sulfuric acid and the phosphate rock has taken place, the precipitated gypsum is separated from the liquor, usually by means of Type 316L or 317L stainless steel filters. Corrosion rates are generally lower in

TABLE LII
Plant Test In Sulfuric Acid Dilution With
Recirculated Phosphoric Acid

Alloy	Corrosion Rate		Maximum Depth of Crevice Corrosion	
	mm/y	mpy	mm	mils
CARPENTER alloy 20Cb	0.03	1.1	—	—
ALOYCO 20	0.04	1.5	—	—
INCOLOY alloy 825	0.07	2.7	0.13	5
HASTELLOY alloy C	0.07	2.8	—	—
ILLIUM alloy G	0.08	3.0	—	—
INCONEL alloy 718	0.08 (a)	3.2 (a)	—	—
WORTHITE	0.11	4.3	0.08	3
INCOLOY alloy 901	0.15	6.1	0.13	5
ILLIUM alloy R	0.18	6.9	—	—
	0.36 (b)	14.3 (b)	—	—
MONEL alloy K-500	0.79	31	(c)	(c)
MONEL alloy 400	0.97	38	—	—
HASTELLOY alloy B	1.96	78	—	—
Type 317 stainless steel	>3.81 (s)	>150 (s)	—	—
Type 316 stainless steel	>4.57 (s)	>180 (s)	—	—

(a) Pitted to a maximum depth of 0.13 mm (5 mils)

(b) Duplicate specimens did not corrode at the same rate

(c) Pitted to a maximum depth of 0.08 mm (3 mils)

(s) Stress corrosion cracking around markings

Phosphoric acid (wet-process) 28% (20% P₂O₅), sulfuric acid 20-22%, fluoride approx. 1-1.5%, probably as hydrofluosilicic acid. Continuous dilution of concentrated sulfuric acid with recirculated phosphoric acid. Specimens exposed at bottom of dilution tank.

Temperature: 82-110°C (180-230°F) average 93°C (200°F)

Duration of test: 42 days; moderate aeration, agitation by convection only

All specimens were badly scaled

TABLE LIII
Plant Test In
Phosphoric Acid Reactor

Alloy	Corrosion Rate	
	mm/y	mpy
INCONEL alloy 625	0.02	0.7
HASTELLOY alloy G	0.03	1.1
ILLIUM alloy 98	0.07	2.7
Lead, antimonial	0.08	3.2
HASTELLOY alloy C	0.09	3.4
CARPENTER alloy 20Cb-3	0.17	6.5
WORTHITE	0.17	6.8
CARPENTER alloy 20Cb	0.17	6.8
INCOLOY alloy 825	0.19	7.4
DURIMET alloy 20	0.29	11.6
CHLORIMET alloy 3	0.31	12.2
ILLIUM alloy G	0.38	14.8
Type 317 stainless steel	0.56	22
ILLIUM alloy P	0.69	27
Type 316L stainless steel	1.04	41
Type 316 stainless steel (sensitized)	1.27	50
Cast ACI CF-8M	>5.23	>210 (a)
HASTELLOY alloy B	>1.68	>66 (a)
ILLIUM alloy R	>2.31	>91 (a)
CHLORIMET alloy 2	>7.87	>310 (a)

(a) Corroded away

Environment: Phosphoric acid (wet-process) 39% (28% P₂O₅), sulfuric acid 2% hydrofluosilicic and hydrofluoric acid trace amounts, total fluoride equivalent about 1.2% suspended gypsum about 20%. Specimens in primary digestion tank.

Temperature: 77-84°C (170-183°F), average 82°C (180°F)

Duration of Test: 96 days; moderate aeration, vigorous agitation.

No pitting



This pump volute cast by Stainless Foundry & Engineering Co., Inc. of ILLIUM alloy P will be used to handle phosphoric acid slurries in a wet process phosphoric acid plant. This alloy was developed to withstand the abrasive effects of the gypsum and phosphate rock saturated with sulfuric and phosphoric acids.

the filters than in the reactors as shown by Table LV.

Pumps and valve bodies may utilize the cast equivalents of the wrought alloys mentioned and in some cases there are cast alloys specifically engineered for the mixed acid slurries containing abrasive solids encountered in phosphoric acid service such as ILLIUM alloy P.

Although there may be further concentration and purification steps, they are beyond the scope of this bulletin.

C. HYDROMETALLURGY

1. General

Hydrometallurgical techniques have been known since the 1700's, but they did not achieve great significance until this century. Extractive hydrometallurgy (leaching) now accounts for about 35 percent of North America's combined output of copper, nickel, cobalt, zinc and uranium. (Uranium is totally dependent on hydrometallurgy). A very significant proportion of these leaching processes utilize sulfuric acid. With the present emphasis on pollution control, hydrometallurgy is expected to grow at an unprecedented rate. From the standpoint of non-ferrous metal refining, hydrometallurgy has already achieved overwhelming dominance.

The corrosiveness of the sulfuric acid solutions employed in

TABLE LIV
Plant Test In A Hemihydrate Process
Phosphoric Acid Reactor

Alloy	Corrosion Rate		Maximum Depth of Pitting or Crevice Corrosion	
	mm/y	mpy	mm	mils
INCONEL alloy 625	0.02	0.6	Incipient ^a	Incipient ^a
HASTELLOY alloy G	0.02	0.6	Incipient	Incipient
Alloy 904L	0.02	0.8	Incipient	Incipient
INCOLOY alloy 825	0.02	0.9	0.05	2
ALLEGHENY LUDLUM 6X	0.03	1.0	Incipient	Incipient
ILLIUM alloy G	0.03	1.0	Incipient	Incipient
CARPENTER alloy 20 Cb-3	0.03	1.0	0.03	1
JESSOP alloy JS-777	0.03	1.0	Incipient	Incipient
ILLIUM alloy P	0.03	1.2	Incipient	Incipient
JESSOP alloy JS-700	0.03	1.2	Incipient	incipient
Cast ACI CD4 MCu stainless steel	0.04	1.4	Incipient	Incipient
HASTELLOY alloy M-532	0.04	1.4	0.03	1
Type 317 stainless steel	0.04	1.6	Incipient	incipient
HASTELLOY alloy C-276	0.05	2.1	Incipient	Incipient
Type 316 stainless steel	0.06	2.4	0.03	1
Type 316 stainless steel (sensitized)	(b)	(b)	Incipient	incipient
Type 329 stainless steel	0.08	3.2		

(a) Incipient = <0.0254 mm (<1 mil). Since pitting and crevice corrosion can be divided into periods of incubation and propagation, the exact meaning of incipient is not clear. For instance, propagation would not be expected to proceed at as high a rate for a highly alloyed material like Alloy 625 as it would in say Type 316 stainless steel.

(b) This specimen showed intergranular corrosion.

Phosphoric Acid 40-43%. Impurities not defined but phosphate rock was from Florida and should therefore be similar to those reported in Table LIII. A greater tendency for localized attack in this exposure may be the result of the higher temperatures employed, a greater amount of chloride or both, specimen holder attached to dissolved draft tube.

Temperature: 85-105°C (185-221 °F)

Duration of test: 47 days, moderate aeration, vigorous agitation.

hydrometallurgy varies widely. Unprotected carbon steel is severely attacked even in the ambient temperature, low acid concentrations that exist in certain leaching methods. However, austenitic stainless steels, especially Type 316L, are utilized to advantage in great quantities. The sulfuric acid solutions employed, or being considered for use, in hydrometallurgy vary in concentration from less than one percent to 98 percent and vary in temperature from ambient to 270°C (518°F). Obviously, stainless steels are not applicable in the more aggressive environments, but are used extensively in the dilute leaching solutions.

There are two important variables, aside from acid temperature and concentration, that can influence the applicability of alloys that exhibit active-passive behavior, especially the stainless steels, in leaching and refining operations. The first variable is chloride content of the solution which may limit usefulness of these alloys; the second is oxidizing agents which may extend the usefulness of alloys. Since chlorides are often present in both ore and overburden, they may limit the use of stainless steel in processes where temperatures or acid concentrations are high. Although the concentrations of the metal being extracted or refined and the acid concentration, temperature and other important variables are usually pre-

TABLE LV
Plant Test In Phosphoric
Acid-Gypsum Slurry

Alloy	Corrosion Rate	
	mm/y	mpy
Type 309 stainless steel	0.02	0.6
Type 317 stainless steel	0.04	1.6
Type 316 stainless steel	0.11	4.4
Type 304 stainless steel	0.34	13.5
INCOLOY alloy 800	0.37	14.6
Lead, chemical	0.43	17.1
MONEL alloy 400	1.14	45
INCONEL alloy 600	>1.85 a	>73 a

(a) Corroded away

Slurry composition: 30% solids, 39% phosphoric acid (29% P₂O₅), 1.4% sulfuric acid, 2% fluoride probably combined as hydrofluosilicic acid. Specimens in launder between reactors.

Temperature: 71-91°C (160-195°F), average 82°C (180°F)

Duration: 35 days; extensive aeration; flow rate of slurry 5 feet per second. No pitting.

cisely reported, the chloride content is often overlooked, or else goes unreported. This makes the interpretation of corrosion tests and delineation of limiting conditions difficult. Oxygen, bacteria and metal ions in solution that act as oxidizing agents often inhibit the corrosion of alloys, and isocorrosion charts or laboratory corrosion tests in pure sulfuric acid are often too conservative for use in hydrometallurgical operations.

2. Copper

a. Leaching

Mikesell indicates four different leaching methods: (1) vat leaching, (2) heap leaching, (3) dump leaching, and (4) *in situ* leaching.⁹⁴ To these methods might be added pressure leaching which has been utilized mainly as proprietary processes of several manufacturers or is being investigated on a research basis.

The environments of principal concern in vat leaching are solutions usually containing less than 230 g/l (~20%) sulfuric acid but occasionally higher concentrations plus various concentrations of copper sulfate and other metal sulfates. Table LVI shows the results of a corrosion test in a strong and aggressive copper extraction leach system. There is a tendency for crevice corrosion in this environment which may be the result of some unreported chloride content (see Part IIB4). In addition, the crevices incorporated in the test spool assembly by the flourinated polymer insulating-spacers between specimens may be more severe than those in the actual equipment. Type 316L stainless steel has given one year of trouble-free service in this application and continues in service.

Most leach solutions involve lower sulfuric acid concentrations and temperatures and are less aggressive than that shown in Table LVI. Here Type 316L or even Type 304L stainless steel can be successfully utilized as a material of construction, unless the leach solutions contain halide conta-



Vat leaching of copper ore is carried out in these vats which are 34.1 x 31 x 5.6m (110 x 100 x 18 ft.) in size. Most of piping, pumps, valves and clarifier arms are fabricated from Types 316 and 316L stainless steels and their cast equivalents (ACI CF-8M and CF-3M) at this plant.

minants. In those instances involving halides, consideration should be given to the use of more highly alloyed materials than Type 316L stainless steel.

Heap and dump leaching are quite similar and by their nature do not require elaborate equipment. The acid content of these leaching solutions may be as strong as 50 g/l (5%) depending on ore type and quality, and the presence of acid-consuming gangue.⁹⁵ Usually the leach liquor is diluted, spent electrolyte from refining or spent solution from cementation where Type 316L stainless steel is used successfully for tanks, hangers and other equipment. Most oxide containing copper minerals are directly soluble in dilute sulfuric acid solutions and these types of leaching methods find greatest use with them. However, ores containing some sulfides may also be leached by these methods. Pyritic copper sulfide ores oxidize slowly with the help of bacteria, oxygen and ferric sulfate (which is usually developed in the dump itself). Heat is generated by the oxidation reactions that take place and the optimum temperature for bacterial action on sulfides and ferrous iron is about 35°C (95°F).⁹⁶

This combination of weak sulfuric acid containing strong oxidizing agents (Cu⁺⁺, Fe⁺⁺⁺, O₂, and sometimes oxidizing bacteria), at low to moderate temperature, allows the use of Type 316L stainless steel and sometimes Type 304L stainless steel as shown by the numerous corrosion test results indicated previously in Parts II B-2 and II B-3 of this bulletin.

Heap leaching of an all oxide ore at Ranchers Bluebird Mine in Miami, Arizona was described in detail by Power.⁹⁷ A leach

TABLE LVI
Field Test In A Copper
Extraction Leach System

Alloy	Corrosion Rate		Maximum Depth Of Localized Attack	
	mm/y	mpy	mm	mils
INCOLOY alloy 825	0.01	0.5	Incipient ^a	Incipient ^a
Cast IN-862	0.02	0.7		
Alloy 904L	0.02	0.9		
Type 304 stainless steel	0.02	0.9	Incipient	Incipient
DURIMET alloy 20	0.03	1.0	Incipient	Incipient
Type 316 stainless steel	0.03	1.0	Incipient	Incipient
CARPENTER alloy 20 Cb-3	0.03	1.1	Incipient	Incipient
INCONEL alloy 625	0.03	1.2		
Titanium	0.03	1.3		
Type 317 stainless steel	0.04	1.4	Incipient	Incipient
HASTELLOY alloy G	0.05	2.1		
Lead, Chemical	0.95	37.3		
Type 316 stainless steel (sensitized)	b	b		

a. Incipient is less than 0.0254 mm (<1 mil).

b. Sensitized by holding at 677°C (1250°F) for one hour. Specimens suffered intergranular corrosion.

Environment: Leach solution containing 265-345 g/l H₂SO₄ (23-29% H₂SO₄), 150-190 g/l Copper Sulfate and 7 g/l Nickel

Temperature: 93-99°C (199-210°F)

Test Duration: 33 leaches of 2.5 hours each (3.5 days total exposure to leach solution)

Agitation & Aeration: Extensive

cycle of 180 days was employed that consisted of exposure to various sulfuric acid concentrations as shown below:

50 g/l (5%)	H ₂ SO ₄	first 10 days
30 g/l (3%)	H ₂ SO ₄	next 20 days
20 g/l (2%)	H ₂ SO ₄	next 30 days
7-10 g/l (<1-1%)	H ₂ SO ₄	straight raffinate solution for about 120 days

Although no corrosion data were included, Power indicated that Type 316L stainless steel was utilized for handling the leach solutions and subsequent solvent extraction wherever metallic components were desired. Acid concentrations in the solvent extraction and stripping units were 145.0-150.7 g/l (about 13-14%).

The results of a number of corrosion tests in a variety of leach solutions are shown in Table LVII. These tests were all field tests in vat type leaching operations, but exposures 1-5 are similar to heap and dump leaching. Exposure 6 was an aggressive, high temperature leach involving sulfides. The high corrosion rates are a result not only of the 100°C (212°F) temperature but are indicative of some unreported chlorides and an activation of the alloys during periods when oxidizing agents (Cu⁺⁺) were at too low a level to maintain passivity.

In addition to the leaching of ores, slimes from refinery operations are also leached for recovery of metals, including

precious metal content. Table LVIII shows the results of a test in the acid leach circuit of a copper anode slime slurry in the silver refinery of a copper company. Type 316L stainless steel, 6.35 mm (1/4-inch) thick, was the material of construction of the vessel in which the test was run and had given eight years of service, although some corrosion was reported at welds.

In order to speed up chemical reactions, there have been laboratory attempts to pressure leach ores at temperatures above the atmospheric boiling point. These have led to commercialization of a few proprietary processes but little information is available about them in regard to corrosion rates or materials of construction.

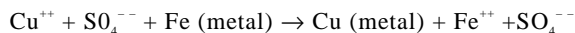
One such process, which is patented by Inco Limited, originally utilized a second-stage batch leach vessel of carbon steel clad with 316L stainless steel. The environment consisted of:

150 g/l H₂SO₄ (~14%)
 35-50 g/l CuSO₄ at start, 90-125 g/l at finish
 60°C (140°F) start, 110°C (230°F) finish
 Violent agitation
 Pressurized with oxygen to 13 kg/cm²

Although no chlorides were reported, the leach vessel showed some pitting due to lack of oxygen and resulting reducing conditions. It would have been possible to electrochemically protect the vessel by controlling its corrosion potential in the passive region, but this was not done. The process was modified instead: the sulfuric acid concentration was reduced quite simply by not intentionally adding it at the start of the batch cycle and relying on the oxidation of sulfides to generate sulfuric acid during the oxidative leach.*

b. Cementation

In one recovery method, copper is precipitated from solution by contact and cementation with metallic iron, such as shredded scrap detinned cans, with the spent solution reused for further leaching. The precipitation reaction is:



One plant uses cone-type precipitators. The annular space between the inner cone and the tank is covered by a heavy gage Type 304 stainless steel screen and it holds about 13,600 kg (about 15 tons) of iron scrap. The iron scrap not only serves to reduce the copper in solution but also affords cathodic protection to the stainless steel. Pregnant leach solution is pumped up through the scrap, while the copper precipitate settles down through the stainless steel screen to be discharged intermittently.

Precipitates from the cones are pumped to a filter plant where they are dewatered in a 122 cm (48-inch) Type 304L stainless steel filter press equipped with Type 304 stainless steel filter screens.

* This technology and consultation on similar technology, is available through INCO TECH**, a worldwide consulting service for exploration, mining, processing and refining of metal ores, with headquarters in Toronto.

c. Solvent Extraction

Liquid ion exchange (solvent extraction) is also used for handling copper leach solutions. The process utilizes a reagent such as a mixture of 2-hydroxybenzophenoximes that has a relatively high affinity for copper ions but a low affinity for other metal ions. Feed to such a process might typically be:

0.25 g/l H₂SO₄
 2.62 g/l Cu⁺⁺
 1.37 g/l Fe (both Fe⁺² and Fe⁺³)
 pH 2.5
 Temperature 20-35°C (68-95°F)

The reagent, usually in a kerosene solvent, operates on a hydrogen ion cycle in which hydrogen ions are exchanged for cupric ions. Thus, the leach solution is regenerated while the copper solution would be:

4.16 g/l H₂SO₄
 0.08 g/l Cu
 1.37 g/l Fe
 pH 1.4
 Temperature: Ambient

The first plant utilizing this technology went into operation in 1970 and utilized Types 316 and 316L (where welding was employed) stainless steel for all wetted surfaces in the solvent extraction area. Plant operating personnel report that there have been no corrosion difficulties after 12 years of operation and the plant continues to operate.

d. Refining (Electrowinning)

Electrolytic refining provides the high purity grades of copper needed for electrical conductors and also permits the recovery of the small quantities of precious metals from tank house slimes. The copper sulfate – sulfuric acid solution can vary widely in chemical composition, specific gravity and temperature and still give satisfactory results. Usually the sulfuric acid concentration is maintained at about 200 g/l (16%) for reasons of electrolyte conductivity but may vary from 150 to 235 g/l. The copper content of the electrolyte may vary from 35-55 g/l but is usually maintained at the mid-point of this range to insure pure copper deposition and yet allow for the presence of reasonable amounts of soluble impurities. The temperature of the electrolyte is important and, although it may range from 50-66°C (120-150°F), it is usually maintained at the upper end of this range in order to insure high solubility as well as to lower specific gravity which facilitates the continuous circulation required to maintain concentration and temperature levels.

Corrosion rates in tank house electrolytes are shown in Table LIX. Most modern refineries utilize Type 316L stainless steel as the major material of construction for equipment

** Trademark. The Inca family of companies

in the tank house. Inco utilizes ACI CN-7M cast stainless steel for circulating pumps although other manufacturers have used pumps of ACI CF-8M or its low carbon counterpart CF-3M.

The electrolyte temperature is maintained by the use of

shell and tube heat exchangers supplied with low pressure steam at Inco's Copper Cliff refinery. Impregnated graphite tubes were used for many years but, although their corrosion resistance was very good, they had two shortcomings: slime

TABLE LVII
Field Corrosion Tests In Leach Solutions

Exposure

Alloy	1				2				3	
	Corrosion Rate		Maximum Depth of Crevice Corrosion		Corrosion Rate		Maximum Depth of Crevice Corrosion		Corrosion Rate	
	mm/y	mpy	mm	mils	mm/y	mpy	mm	mils	mm/y	mpy
Type 316 stainless steel	Nil*	Nil*	0	0	Nil	Nil	0	0	Nil	Nil
Type 304 stainless steel	Nil	Nil	0	0	Nil	Nil	0	0	Nil	Nil
INCONEL alloy 600	Nil	Nil	0	0	Nil	Nil	0	0	Nil	Nil
Nickel 200	0.08	3.3	0.23	9	0.50	19.6	Perf.	Perf.	0.47	18.5
MONEL alloy 400	0.68	26.9	0	0	-	-	-	-	0.44	17.5
Ni-Resist Type 2	1.52	59.9	0.36**	14**	-	-	-	-	-	-
Mild Steel	2.05	80.9	Perf.	Perf.	-	-	-	-	-	-
Gray Cast Iron	2.47	97.4	0.46	18**	-	-	-	-	-	-
Type 1100 Aluminum	>2.05	>80.9	Corroded away		-	-	-	-	-	-
Lead—Chemical	-***	-	-	-	0.01	0.2	0	0	-	-
WORTHITE	-	-	-	-	-	-	-	-	Nil	Nil
HASTELLOY alloy C	-	-	-	-	-	-	-	-	0.02	0.6
HASTELLOY alloy G	-	-	-	-	-	-	-	-	-	-
Alloy 904L	-	-	-	-	-	-	-	-	-	-
JESSOPJS-700	-	-	-	-	-	-	-	-	-	-
Type 317 stainless steel	-	-	-	-	-	-	-	-	-	-
DURIMET 20	-	-	-	-	-	-	-	-	-	-
ACI CD4-MCu	-	-	-	-	-	-	-	-	-	-
CARPENTER alloy 20Cb-3	-	-	-	-	-	-	-	-	-	-
INCOLOY alloy 825	-	-	-	-	-	-	-	-	-	-

NOTE: Localized attack was in the form of crevice corrosion beneath a fluropolymer unless otherwise noted.

* Nil is less than 0.00254 mm/y (<0.1 mpy)

** Actually pitting rather than crevice corrosion

*** A dash indicates alloy was not tested

EXPOSURES:

1. 52 day test in leach solution containing:

23 g/l copper

16 g/l cobalt

5 g/l zinc

4 g/l iron

2 g/l nickel

106 g/l sulfate

pH 2.5-3.0

Temperature 26.7°C (80°F)

Moderate aeration and mild agitation

2. 229 day test in dilute sulfuric acid leach solution for copper extraction from residue formed during nickel refining:

50 g/l Cu as CuSO₄

5 g/l Ni as NiSO₄

2 g/l Co as CoSO₄

pH 2.0

Temperature ambient to 65°C (ambient to 149°F)

Aeration associated with impeller agitation

3. 194 day test half submerged in leach solution containing:

16-27 g/l CuSO₄

0-2 % Na₂SO₄

25-48 g/l H₂SO₄ (2½-4½%)

Temperature 20-60°C (68-140°F)

Slight aeration-intermittent agitation

accumulated that reduced heat transfer and they were susceptible to breakage during cleaning. These impregnated graphite tube exchangers were replaced by units tubed with either INCOLOY alloy 825 or CARPENTER alloy 20 Cb-3.⁹⁸

Other refineries have utilized Type 316L stainless steel for heating coils.

Some copper refineries have utilized PVC piping for headers and drop pipes but replaced this plastic with Type 316L

TABLE LVII
Field Corrosion Tests In Leach Solutions

												Exposure	
4				5				6					
Maximum Depth of Crevice Corrosion		Corrosion Rate		Maximum Depth of Crevice Corrosion		Corrosion Rate		Maximum Depth of Crevice Corrosion		Corrosion Rate		Maximum Depth of Crevice Corrosion	
mm	mils	mm/y	mpy	mm	mils	mm/y	mpy	mm	mils	mm/y	mpy	mm	mils
0.05	2	Nil	Nil	0.23	9	Nil	Nil	0.20	8	0.34	13.3	0.03	1
0.05	2	Nil	Nil	0.43	17	Nil	Nil	0.23	9	-	-	-	-
0.05	2	Nil	Nil	0.15	6	Nil	Nil	0.08	3	-	-	-	-
Perf.	Perf.	0.5	2.1	0.28	11	1.77	69.5	Perf.	Perf.	-	-	-	-
Perf.	Perf.	>4.39	>173	Corroded away		>4.39	>173	Corroded away		-	-	-	-
-	-	-	-	-	-	-	-	-	-	-	-	-	-
-	-	-	-	-	-	-	-	-	-	-	-	-	-
-	-	-	-	-	-	-	-	-	-	-	-	-	-
-	-	0.05	2.1	0	0	0.05	1.8	0	0	-	-	-	-
0	0	-	-	-	-	-	-	-	-	-	-	-	-
0	0	1.40	55.0	0	0	1.34	52.7	0	0	-	-	-	-
-	-	-	-	-	-	-	-	-	-	0.14	5.7	0.05	2
-	-	-	-	-	-	-	-	-	-	0.18	7.0	0.18	7
-	-	-	-	-	-	-	-	-	-	0.21	8.3	0.15	6
-	-	-	-	-	-	-	-	-	-	0.28	11.2	0	0
-	-	-	-	-	-	-	-	-	-	0.34	13.4	0.36	14
-	-	-	-	-	-	-	-	-	-	0.54	21.2	0	0
-	-	-	-	-	-	-	-	-	-	0.58	23.0	0.05	2
-	-	-	-	-	-	-	-	-	-	0.84	33.0	0.33	13

4. 32 day test in "Low Acid" leach solution containing:

40-60 g/l Cu as CuSO₄

2-5 g/l Ag as AgSO₄

1-3 g/l Mn

4-7 g/l Zn

0-3 g/l H₂SO₄ (0-0.3%)

Temperature 60-77°C (140-170°F)

Good aeration and continuous agitation

Because of crevice corrosion suffered by many of the specimens, it is suspected unreported chlorides were present.

5. 32 day test in "High Acid" leach solution containing:

40-60 g/l Cu as CuSO₄

1-4 g/l Ag as AgSO₄

2-3 g/l Mn

5-7 g/l Zn

30-62 g/l H₂SO₄ (3-6%)

Temperature 60-77°C (140-170°F)

Good aeration and continuous agitation

Because of crevice corrosion suffered by many of the specimens, it is suspected unreported chlorides were present.

6. First stage leach slurry of CuS with Ni, Co and iron sulfides in solution. 10-20 g/l H₂SO₄ (1-2%), cupric ion usually 2 g/l has been as low as 10 ppm.

Temperature 100°C (212°F)

Moderate aeration and agitation

TABLE LVIII
Field Test in Acid Leach Circuit
For Copper Anode Slimes

Alloy	Corrosion Rate		Maximum Depth of Localized Attack	
	mm/y	mpy	mm	mils
INCONEL alloy 625	0.00	0.0		
Tantalum	0.00	0.0		
Titanium	0.00	0.0		
INCOLOY alloy 825	0.00	0.0	Incipient	Incipient
HASTELLOY alloy C-276	<0.01	0.1	Incipient	Incipient
Type 317 stainless steel	<0.01	0.1	Incipient	Incipient
DURIMET alloy 20	<0.01	0.1	0.03	1
Type 316 stainless steel	<0.01	0.1	0.05	2
CARPENTER alloy 20Cb-3	<0.01	0.1	0.08	3
Type 316 stainless steel—sensitized	a	a		5
ILLIUM alloy B	0.03	1.2		
Load, chemical	0.04	1.5	Incipient	Incipient
HASTELLOY alloy B	>3.23 ^b	>127 ^b		

^a Sensitized by heat treating at 677°C (1250°F) for one hour. Specimens suffered intergranular corrosion.

^b Corroded away

Media: Slurry containing 100-150 g/l (9½-14%) H₂SO₄, 30 g/l Cu, filtered slime containing 30 percent Cu, 12 percent selenium, 20 percent Te and As and some Au and Ag
During test, a solution containing 3 g/l H₂SeO₃ and 150 g/l (14%) H₂SO₄ added twice a week

Temperature: 16-82°C (60-180°F)
Location: Specimens exposed 91.4 cm (3 ft.) from top of tank in the slurry most of the time
Agitation: Slight
Aeration: None Test
Duration: 55 days

TABLE LIX
Corrosion Tests in Copper Refinery Electrolytes

Alloy	Test 1*		Test 2*	
	mm/y	mpy	mm/y	mpy
Type 304 stainless steel	nil**	nil	nil	nil
Type 304 stainless steel — sensitized	corroded away	—	—	—
Type 316 stainless steel	nil	nil	nil	nil
Type 316 stainless steel — sensitized	Intergranular Corrosion	Intergranular Corrosion	Intergranular Corrosion	Intergranular Corrosion
Type 317 stainless steel	nil	nil	—	—
INCOLOY alloy 825	nil	nil	—	—
INCONEL alloy 625	nil	nil	—	—
CARPENTER alloy 20 Cb-3	nil	nil	0.002	0.1
DURIMET alloy 20	—	—	0.002	0.1
JESSOP alloy JS-700	0.002	0.1	—	—
HASTELLOY alloy G	—	—	0.002	0.1
HASTELLOY alloy C-276	0.008	0.3	0.008	0.3
Chemical Lead	—	—	0.05	2.0
HASTELLOY alloy B	corroded away	—	—	—

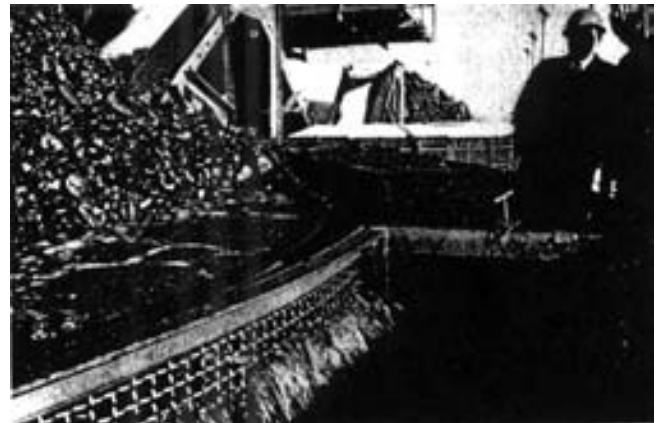
* Test 1: Electrolyte Composition: 194 g/l H₂SO₄, 49 g/l CuSO₄, 1 g/l CaO
Aeration: None
Agitation: Moderate
Temperature: 66°C (151°F)
Exposure Time: 458 days

Test 2: Electrolyte Composition: 200-235 g/l H₂SO₄, 36-40 g/l Cu, 20-22 g/l Ni
Aeration: None
Agitation: Moderate
Temperature: 66°C (151°F)
Exposure Time: 33 days

** Nil is less than 0.00254 mm/y (<0.1 mpy)



A vat leaching plant originally used PVC-lined piping for dilute sulfuric acid mixtures. High maintenance costs with the original system led to replacement of this system with Type 316L stainless steel piping as leaks occurred. Old and new pipe can be seen above.



A portion of a Cone Type precipitator developed by the Kennecott Copper Corporation. An inverted 3 x 3m (10 x 10 ft.) cone in a tank contains shredded, scrap detinned cans and is separated from the tank wall by the heavy gauge Type 304 stainless steel screen shown.

stainless steel because the plastic had a tendency to get out of round or enlarged in diameter and was very difficult to repair. Stray currents are stopped with a short length of rubber hose.

In a number of instances, both Type 304L and 316L stainless steels have replaced antimonial-lead linings in holding equipment as their greater resistance to mechanical damage has considerably reduced the incidence of repairs. In many cases, upgrading from mild steel to Type 304 stainless steel has brought substantial increases in equipment life that far outweigh the cost differential.

3. Uranium

The method used to extract uranium from its ore is primarily dependent upon the type of ore being processed. Some uranium-containing ores are hard and others soft; some non-reactive with acids and others, which contain calcite, highly reactive, consuming large amounts of acid in their treatment.

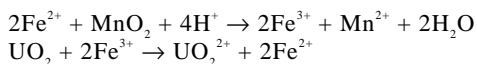
The general practice is to crush the rock in jaw crushers to a size easily accommodated in the secondary crushing step which is usually by gyratories or hammer mills. Product from these mills is ground further in rod, ball, or hammer mills until a uniform product is obtained that lends itself readily to leaching. Either acid or caustic leaching practice can be followed utilizing mechanically agitated tanks or air agitated columns. This is followed by liquid-solid separation using classifiers or thickeners.

The choice of the acid or alkali (carbonate) leach procedure does not follow any hard or fast rule. In general, ores containing limestone or sandstone with grains cemented with calcite are leached by alkalis; ores cemented with clay or silica are leached in acid. In the latter case, if the acid consumption exceeds 150 pounds per ton of ore treated, the alkali process will usually be practiced. On-site costs of leaching acids (sulfuric) and alkalis (sodium carbonate and hydroxide) due to plant locations and shipping costs may determine the choice of leachant used.

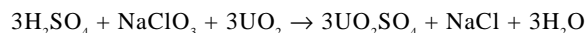
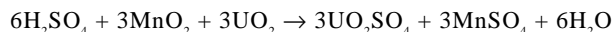
In general, acid treatment which allows for high uranium recovery and is the easiest to control is the most economical process due to lower capital costs. The alkali process requires more expensive high pressure autoclaves.

In the Colorado area, sulfuric acid leaching is almost universal with uranium recovery efficiencies of 95-98%. These efficiencies are achieved by oxidizing tetravalent uranium in the ore to the hexavalent state. Tetravalent uranium is obtained by conversion of ferrous iron (Fe^{2+}) to ferric (Fe^{3+}) by reacting it with manganese dioxide. The ferric ion then reacts with uranium dioxide in an acid solution to produce tetravalent uranium. Usually, sufficient iron is present in the ore to accommodate the reaction; if not, iron additions can be made for the purpose.

A typical reaction might be —



Hexavalent uranium is obtained by treatment of the tetravalent product above with low cost MnO_2 and NaClO_3 in the presence of additional quantities of sulfuric acid:



Colorado Plateau ores can usually be leached in 8 hours with agitation and with temperatures up to 71°C (160°F) in the first leach tanks, where several of a dozen or more tanks may be heated to speed up the reaction. Reaction temperature in unheated tanks extends down to slightly above ambient temperatures.

Chlorides are sometimes associated with the uranium ores and the processing steps include chloride ion and strong oxidizing agents in addition to the dilute sulfuric acid. There is a strong tendency for crevice corrosion, pitting, or activation and high corrosion rates with Types 304L or 316L stainless steels. More highly alloyed materials have to be carefully selected (usually a corrosion test is necessary to determine the most economical alloy) in order to determine compatibility in a particular leach environment. Alloys with resistance to some of the more aggressive environments, as shown in Tables LX - LXVI, include HASTELLOY alloys G-3, G and C-276, INCONEL alloy 625, CARPENTER alloy 20 Cb-3, INCOLOY alloy 825 and other alloys.

Table LXVII shows the results of laboratory tests which were run to select a material of construction for a belt filter. Although both solutions contained the same sulfuric acid concentration, the solution with the higher chloride content had a greater tendency for localized attack in the form of pitting and crevice corrosion even though it was at a lower temperature. The alloys that suffered practically no attack at all in either environment were HASTELLOY alloy G, INCONEL alloy 625 and HASTELLOY alloy C-276.

Material requirements for the storage of pregnant liquor after leaching are much less demanding than the leaching itself, as will be noted in Table LXVIII where Type 316 stainless steel is shown to have adequate corrosion resistance. The low carbon grade (316L) would be necessary to avoid intergranular corrosion if welded construction were employed.

4. Other Metals

Among other important metals, zinc is also processed by hydrometallurgical techniques. Leaching of the roasted ore and ore concentrates with sulfuric acid is followed by electrolytic deposition of the zinc content of the liquors with insoluble anodes.

The feed to the cells usually averages about 110-135 g/l zinc, but sometimes as high as 215 g/l. The sulfuric acid concentration may vary from 3 to 28 percent and is cooled to $27-45^\circ\text{C}$ ($80 - 113^\circ\text{F}$) by means of Types 316 or 316L stainless steel internal coils or an external heat exchanger. Metallic impurities, mainly ferric and cupric ions, serve as oxidizing agents. WORTHITE pumps and ALOYCO 20 valves to circulate the electrolyte through coolers to the main cell feed launder have an enviable record of long-term, practically maintenance free operation in this service.⁹⁹

The austenitic stainless steels were also resistant in a leach process for manganese ore as shown by Table LXIX.

TABLE LX
Uranium Recovery
Acid Process Data

Alloy	Corrosion Rate		Maximum Depth of Pitting	
	mm/y	mpy	mm	mils
HASTELLOY alloy G-3	0.003	0.1		
	0.041	1.6		
Alloy 904 L	0.064	2.5		
	0.066	2.6		
JESSOP alloy JS-777	0.003	0.1		
	0.211	8.3		
HASTELLOY alloy G	0.099	3.9		
	0.119	4.7		
CARPENTER alloy 20Cb-3	0.069	2.7		
	0.206	8.1		
CARPENTER alloy 20Mo-6 ¹	0.150	5.9		
INCOLOY alloy 825	0.066	2.6		
	0.594	23.4		
Type 317L stainless steel	0.003	0.1		
	1.367	53.8		
Type 316 stainless steel—sensitized	0.457	18.0	Intergranular Corrosion Perforated	
	1.643 ²	64.7 ²		
Type 316 stainless steel	1.242 ²	48.9 ²		
	1.943 ²	76.5 ²		

¹ Only one sample exposed

² Partially corroded away

Process Unit: Pachuca Tank
 Corrosive Media: Uranium ore leaching slurry containing 70 g/l 93% H₂SO₄
 Location of Specimens: In vapor .46 m (18 inches) above slurry
 Temperature: 75-85°C (167-185°F)
 Duration: 90 days
 Agitation & Aeration: Extensive
 Remarks: Corrosion rates of the duplicate specimens were not consistent so both rates are reported. Apparently the conditions at one end of the test spool were much more severe (splashing?) than at the other end where the duplicate specimens were located.

TABLE LXII
Uranium Recovery
Acid Process Data

Alloy	Corrosion Rate		Maximum Depth of Localized Attack	
	mm/y	mpy	Pitting	Crevice
INCOLOY alloy 825	nil*	nil		Incipient
HASTELLOY alloy C-276	0.04	1.4		
DURIRON	0.06	2.2		
Type 317 Stainless Steel	0.02	0.9		1.52 60.0
CARPENTER alloy 20Cb	0.03	1.3		Perforated**
Type 316 Stainless Steel	0.05	1.9	Perforated**	Perforated**
Type 316L Stainless Steel	0.05	2.0		Perforated**
HASTELLOY alloy D	2.21	87.0		

* nil is less than 0.00254 mm/y. (<0.1 mpy)

** 0.79 mm (31 mils)

Process Unit: Uranium ore leach tank 9.75 x 9.14m (32' dia. x 30' deep)
 Corrosive Media: 5-5¼% sulfuric acid (50-60 g/l); 0.2-0.3 g/l chlorate; 5.6 g/l dissolved iron; 1 g/l U₂O₅; 70% solids
 Location of Specimens: Suspended in acid leach pulp 0.61 m (2') below surface and 3.66m (12') from tank center
 Temperature: 45-48°C (113-118°F)
 Duration: 60 days
 Aeration: Air lift agitated
 Agitation: Approx. 0.3 m/sec. (1 fps)

TABLE LXI
Uranium Recovery
Acid Process Data

Alloy	Corrosion Rate		Maximum Depth of Crevice Corrosion	
	mm/y	mpy	mm	mils
INCOLOY alloy 825	nil*	<0.1		
Type 316 Stainless Steel	nil	<0.1		
CARPENTER alloy 20 Cb	0.005	0.2		
HASTELLOY alloy C	0.03	1.3		
Chemical Lead	0.05	2.0		
Type 317 Stainless Steel	0.005	0.2		Incipient**
Type 302 Stainless Steel	0.005	0.2	.15	6.0
Type 347 Stainless Steel	0.04	1.4	.64	25.0

* nil is less than 0.00254 mm/y (<0.1 mpy)

** Incipient is less than 0.0254 mm (<1 mil)

Process Unit: Uranium ore leach tank #1
 Corrosive Media: Pulped uranium ore containing 60% solids, 3-5.5% H₂SO₄ (28-55 g/l), 5-10 g/l ferric iron, some ferrous iron and approximately 0.1% NaClO₃
 Location of Specimens: Immersed in pulp near steam coil
 Temperature: 45°C (113°F)
 Duration: 41 days
 Aeration: None
 Agitation: Moderate

TABLE LXIII
Uranium Recovery
Acid Process Data

Alloy	Corrosion Rate		Remarks
	mm/y	mpy	
CARPENTER alloy 20 Cb	0.71	28	Smooth general attack less under spacers
Type 316 Stainless Steel	1.68	66	General attack with pitting
INCOLOY alloy 825	1.78	70	General attack; less under spacers
Type 304 Stainless Steel	2.77	109	Severe general attack — mostly corroded away
Type 321 Stainless Steel	3.22	127	Completely corroded except for area under spacer
Type 347 Stainless Steel	3.71	146	Same as above
MONEL alloy 400	4.14	163	Completely corroded except for area under spacers

Process Unit: Dorr Agitator
 Corrosive Media: 5% Sulfuric acid plus 0.5 g/l ferric ion and 6 g/l ferrous ion in a pulped silicate ore
 Location of Specimen: 0.3m (1') below surface of pulp
 Temperature: 40-47°C (104-117°F)
 Duration: 42 days
 Agitation: Air Agitated

TABLE LXIV
Uranium Recovery
Acid Process Data

Alloy	Corrosion Rate	
	mm/y	mpy
INCOLOY alloy 825	0.005	0.2
HASTELLOY alloy C-276	0.01	0.4
DURIMET alloy 20	0.013	0.5
INCOLOY alloy 901	0.015	0.6
DURIRON	0.12	4.9
Type 316 Stainless Steel	1.7	67.0
NI-Cu Cast alloy 505	6.1	240.0

Process Unit: Tank #1-Acid leaching of uranium ore
 Corrosive Media: Sulfuric acid solution containing uranium and other metal salts — pH 0.4-1.0
 Location of Specimens: Immersed in solution
 Temperature: 38-71°C (100-160°F)
 Duration: 100 days
 Aeration: Considerable
 Agitation: Considerable

TABLE LXV
Uranium Recovery
Acid Process Data

Alloy	Corrosion Rate		Maximum Depth Of Crevice Corrosion	
	mm/y	mpy	mm	mils
CARPENTER alloy 20 Cb	nil*	nil	.15	6.0
Type 302 Stainless Steel	nil	nil	.43	17.0
INCOLOY alloy 825	0.005	0.2	.28	11.0
MONEL alloy 400	Corroded away			
Ni Resist, Type 2	Corroded away			
Cast Iron	Corroded away			

* Nil is less than 0.00254 mm/y (<0.1 mpy)

Process Unit: No. 3 Leach Tank (12-hour retention)

Corrosive Media: Leach pulp containing approximately 68% solids with S/SO₄ at 12.0 g/l (1.2% acid) and pH 2.05; Cl⁻ 1.2 g/l; F⁻ 2.3 g/l; Fe⁺⁺⁺ 2.6 g/l; Fe⁺⁺ 6.1 g/l; NaClO₃ - nil

Location of Specimens: Center of leach tank just under surface of pulp

Temperature: 25-32°C (78-90°F)

Duration: 35.5 days

Aeration: None

Agitation: Slow

Comments: Specimens installed in tank for 3 separate leach runs which were interrupted by intervals of 5 and 13 days. During interruption, specimens were kept in pregnant solution.

TABLE LXVI
Uranium Recovery
Acid Process Data

Alloy	Corrosion Rate		Maximum Depth of Localized Attack Pitting		Maximum Depth of Crevice
	mm/y	mpy	mm	mil	
CARPENTER alloy 20 Cb	0.03	1.1			
HASTELLOY alloy C	0.05	2.0			
INCOLOY alloy 825	0.02	0.7			
Type 317 Stainless Steel	0.10	4.0			0.025 1.0
DURIRON	0.13	5.0			Perforated*
Chemical Lead	0.23	9.0			
Type 316 Stainless Steel	0.30	12.0	Perforated		Perforated*
Type 304 Stainless Steel	2.54	100	Perforated		Perforated*

* 0.79 mm (31 mils)

Process Unit: Uranium ore leach tank—Agitator #9

Corrosive Media: Uranium leach circuit; 68% solids (55-62% <200 mesh); 5.5% H₂SO₄ (55 g/l); 0.25-0.35 g/l sodium chlorate

Location of Specimens: In #9 leach tank for 6 days; in overflow box for 35 days

Temperature: 60-65°C (140-149°F)

Duration: 41 days

Aeration: Air

Agitation: None in overflow

TABLE LXVII
Uranium Recovery
Acid Process Data

Alloy	Test 1				Test 2			
	Corrosion Rate		Maximum Depth of Pitting or Crevice Corrosion		Corrosion Rate		Maximum Depth of Pitting or Crevice Corrosion	
	mm/y	mpy	mm	mils	mm/y	mpy	mm	mils
HASTELLOY alloy G	nil ¹	nil			nil	nil		
INCONEL alloy 625	-	-			nil	nil		
INCOLOY alloy 825	nil	nil			nil	nil	Incipient ²	Incipient
HASTELLOY alloy C-276	0.003	0.1			nil	nil		
Alloy 904L	nil	nil			nil	nil	0.05	2
Type 317 Stainless Steel	nil	nil	Incipient	Incipient	0.003	0.1	0.06	3
CARPENTER alloy 20 Cb-3	nil	nil	0.03	1	nil	nil	0.36 ³	14 ³
Type 316 Stainless Steel	0.13 ⁴	5.1 ⁴	Perforated	Perforated	0.03 ⁴	1.3 ⁴	Perforated	Perforated
Type 304 Stainless Steel	1.68 ⁴	66 ⁵	Perforated	Perforated	0.48 ⁵	19 ⁵	Perforated	Perforated

¹ Nil is less than 0.00254 mm/y (<0.1 mpy)

² Incipient is less than 0.0254 mm (<1 mil)

³ Single pit

⁴ Severe localized attack makes this corrosion rate based on weight loss misleading

⁵ Severe Tunneling corrosion

Process Unit: Laboratory

Corrosive Media: Test 1-Two liters of 20 g/l H₂SO₄, 350 mg/l chloride and 1 g/l uranium. Solution changed after 50 days.

Test 2-Two liters of 20 g/l H₂SO₄, 1 g/l chloride and 1 g/l uranium. Solution changed after 50 days.

Location of Specimens: Submerged in solution

Temperature: Test 1 60°C (140°F)
Test 2 40°C (104°F)

Duration: 90 days

Aeration: Test 1 Moderate
Test 2 None

Agitation: None

D. AMMONIUM SULFATE MANUFACTURE

Ammonium sulfate is a crystalline salt produced by the direct reaction between ammonia and sulfuric acid, but it is produced in even greater quantities as a by-product or co-product of coke production, caprolactam production, and metal refining.

TABLE LXVIII
Uranium Recovery
Acid Process Data

Alloy	Corrosion Rate	
	mm/y	mpy
Type 316 Stainless Steel	nil*	nil
INCOLOY alloy 825	nil	nil
HASTELLOY alloy C	nil	nil
INCOLOY alloy 901	nil	nil
DURIMET alloy 20	nil	nil
DURIRON	nil	nil
Ni-Cu cast alloy 505	0.94	37.0
HASTELLOY alloy D	0.99	39.0

Nil is less than 0.00254 mm/y (<0.1 mpy)

Process Unit: Storage of filtered pregnant liquor after leaching

Corrosive Media: Sulfuric acid solution containing uranium and other metal salts from leaching of uranium ores; PH 0.9-1.4

Location of Specimens: In filtered solution derived from leach tanks

Temperature: 38°C (100°F)

Duration: 100 days

Aeration: Slight

Agitation: Mild

TABLE LXIX
Leaching Of A Reduced
Manganese Ore

Alloy	Corrosion rate		Comments
	mm/y	mpy	
Type 316 Stainless Steel	0.01	0.5	
Type 304 Stainless Steel	0.02	0.7	
Chemical Lead	0.40	15.8	
Nickel 200	2.29	90	
MONEL alloy 400	3.10	122	Crevice corrosion to a maximum depth of .41 mm (16 mils)
Ni-Resist Type 1	13.92	548	
Gray Cast Iron	21.59	850	

Corrosive Media: Leach liquor containing 130 g/l ammonium sulfate, 80 g/l manganese sulfate, 30 g/l sulfuric acid with 5% solids.

Location of Specimens: Near wall of leach tank equidistant from top and bottom.

Temperature: 25-60°C (77-140°F)

Duration: 30 days.

Aeration: None

Agitation: 150 rpm in 2.44 x 3.05 m (8' x 10) vessel

1. Direct Reaction

Usually, concentrated 93% or 98% sulfuric acid is utilized for the direct reaction with ammonia, and Types 316 and 316L stainless steel have been used extensively for the reactor and associated equipment. Table LXX shows the results of corrosion tests in a direct reaction plant producing ammonium sulfate as a prime product. Type 317 stainless steel was exceptionally resistant in all of the test locations including the liquid phase of the reactor. However, one of the specimens of Type 316 stainless steel became active, while its duplicate specimen remained passive, indicating that the use of Type 316 stainless steel was borderline under the conditions of operation of this particular reactor vessel. Temperature control was questionable because the temperature was reported as "at least 110°C (230°F)." Indeed, the 6.35 mm (0.25 inch) wall thickness of this reactor was perforated near the acid feed line after 4 months service. The process of diluting or reacting concentrated sulfuric acid in direct contact with the alloy, with an attendant rise in temperature and impingement effects, must be avoided. HASTELLOY alloy C and cast LEWMET alloy 55 nozzles to inject sulfuric acid into the liquid have been used successfully at other plants.

In general, the experience with Type 316 stainless steel in these plants has been very good, but in locations where the passive limit of this stainless steel may be exceeded, consideration should be given to the use of more corrosion resistant Type 317 and 317L stainless steels or the more sulfuric acid resistant alloys such as CARPENTER alloy 20 Cb-3, INCOLOY alloy 825, HASTELLOY alloy G, etc.

Welded samples of Type 316 stainless steel that were exposed in the liquid and vapor of the reactor (Tests 1 and 2 of Table LXX) showed no evidence of intergranular attack in the heat-affected zones of welds although some of the specimens became active and corroded at high rates, as did the annealed corrosion coupons. However, this may be a borderline situation and the possibility of this type of attack should be taken into account. It would seem prudent to pay a slight premium for the low-carbon grade as a means of assuring greater reliability in the case of an upset.

2. By-Product of Caprolactam

The major source of ammonium sulfate in the United States is from caprolactam production, where sulfur values are recovered as by-product ammonium sulfate which is generated at several different steps in the process. Corrosion rates given in Table LXXI indicate the excellent corrosion resistance of Type 304 and 316 stainless steels in the generation and handling of ammonium sulfate, when the process is controlled in regard to temperature, pH and velocity. Both of these stainless steels are utilized in this equipment because the sulfuric acid feed is neutralized by the ammonia and the equipment is usually only exposed to very dilute sulfuric acid. Type 316 stainless steel is more versatile and can tolerate more stringent conditions. Some plant operators use a pH of 3 and 4 as practical limits for Types 316 and 304 stainless steel respectively. At higher acid concentrations the stainless steels may become active in which case a general, fairly uniform corrosion occurs. Temperature is important but is dependent upon, and secondary to, the process requirements for the

caprolactam process.

Regular carbon grades of stainless steel have been utilized in these plants but the results of Table LXXI show that there is a tendency for furnace sensitized specimens to show higher corrosion rates than the annealed specimens.

3. By-Product of Coke

When coal is carbonized in coke ovens, ammonia, ammonium hydroxide and ammonium chloride are generated. At some plants, the ammonia values from the hydroxide and chloride are liberated in a rectifying column before ammonia absorption.

Ammonia is absorbed from coke oven gas utilizing sulfuric acid by one of three processes.^{100, 101} The same principles apply to each process but the crystal size of the product, which affects its sales appeal, varies according to the process. Large dust-free, free-flowing crystals are preferred for storage, blending with other fertilizers and application on the soil.

The oldest process, with the least effective control of crystal size, is the Saturator Process. Type 316 and 316L stainless steels and Alloy 400 have been successfully used as materials of construction for this type of plant. In this process, the ammonia laden gas is introduced into the saturator vessel through a distributor called a "cracker pipe" and bubbles up through an ammonium sulfate solution containing about 5 to 6

TABLE LXX
Ammonium Sulfate Production—Direct Reaction Of
Ammonia and Sulfuric Acid

Alloy	Corrosion Test									
	Test 1		Test 2		Test 3		Test 4		Test 5	
	mm/y	mpy	mm/y	mpy	mm/y	mpy	mm/y	mpy	mm/y	mpy
Type 317 stainless steel	0.03	1.0	0.003	0.1	0.02	0.9	nil	nil	nil	nil
ALLOYCO alloy 20	0.01	0.4 ¹								
	0.25	10.0	0.05	2.0	nil	nil	nil	nil	nil	nil
Type 316 stainless steel	0.01	0.5 ¹								
	1.07	42.	0.003	0.1	0.03	1.1	0.10	4.0	0.003	0.1
Type 304 stainless steel	0.01	0.3								
	— ₂	— ₂	0.003	0.1	0.05	2.0	0.81	32.0	0.09	3.5
Chemical Lead	6.35	250								
	— ₂	— ₂	6.10	240.	0.41	16.	0.25	10.0	0.61	24.
Nickel 200	6.10	240								
	— ₂	— ₂	1.40	55.	0.36 ⁴	14. ⁴	0.28 ⁴	11. ⁴	0.89 ⁵	35. ⁵
MONEL alloy 400	10.67	420.	1.40	55.	0.43	17.	0.38	15.	1.02	40.
INCONEL alloy 600	11.68 ³	460. ³	1.75	69.	0.43 ⁴	17. ⁴	0.20 ⁵	8. ⁵	0.69 ³	27. ³

nil = <.00254 mm/y (<0.1 mpy)

¹ Duplicate specimens were exposed and averages are given where one number appears. However, in this test one specimen became active while the duplicate specimen remained passive.

² Duplicate specimen lost or corroded away.

³ Perforated.

⁴ Pitted to a maximum depth of 0.41 mm (16 mils).

⁵ Pitted to a maximum depth of 0.30 mm (12 mils).

Test 1—In liquid phase of Type 316 stainless steel reactor. Reactor operated for 219 hours during a 27-day exposure. Corrosion rates based on 9 days of actual operation. No aeration, violent agitation. Temperature 110°C (230°F) or higher.

Test 2—In vapor phase of above reactor. Otherwise the same.

Test 3—Exposed in No. 2 crystallizer which operated for total of 30 days during 77 days of total exposure. Corrosion rates based on 30 days. No aeration, medium agitation. Temperature 71°C (160°F) average, 69-80°C (155-175°F) range.

Test 4—Exposed in No. 5 crystallizer. Same as Test 3 except average temperature was 66°C (150°F), 63-74°C (145-165°F) range.

Test 5—Exposed in liquid of vacuum drum-filter. Operated for total of 30 days during 77 days of total exposure. Corrosion rates based on 30 days. No aeration, considerable agitation. Temperature 54°C (130°F) average, 52-63°C (125-145°F) range.

TABLE LXXI
Ammonium Sulfate Production—BY Product of Caprolactam

Alloy	Corrosion Rate											
	Test 1		Test 2		Test 3		Test 4		Test 5		Test 6	
	mm/y	mpy	mm/y	mpy	mm/y	mpy	mm/y	mpy	mm/y	mpy	mm/y	mpy
Type 316 stainless steel	0.01	0.2	—	—	0.02	0.9	0.00	0.1	0.00	0.1	nil ²	nil
Type 316 stainless steel furnace sensitized	—	—	—	—	—	—	0.16	6.2	0.05	1.8	nil	nil
Type 316L stainless steel	—	—	—	—	—	—	0.00	0.1	0.01	0.2	nil	nil
Type 317 stainless steel	—	—	—	—	—	—	nil	nil	nil	nil	nil	nil
Type 304 stainless steel	—	—	—	—	0.02	0.7	—	—	—	—	nil	nil
Type 304 stainless steel furnace sensitized	—	—	—	—	—	—	—	—	—	—	nil	nil
CARPENTER alloy 20Cb	0.02	0.9	—	—	0.09	3.5	0.03 ³	1.1 ³	0.04	1.5	nil	nil
INCOLOY alloy 825	—	—	—	—	—	—	0.08	3.1	0.06	2.2	nil	nil
DURIMET alloy 20	0.01	0.2	0.00	0.1	—	—	—	—	—	—	—	—
HASTELLOY alloy B	0.79	31.	>8.89	>350. ⁴	2.79	110.	—	—	—	—	—	—
HASTELLOY alloy C	0.01	0.3	—	—	—	—	—	—	—	—	—	—
MONEL alloy 400	—	—	0.76	30.	2.29	90.	>3.30 ⁴	>130.4	>3.30 ⁴	>130. ⁴	0.04	1.7
Chemical Lead	—	—	0.30	12.	1.35	53.	>4.57 ¹	>180.4	3.05 ⁵	120. ⁵	6.10	240.

¹ Heat treated at 677°C (1250°F) for one hour to precipitate chromium carbides.

² Nil = <0.00254 mm/y (<0.1 mpy).

³ Duplicate samples showed different corrosion rates.

⁴ Corroded away

⁵ Partially corroded away.

Test 1: Pilot plant test in Disulfonate tank. 12% ammonium nitrate reduced with pure SO₂ gas to produce 34% ammonium hydroxylamine disulfonate plus several percent ammonium sulfate and less than 1 % ammonium nitrate. Average pH 5 during batch, final pH = 3. Operated total of 4.2 days over 100-day period. Temperature 0-10°C (32-50°F). Test spool attached to cooling coil.

Test 2: Pilot plant test in Hydrolysis Kettle. Hydrolysis of 34% ammonium hydroxylamine to yield 10% hydroxylamine sulfate, 7% sulfuric acid, 20% ammonium sulfate and <1 % ammonium nitrate. Operated 18.8 days-50 hours at 100°C (212°F), balance at 30°C (86°F), in liquid.

Test 3: Pilot plant test immersed in Oxime Kettle. Cyclohexanone added to solution from Hydrolysis Kettle and agitated followed by an ammonia addition. After the free acid is neutralized, further ammonia causes formation of cyclohexanone oxime, ammonium sulfate and water. Operated 25 hours over 45-day period. Temperature 40°C (104°F) average, 20-50°C (68-122°F) range.

Test 4: Plant test in stripping column for removal of cyclohexanone from ammonium sulfate. Specimens exposed for 54 days at liquid level in the reboiler. Temperature 110°C (230°F) average, 100-135°C(212-275°F)range.

Test 5: Plant test in same stripping column as above except samples exposed at first tray level of the bubble-cap column.

Test 6: Plant test in ammonium sulfate crystallizer. Corrosion test spools exposed in liquid for 30 days, vapor and splash area for 78 days. Liquid varied from 37% solution to 30% slurry in saturated solution containing 2% hydroxylamine ammonium monosulfonate and a trace of sulfuric acid, pH 3.5-4.5. Temperature 96°C (205°F) average, 85-105°C (185-221°F) range. Corrosion rates in all three test areas were equivalent.

percent sulfuric acid. Since sulfuric acid in this concentration range will cause intergranular corrosion in weld heat-affected zones, it is necessary to utilize the low carbon grades of stainless steel when weld fabrication is employed.¹⁰² Table LXXII shows the results of a corrosion test in which the specimens were exposed on the cracker pipe. The Saturator Process has been largely replaced by the Absorption and Controlled Crystallization Processes.

In the Ammonia Absorption Process, the ammonia laden gas enters the base of an unpacked, spray-type absorber and is scrubbed by a countercurrent flow of ammonium sulfate solution containing from 4 to 10 percent sulfuric acid, sprayed in at the top. The solution leaving the scrubber drains to a crystallizer from which the crystal slurry is pumped to a slurry tank where the salt settles. Another portion of the crystallizer solution is diverted to a mother liquor tank where 66° Baume sulfuric acid is added so as to maintain the acid concentration within the desired range, before returning to the scrubber. Concentrated ammonium sulfate slurry withdrawn from the bottom of the slurry tank is fed continuously to centrifugal dryers where the moisture is reduced to about two percent and then on to vacuum rotary-drum-dryers for final drying.

The results of corrosion tests in a plant employing the Absorption Process are shown in Table LXXIII.

The third process for recovering ammonia from coke oven gas is the Low Differential Controlled Crystallization Process. The acid concentration is maintained at 6-7 percent, temperatures are generally below 60°C (140°F) and the equipment utilized is similar to that used in the Absorption Process except that a vaporizer is incorporated into the system. By varying the circulation rate and the degree of crystal concentration in the crystallizer, the size range of the ammonium sulfate crystals can be controlled within narrow limits, the product is clear, crystalline, rice sized, dust free, free flowing and more resistant to degradation than ammonium sulfate made by the preceding two processes.

TABLE LXXII
Ammonium Sulfate Production—Coke Oven
By-Product, Saturator Process

Alloy	Corrosion Rate	
	mm/y	mpy
Type 316 stainless steel	0.003	0.1
Type 304 stainless steel	0.003 ¹	0.1 ¹
	0.13	5.0
INCONEL alloy 600	0.02 ²	0.7 ²
MONEL alloy 400	0.15	6.0
Nickel 200	0.18	7.0
Ni-Resist Type 1	0.48	19.0
Carbon Steel	0.91	36.0
Gray Cast Iron	1.52	60.0

(1) Rates for duplicate specimens. Apparently one specimen became active for short periods while other specimen remained passive.

(2) Pitted to a maximum depth of 0.15 mm (6 mils)

Attached to cracker pipe of saturator, saturated solution of ammonium sulfate in 3-10% sulfuric acid plus coke oven gas containing 1-2% ammonia at 50-60°C (122-140°F) for 77 days.

Although specific corrosion test results for the Differential Controlled Crystallization Process are unavailable it is known that Types 316 and 316L stainless steels and cast WORTHITE pumps are the predominant materials of construction and have given many years of excellent service.¹⁰³ Since the process conditions are similar to the absorption process, similar low corrosion rates are encountered.

4. By-Product of Hydrometallurgical Operations Utilizing Ammonia for Leaching

Ammonium sulfate is generated during the ammoniacal leaching of metal ores and it is recovered from the spent or “barren” solutions. The metals extracted in this manner are mainly (but not restricted to) nickel and copper. The ammonium sulfate content varies at different points in the process and the oxidizing conditions that exist during leaching favor the use of austenitic stainless steels as shown in Table LXXIV.

The corrosiveness of the solutions vary, but Type 316L stainless steel is usually corrosion resistant. Occasionally, more resistant alloys are required and crystallizers fabricated from INCOLOY alloy 825 have been successfully utilized by several companies.

E. ALUMINUM SULFATE MANUFACTURE

Aluminum sulfate* also known as “alum”**, “filter alum”, or “papermakers alum” is produced from finely ground bauxite, alumina or clays by digestion with sulfuric acid. Sulfuric

* Crude aluminum sulfate is called “alum cake” or if much iron is present, “alum ferric cake”.

** Aluminum sulfate has largely replaced “alum” markets formerly dominated by potassium aluminum sulfate [KAl(SO₄)₂•12H₂O] and ammonium aluminum sulfate [NH₄Al(SO₄)₂•12H₂O].

TABLE LXXIII
Ammonium Sulfate Production—Coke
Oven By-Product, Absorption Process

Alloy	Corrosion Rate			
	Test 1		Test 2	
	mm/y	mpy	mm/y	mpy
WORTHITE	nil*	nil*	nil	nil
Type 317 Stainless Steel	nil	nil	nil	nil
Type 316 Stainless Steel	nil	nil	nil	nil
Type 304 Stainless Steel	nil	nil	nil	nil
MONEL alloy K-500	0.10	3.8	0.04	1.6
MONEL alloy 400	0.14	5.5	0.07	2.9
Nickel 200	0.13	5.2	0.07	2.9
INCONEL alloy 600	0.09	3.7**	0.02	0.9
Ni-Resist, Type 1	0.14	5.4	0.13	5.2
Chemical Lead	0.03	1.1	0.13	5.1
Gray Cast Iron	1.14	45.0	0.91	36.0

* Nil = <0.00254 mm/y (<0.1 mpy)

** Pitted to a maximum depth of 0.15 mm (6 mils)

Test 1: Immersed in mother liquor mixing tank containing a saturated solution of ammonium sulfate and 5% sulfuric acid at 38-47°C (100-116°F) for 33 days.

Test 2: Immersed in crystallizer containing saturated solution of ammonium sulfate and 5% sulfuric acid at 38-47°C (100-116°F) for 33 days.

acid of various concentrations, frequently with air agitation, is used for the digestion. Solids are removed by sedimentation and the solution is treated to precipitate iron, thereby rendering a commercial product (0.5% Fe max.). High purity, iron-free aluminum sulfate (0.005% Fe max.) is made in a similar manner except that high purity reactants are utilized.

The commercial product is sold as the decanted liquid (8.25% Al_2O_3) or concentrated by evaporation to about 61.5 Bé. On cooling, the concentrated syrupy solution solidifies. This product is either sold in brick or slab form or crushed into a powder product which corresponds to 57% $Al_2(SO_4)_3$ or 17% Al_2O_3 .

In producing commercial grade aluminum sulfate from crude bauxite, the conversion of iron impurities to ferric sulfate makes the solution highly oxidizing. This, combined with the boiling temperature and possible small amounts of chloride impurities, makes the digestion process quite corrosive. Results of plant corrosion tests in dissolving tanks are shown in Table LXXV.

It will be observed that MONEL alloy 400, HASTELLOY alloy C-276 and DURIMET 20 would be useful under the conditions obtained in the production of iron-free grade aluminum sulfate (Test 1). These data also suggest that alloys

such as CARPENTER alloy 20 Cb-3 and INCOLOY alloy 825 would also be useful but, unfortunately, they were not included in the test.

In the digestion of crude bauxite, corrosive conditions are considerably less severe in the acid vapor above the liquid since ferric sulfate is not present to an appreciable extent, so that Alloy 400 could be used for parts which do not enter the liquid. However, acid-resistant-brick-lined steel or lead-lined steel are often utilized for the digester tanks in this case. Corrosion rates are shown in Test 2.

In the evaporation of commercial grades of aluminum sulfate, corrosion rates due to the oxidizing effect of the ferric ion usually will preclude the economical use of Alloy 400 evaporators as shown by most of the tests in Table LXXVI. Under such conditions, some other alternate material might be used for evaporating equipment. Based on operating experience, alloys such as HASTELLOY alloy C-276, Alloy 625, CARPENTER alloy 20 Cb-3, and INCOLOY alloy 825, frequently can be used and should be tested for suitability. Alloy 400 is sometimes used for evaporator covers where in contact with acid vapor only. Tests 7-9 of this Table show the results of corrosion tests in the evaporation of low-iron aluminum sulfate and indicate the suitable performance of a number of nickel containing alloys under these conditions.

TABLE LXXVI
Plant Corrosion Tests in Evaporation of Aluminum Sulfate

Alloy	Corrosion Rate									
	Test 1		Test 2		Test 3		Test 4			
					In Vapor		In Condensate			
	mm/y	mpy	mm/y	mpy	mm/y	mpy	mm/y	mpy	mm/y	mpy
MONEL alloy 400	0.14	5.5	0.41	16.0	0.56	22.0	0.03	1.2	0.81	32.0
Nickel 200	—	—	1.5	59.0	—	—	—	—	0.74	29.0
INCONEL alloy 600	—	—	1.3	51.0	—	—	—	—	—	—
Stainless Steels										
Types 304 & 304L	—	—	x	x	0.25*	10*	nil"	nil"	—	—
70-30 Copper-Nickel	—	—	—	—	0.61	24.0	0.11	4.5	1.65	65.0
Ni-Resist, Type 1	—	—	7.6	300.0	—	—	—	—	—	—
Cast Iron	—	—	—	—	—	—	—	—	0.16	6.6
Mild Steel	—	—	—	—	—	—	—	—	—	—
Chemical Lead	0.08	3.2	—	—	0.05	2.0	0.17	6.6	0.03	1.3
0.7% Te Lead										
INCOLOY alloy 825										
HASTELLOY alloy B										
CARPENTER alloy 20 Cb										
Type 316 stainless steel										
Type 1100 Aluminum										

x Corroded entirely away during test. Original thickness 1.63mm (62 mils).

* Pitted up to a depth of 0.15mm (6 mils)

** <0.00254 mm/y (<0.1 mpy)

*** Perforated

Test 1: Immersed in liquid in alum evaporator. Duration of test 100 days. Temperature 60-166°C (140-240°F).

Test 2: Immersed in liquid in alum evaporator during concentration from 26 to 57% $Al_2(SO_4)_3$. Iron content 0.02% as Fe_2O_3 and 0.8% as FeO. Duration of test 44 days. Temperature 60-116°C (140-240°F).

Test 3: In vapor and condensate from alum evaporation from 26 to 57% $Al_2(SO_4)_3$. Duration of tests 81 days. Temperature of vapor 60-116°C (140-240°F).

a) In vapor in evaporator.

b) In condensate from vapor.

Test 4: Immersed in liquid in alum evaporator during concentration from approx. 24 to 57% $Al_2(SO_4)_3$. Iron content 0.04% as Fe_2O_3 and 0.14% as FeO. Duration of test 20 days.

TABLE LXXIV

Ammonium Sulfate Production-Ammonia Leaching By-Product

Alloy	Corrosion Rate					
	Test 1		Test 2		Test 3	
	mm/y	mpy	mm/y	mpy	mm/y	mpy
HASTELLOY alloy C	–	–	–	–	nil ¹	nil ¹
Type 316L stainless steel	0.01	0.3	nil ¹	nil ¹	–	–
Type 316 stainless steel	0.01	0.4	nil	nil	nil	nil
Type 304 stainless steel	0.01	0.2	nil	nil	16.00	630 ²
Type 321 stainless steel	0.01	0.3	nil	nil	18.64	734 ²
Type 347 stainless steel	0.01	0.3	nil	nil	–	–
Type 430 stainless steel	0.01	0.2	nil	nil	–	–
Carbon Steel	0.05	2.0 ³	0.64	25.0	–	–

¹ nil = less than 0.00254mm (<0.1 mil)

² Perforated

³ Pitted to a depth of 0.08mm (3 mils)

Test 1: Immersed in the liquid of the final leach autoclave. Liquid contains 80 g/l (NH₄)₂SO₄ (about 8 percent), 80 g/l NH₃ plus substantial amounts of nickel, copper and cobalt in their higher valence state. Solution agitated and air was sparged in the bottom. Exposed at 77-82°C (170-180°F) for 102 days.

Test 2: Immersed in the liquid of the adjustment leach autoclave. Liquid contains 150 g/l (NH₄)₂SO₄ (about 14 percent), 80 g/l free NH₃ plus nickel, copper and cobalt in their higher valence state. Solution agitated and air was sparged in the bottom. Exposed at 80-82°C (175-180°F) for 107 days.

Test 3: Exposed in centrifuge basket separating ammonium sulfate from 8.4 g/l H₂SO₄ solution. Tested at 69°C (156°F) for 6 days.

TABLE LXXV

Aluminum Sulfate Digestion

Alloy	Corrosion Rate					
	Test 1			Test 2		
	In Liquid		In Vapor			
	mm/y	mpy	mm/y	mpy	mm/y	mpy
MONEL alloy 400	0.10	4.1	4.32	170.0	.20	8.0
Nickel 200	2.34	92.0	x	x	–	–
INCONEL alloy 600	–	–	x	x	–	–
HASTELLOY alloy C	0.15	6.0	–	–	–	–
DURIMET 20	0.36	14.0	–	–	–	–
Ni-Resist, Type 1	–	–	18.8	740.0	–	–
Chemical Lead	–	–	0.41	16.0	.13	5.0

x Completely corroded away. Original thickness 0.79 mm (31 mils)

Test 1: Immersed in dissolving tank during treatment of very low iron-content alumina with sulfuric acid to produce "iron-free" aluminum sulfate. Agitated with air for short periods. Duration of test 21 days. Temperature boiling at 104-120°C (220-250°F).

Test 2: Dissolving of high iron-content bauxite in sulfuric acid to produce aluminum sulfate. Duration of tests 50 and 81 days. Temperature of solution, boiling.

- a) Immersed in liquid in tank, 50 days.
- b) In vapor above liquid, 81 days.

TABLE LXXVI (Continued)

Plant Corrosion Tests in Evaporation of Aluminum Sulfate

Corrosion Rate													
Test 5		Test 6				Test 7		Test 8		Test 9			
In Liquid		In Vapor		In Liquid		In Vapor							
mm/y	mpy	mm/y	mpy	mm/y	mpy	mm/y	mpy	mm/y	mpy	mm/y	mpy	mm/y	mpy
–	–	0.46	18.0	1.55	61.0	1.2	47.0	0.01	0.4	0.09	3.7	0.10	3.9
–	–	1.2	47.0	3.3	130.0	2.8	110.0	0.04	1.5	0.48	19.0	0.38	15.0
–	–	1.14	45.0	4.1	160.0	2.8	110.0	0.08	3.3	x	x	x	x
–	–	–	–	0.20	8.0	1.7	66.0	–	–	0.08	3.0	0.09	3.5
1.55	61.0	0.99	39.0	0.66	26.0	2.54	100.0	–	–	–	–	–	–
6.6	260.0	2.1	83.0	4.3	170.0	3.3	130.0	–	–	–	–	–	–
–	–	2.8	110.0	x	x	3.81	150.0	–	–	–	–	–	–
0.08	3.0	0.08	3.0	0.02	0.7	0.025	1.0	0.06	2.3	–	–	–	–
										nil	nil	0.02	0.9
										0.02	0.8	0.02	0.7
										0.02	0.9	0.03	1.1
										0.03	1.0	0.02	0.9
										1.14	45.0***	1.28	50.5***
										x	x	x	x

Test 5: In alum evaporator during concentration of aluminum sulfate. Duration of tests 48 and 90 days. Temperature 66-120°C (150-245°F). Free H₂SO₄ 0.03%.
a) In liquid, 48 days.
b) In vapor, 90 days.

Test 6: In alum evaporator during concentration from 20 to 60% Al₂(SO₄)₃. Duration of tests 36 days. Temperature 66-120°C (150-245°F).
a) In liquid.
b) In vapor.

Test 7: Immersed in evaporator during concentration of "iron free" aluminum sulfate to 55% Al₂(SO₄)₃ concentration. pH 2-3. Duration of tests 27 days. Temperature boiling at 106-112°C (225-235°F).

Test 8: Immersed in liquid in batch alum evaporator during 423 cycles while concentrating from 28.2 to 57.7% aluminum sulfate. Iron content 0.1 ferric and 0.3 ferrous at start. Temperature 90-120°C (195-250°F).

Test 9: Same as Test 8 but exposed for an additional four hours to 4% NaOH at an average temperature of 102°C (215°F) as a coil descaling treatment.

In the use of aluminum sulfate, the solid salt is usually dissolved in hot water to provide the desired solution concentration. Some free sulfuric acid may be present and the corrosiveness of the solution to particular alloys depends upon the concentration of ferric ion present. The best grades of paper-makers' alum are iron-free with very little free acid content and, under these conditions, Types 316 or 316L stainless steels and Alloy 400 can be used for alum dissolving and storage tanks. Where the ferric ion is present, Type 316 stainless steel, or when welding is required, its low carbon counterpart, Type 316L, is often the preferred material of construction because of the strong passivating effect of this oxidizing agent.

The corrosion test results given in Table LXXVII were obtained during the dissolving of 2 lbs. of alum per gallon of water in a paper mill.

The test results in Table LXXVIII were obtained during storage and handling of alum solutions in paper mills.

Table LXXIX provides the results of a test in the cylinder vat of paper board machine where pH ranged from 2.8 to 8.5 and there was some aeration of the solution due to movement of the cylinder.

F. ORGANIC SULFATIONS AND SULFONATIONS

1. General

Sulfation and sulfonations are among the processes used to change the properties of organic materials such as to introduce greater solubility, or to make a hydrocarbon more reactive for further synthesis. These processes are used particularly in the preparation of surface - active materials including detergents,

emulsifiers, wetting agents, and penetrants from animal and vegetable oils and from fatty alcohols, aromatics and other hydrocarbons. Sulfation occurs when an OSO₂OH group is attached to carbon. Sulfonation is any procedure to attach the sulfonic acid group SO₂OH, or the corresponding salt or sulfonyl halide to a carbon atom.

TABLE LXXVIII
Plant Corrosion Test in Storage of Alum in Paper Mills

Alloy	Corrosion Rate					
	Test 1		Test 2		Test 3	
	mm/y	mpy	mm/y	mpy	mm/y	mpy
Type 316						
stainless steel	nil*	nil*	nil	nil	nil	nil
MONEL alloy 400	0.07	2.6	0.15	6.0	-	-
Nickel 200	0.08	3.0	0.15 ^a	6.0 ^a	-	-
INCONEL alloy 600	-	-	nil	nil	-	-
HASTELLOY alloy B	-	-	0.13	5.3	-	-
HASTELLOY alloy C	-	-	nil	nil	-	-
Ni-Resist, Type 3	-	-	0.22	8.6	-	-
Ni-Resist, Type 1	0.09	3.6	0.36	14.0	-	-
Cast Iron	-	-	16.56 ^b	650.0 ^b	-	-
Mild Steel	0.28	11.0	4.8	190.0	-	-
Chemical Lead	0.02	0.6	-	-	0.5	2.0
Type 304						
stainless steel	-	-	-	-	nil	nil
INCOLOY alloy 825	-	-	-	-	nil	nil
CARPENTER alloy 20Cb	-	-	-	-	nil	nil

* <0.00254 mm/y (<0.1 mpy)

^a Perforated by pitting. Original thickness. 79mm (31 mils).

^b Completely graphitized.

Test 1: Immersed in 24% aluminum sulfate solution in storage tank. Duration of test 62 days. Temperature 32-38°C (90-110°F).

Test 2: Immersed in 15% aluminum sulfate solution in alum head tank. Duration of test 45 days. Temperature 43°C (110°F). pH 3.0.

Test 3: Immersed in 21.8% of aluminum sulfate solution in storage tank. Air agitated 45 minutes each day. Duration of test 60 days. Temperature 48-66°C (120-150°F).

TABLE LXXVII
Plant Corrosion Tests In
Dissolving Of Alum In Paper Mill

Alloy	Corrosion Rate			
	In Use 4 Hrs. Per Day		Continuous Use	
	mm/y	mpy	mm/y	mpy
Type 316 stainless steel	nil*	nil*	nil	nil
Chemical Lead	0.07	2.7	0.41	16.1
MONEL alloy 400	0.15	6.0	0.91	36.0
Nickel 200	0.20	8.0	1.24	49.0
Mild Steel	1.37	54.0	8.13	320.0
Cast Iron	1.65	65.0	9.91	390.0
Ni-Resist, Type 1	2.3	90.0	13.5	530.0

Conditions: Immersed in alum dissolving tank during dissolving of alum in water. Temperature 43-49°C (110-120°F). Tank in use 4 hours per day for 44 days. Rates based on this use and on continuous exposure.

* nil <0.00254 mm/y (<0.1 mpy)

TABLE LXXIX
Plant Corrosion Test In Alum Solution In
Paper Board Cylinder Vat

Alloy	Corrosion Rate	
	mm/y	mpy
	INCONEL alloy 600	nil*
Type 316 stainless steel	nil	nil
Nickel 200	0.06	2.4
MONEL alloy 400	0.15	6.0
Mild Steel	0.38	15.0
Ni-Resist, Type 1	0.53	21.0
Cast Iron	0.61	24.0

* <0.00254 mm/y (<0.1 mpy)

Conditions: Immersed in alum solution in cylinder vat. pH range from 2.8 to 8.5. Average pH 5.65. Duration of test 33 days. Temperature 33°C (91°F.)

The agents commonly employed for sulfation or sulfonation are sulfur trioxide itself or various strengths of SO₃ in water, from 66° Bé sulfuric acid, or even weaker, to strong oleums. The strength of acid used and temperature will usually depend upon the degree of saturation of the hydrocarbon, the location to which the attachment is to be directed and other factors. In some cases chlorosulfonic acid and even bisulfite solutions are used as sulfonating agents.

The selection of corrosion resistant materials of construction for sulfations and sulfonations is dependent upon such factors as the reagents utilized, the temperature and the amount of dilution which occurs during processing. If the reaction involves conditions which are generally reducing, Alloy 400 may be a preferred material whereas under oxidizing conditions an austenitic alloy in the stainless steel or high nickel alloy family would be desirable. Sulfonations at high temperatures and pressures can be very stringent.

2. Sulfated Fatty Acids

The first sulfonate-type chemical introduced commercially was "sulfonated" castor oil (Turkey red oil) which first appeared in 1875. (Although referred to as sulfonated, it is more correctly termed sulfated since the bond is mostly through the oxygen of a sulfate group.) Its main use was in the dyeing of textiles. Typical reaction conditions for sulfating a number of oils are shown in Table LXXX.

Normally, cold 96% sulfuric acid is added to the extent of 20-40% of the weight of the oil under agitated conditions. The results of a corrosion test in a succession of sulfation reactions over an extended time are provided in Table LXXXI.

TABLE LXXX
Reaction Conditions For The
Preparation of Sulfated Oils¹⁰⁴

Oil	Sulfating Agent (a)		Time	Temperature	
	lb./lb. Oil	Hr.		C	F
castor	0.25	0.30	3	30	86
castor	0.21		9	25-30	77-86
olive	0.38		3	20	68
shark	0.20		3	25	77
sperm	0.09		3	25	77
neat's foot	0.10		>2	15-25	59-77
cod	0.12			7-18	45-65
cod	0.28		10	35	95
oleic acid	0.23		1	52	89
oleic acid	0.40	b	1.5	20	68
oleic esters	0.30	0.50	3	25	77
oleic N-ethyl anilide	1.0	c	10-15	0	32
butyl ricinoleate	1.0		6.5	0	32

(a) 96% acid used, except as indicated; (b) 98% acid used; (c) 100% acid used.

After sulfation, sodium sulfate or sodium chloride solutions are added to salt-out, the product which is separated, washed with Glaubers salt solution, re-separated, and finally neutralized with caustic soda, soda ash, or ammonia. Corrosion results from one such treatment over an extended time period are given in Table LXXXII.

Corrosion rates in a quick sulfation process using 98% sulfuric acid and acetic anhydride are shown in Table LXXXIII.

These test results are indicative of the good performance of MONEL alloy 400 in the sulfation of animal and vegetable oils, which has been confirmed by its performance in operating reactors over a period of years. Alloy 400 has been used for the construction of complete sulfators, linings, heating coils, agitators, pipe, fittings, pumps and pump rods. Corrosion resistance is favored by the fact that the concentrated acid, when added, is dispersed in the oily media which provides a somewhat protective film.

Frequently, washing and neutralization are done in the sulfation vessel, or it may be done separately. The results of plant corrosion tests in the washing and neutralization of sulfated vegetable oils are shown in Table LXXXIV.

The cast iron-nickel-chromium-molybdenum alloys, such as ACI CN-7M are used for pumps and valves in sulfation and washing systems since they have suitable resistance to both concentrated and dilute sulfuric acid at the temperatures encountered.

3. Sulfated Alcohols and Sulfonated Aromatics

A wide variety of detergents and wetting agents are made by the sulfation of fatty alcohols such as lauryl, myricyl, oleyl,

TABLE LXXXI
Sulfation Of Castor, Soya, Mineral, Sperm And
Red Oils With Other Fatty Acids

Alloy	Corrosion Rate	
	mm/y	mpy
CARPENTER alloy 20 Cb-3	nil ^a	nil ^a
Type 216 Stainless Steel	nil	nil
HASTELLOY alloy C-276	0.003	0.1
Type 316 stainless Steel ^b	0.01	0.5
Type 316 (Sensitized) ^c	0.05	2.1
HASTELLOY alloy B	0.05	2.1
INCONEL alloy 600	0.09	3.6
MONEL alloy 400	0.10	4.1

a) Ni1 < 0.00254 mm/y (<0.1 mpy)

b) Max. pitting 0.05 mm (2 mils), broad pits with small rata of depth to diameter. Non-uniform general corrosion.

c) Non-uniform general corrosion. However, actual Type 316 stainless steel sulfonator failed in weld area indicating the low carbon counterpart, 316L may be needed.

Condition: 96% H₂SO₄, Specimens submerged, moderate aeration, complete agitation, 16-38°C (60-100°F), 529 days total.

palmityl and stearyl alcohols, or of fatty esters such as the mono-glycerides, and can be referred to generally as aliphatic or alkyl sulfates. In some cases, these are converted to corresponding sodium, potassium or ammonium salts by treatment with the corresponding alkali for use as detergents. They generally are stable toward acids, alkalies, and salts and are

not precipitated by the hardness (calcium and magnesium ions) present in most natural waters.

Sulfonation of linear alkylbenzene, with either oleum (10-25% SO₃) or sulfur trioxide itself, has gained considerably in importance since 1965, when domestic household detergent producers switched to biodegradable surfactants which utilize these straight chain linear alkylates. Linear alkylbenzenes in which alkyl groups average C₁₁ – C₁₃ are termed “dodecylbenzene”. Table LXXXV shows the results of some laboratory corrosion tests sulfonating dodecylbenzene with 20 percent oleum. Type 304 or 304L stainless steels or more highly alloyed austenitic alloys such as CARPENTER alloy 20 Cb-3 or INCOLOY alloy 825 are very often selected for sulfonation equipment for reasons of product purity. Carbon steel is sometimes utilized downstream.

There is a report in the literature indicating that an “alloy 20” sulfonator containing Type 304 stainless steel cooling coils and agitator for the sulfonation of dodecylbenzene with 100 percent sulfuric acid at 52°C (125°F) was anodically protected to extend the life of both coils and tank.¹⁰⁵ Anodic protection could be used to advantage in many more of these applications.

Corrosion data for a process to sulfonate dodecylbenzene utilizing vaporized sulfur trioxide in a stream of dry air are lacking. However, one large detergent producer has indicated they have been obtaining good service with alloys such as CARPENTER alloy 20 Cb-3, INCOLOY alloy 825 and similar alloys. Downstream of the sulfonation equipment, Type 316L stainless steel is utilized by that producer.

TABLE LXXXII
Sulfated Oils from Sulfonator with Water, NA₂SO₄, Various Alkalies Including NAOH, KOH, NH₃, And Diethanolamine

Alloy	Corrosion Rate	
	mm/y	mpy
JESSOP alloy JS-700	0.01	0.5
INCOLOY alloy 825	0.01a	0.5a
CARPENTER alloy 20 CB-3	0.01a	0.5a
INCONEL alloy 600	0.02b	0.8b
MONEL alloy 400	0.02	0.8
Type 316 stainless steel	0.03c	1.0c
Type 317 stainless steel	0.03	1.1
Nickel 200	0.04	1.5
Type 304 stainless steel	0.04d	1.7d
Type 316 stainless steel sensitized	0.05e	2.0e
Type 304 stainless steel sensitized	0.08f	3.0f
Chemical Lead	>.56g	>22.1g

- a) A few random pits
- b) Numerous shallow pits <0.02 mm (<1 mil)
- c) Slight crevice corrosion
- d) Intergranular etch
- e) Max. Pitting, 0.05 mm (2 mils); Intergranular etch
- f) Intergranular corrosion
- g) Specimen corroded away

Conditions: pH 1-13, Specimens submerged in wash tank extensive aeration and agitation 49-100°C (120-212°F), 529 days total.

Comments: Lead lining used in past contaminated product and required frequent repair.

TABLE LXXXIII
Plant Test In Quick Sulfation of Vegetable Oils

Alloy	Corrosion Rate	
	mm/y	mpy
HASTELLOY alloy C	0.01	0.4
MONEL alloy 400	0.03	1.0
INCONEL alloy 600	0.04	1.5
Nickel 200	0.07	2.9
Chemical Lead	0.81*	32.0*

*Significant pitting and crevice attack

Conditions: Immersed in sulfation reactor in mixture of vegetable oils and 96% sulfuric acid plus acetic anhydride. Sulfation was being carried out only half of total exposure time. Exposure to vegetable oil only during balance of time. Agitated 90 rpm. under full load. Temperature 27-46°C (80-115°F). Duration of test 210 hours.

TABLE LXXXIV
Plant Tests in Washing and Neutralization of Sulfated Oils

Alloy	Corrosion Rate					
	Test 1		Test 2		Test 3	
	mm/y	mpy	mm/y	mpy	mm/y	mpy
HASTELLOY alloy C	–	–	0.01	0.3	0.01	0.2
HASTELLOY alloy B	–	–	0.06	2.3	0.08	3.0
MONEL alloy 400	0.02	0.5	0.08	3.0	0.08	3.2
INCONEL alloy 600	0.02	0.8	0.08	3.0	0.07	2.9
Nickel 200	0.03	1.3	0.11	4.4	0.11	4.3
DURIMET alloy 20	–	–	0.10	4.1	0.11	4.3
Type 316 stainless steel	–	–	0.13	5.0	0.18*	7.0*
Type 304 stainless steel	–	–	0.23	9.0	0.25**	10.0**
Ni-Resist, Type 1	0.15	6.0	0.43	17.0	0.46	18.0
Chemical Lead	0.23	9.0	–	–	–	–
Gray Cast Iron	4.83	190.0	3.81	150.0	3.05	120.0

* Crevice corrosion to a maximum depth of 0.23 mm (9 mils)

** Crevice corrosion to a maximum depth of 0.36 mm (14 mils)

Test 1: Immersed half-way down in wash tank. Sulfated oil diluted 1 to 1 with water. Neutralized with 10% caustic soda. Agitated. Temperature 40-60°C (104-140°F). Duration of test 60 days.

Tests 2 and 3: Immersed in wash tank during washing, neutralization and panning. Sulfated table oil mixed with approximately 5% sulfuric acid plus small amounts of sodium chloride and sodium sulfate. Agitated about 640 ft. per minute. Test 2 near bottom of tank in aqueous acid layer. Test 3 half-way up tank principally in oil-acid mixture. Temperature 50°C (122°F). Duration of test 45 days.

Another group of surface-active agents are based upon the sulfonation of aromatic hydrocarbons such as benzene and naphthalene. These materials constitute only a small portion of the production of surface active agents but their use as wetting agents and dispersants in paint, dyes and pigments, paper coatings and other applications is significant. Table LXXXVI shows the results of a plant corrosion test in which benzene was sulfonated with oleum. Under the oxidizing conditions of this sulfonation, Alloy 400 is not applicable but austenitic stainless steels or Alloy 600 should be considered as materials of construction.

A class of detergents referred to as alkyl aryl sulfonates are prepared by connecting paraffin hydrocarbon groups such as a keryl or kerosene group to benzene sulfonic acid and treating the resulting material with alkali. Table LXXXVII shows the results of a plant corrosion test in which the sulfonation was carried out utilizing 98 percent sulfuric acid. The mixtures obtained are quite aggressive because of the dilution of the acid and relatively high temperatures. In this case, a glass-lined steel sulfonator would probably be used and DURIRON or HASTELLOY alloy B-2 could be considered if an alloy were required, except in the vapor phase where a number of the alloys exhibited resistance.

Where sulfonations are carried out with strong oleums at high temperatures such as 165-175°C (330-350°F), corrosion rates of all common metals and alloys are likely to be high.

Thus, the conditions of sulfation and sulfonation reactions drastically affect the selection of materials of construction, and hence capital expenditure requirements for the project. This is a point that chemical engineers should take into account during the early design stages of a process, but unfortunately, materials are often not given sufficient consideration at this time. Alloy selection for a particular sulfation or sulfonation has to be made based upon corrosion tests, or a prior knowledge of the resistance of materials under the particular conditions that will exist.

TABLE LXXXV
Laboratory Corrosion Test In
Sulfonation Of Dodecylbenzene

Alloy	Corrosion Rate			
	Test 1*		Test 2*	
	mm/y	mpy	mm/y	mpy
INCONEL alloy 600	0.02	0.9	0.03	1.3
CARPENTER alloy 20 Cb	0.03	1.0	0.03	1.1
Type 316 stainless steel	0.06	2.3	0.05	2.1
HASTELLOY alloy B	0.06	2.5	0.03	1.1
Type 347 stainless steel	0.09	3.4	0.04	1.6
MONEL alloy 400	0.14	5.7**	0.03	1.0
Type 304 stainless steel	0.25	10.0	0.04	1.5
Nickel 200	0.36	14.0	0.03	1.3
Carbon steel	0.41	16.0	1.07	42.0

* Test 1 diluted with 0.139 parts water after reaction. Test 2 not diluted with water after reaction.
** Pitted to a maximum depth of 0.18 mm (7 mils).

Charge consists of 1.32 parts 20% oleum to 1.00 parts dodecylbenzene to give a sulfonic acid. Specimens immersed in agitated mixture at 48-56°C (118-133°F) for test periods of 16 days. Some SO₂ was given off as a side reaction.

G. ORGANIC ESTERIFICATIONS

Sulfuric acid is commonly used as a catalyst in organic esterifications. The sulfuric acid is usually added as 93-98 percent acid in ratios of 0.1 to 2.0 percent of weight of charge. In an anhydrous medium, this would not be excessively corrosive, but in some cases the sulfuric acid may be diluted with water formed by the reaction or by added water. Corrosion rates in these reactions will usually depend upon the amount and concentrations of sulfuric acid involved and upon the temperature (including hot-wall effects) of the reaction.

(Corrosion test results for a number of esterifications and a detailed discussion of those results can be found in INCO's Corrosion Engineering Bulletin No. 6 – "Corrosion Resistance of Nickel-Containing Alloys in Organic Acids and Related Compounds", pp. 58-63.)

TABLE LXXXVI
Plant Corrosion Test In Sulfonation of
Benzene With 20% Or 65% Oleum (Both Were Used)

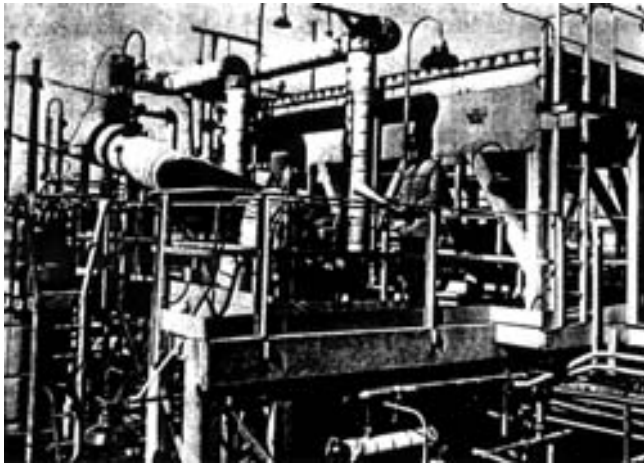
Alloy	Corrosion Rate	
	mm/y	mpy
WORTHITE	0.01	0.4
Type 316 stainless steel	0.03	1.1
INCONEL alloy 600	0.04	1.4
Type 304 stainless steel	0.04	1.7
Ni-Resist-Type 1	0.51	20.0
Ni-Resist-Type 3	0.56	22.0
Gray Cast Iron	0.69	27.0
Type 1100 Aluminum	1.09	43.0
MONEL alloy 400	2.46	97.0
Nickel 200	4.06	160.0
Carbon steel	6.35	250.0

Mixture after sulfonation contains 45-60% benzene sulfonic acid, 0-15% benzene meta disulfonic acid and 30-50% sulfuric acid. Some sulfur dioxide in the vapor space. Test spool in liquid phase which was agitated at 85-90 rpm. Temperature 45°C (113°F) average, range 35-120°C (95-250°F). Duration of test 31 days.

TABLE LXXXVII
Plant Corrosion Test In Sulfonation Of
Alkyl-Aryl Organic Material With
98 Percent Sulfuric Acid

Alloy	Corrosion Rate			
	Liquid		Vapor	
	mm/y	mpy	mm/y	mpy
DURIRON	0.02	0.8	0.01	0.5
HASTELLOY alloy B	0.13	5	0.08	3.0
MONEL alloy 400	0.48	19	0.06	2.3
Chemical Lead	0.64	25	0.10	4.0
WORTHITE	0.97	38	0.01	0.3
CARPENTER 20 Cb	1.22	48	0.03	1.0
Nickel 200	1.37	54	0.08	3.0
INCONEL alloy 600	2.18	86	0.06	2.3
Type 317 stainless steel	3.05	120	0.03	1.3
Carbon steel	3.30	130	0.58	23.0
Gray Cast Iron	3.81	150	0.79	31.0
Type 316 stainless steel	4.32	170	0.03	1.3
Type 304 stainless steel	5.33	210	0.04	1.7

After sulfonation water is added to drop out spent sulfuric acid of 63 percent concentration. temperature 60-77°C (140-170°F) in presence of 98 percent H₂SO₄ and 90-104°C (195-220°F) in presence of 63 percent H₂SO₄. Duration of tests 14 days normal operation (30 hours total exposure to corrosives.) Corrosion rates based on 14 day test period!



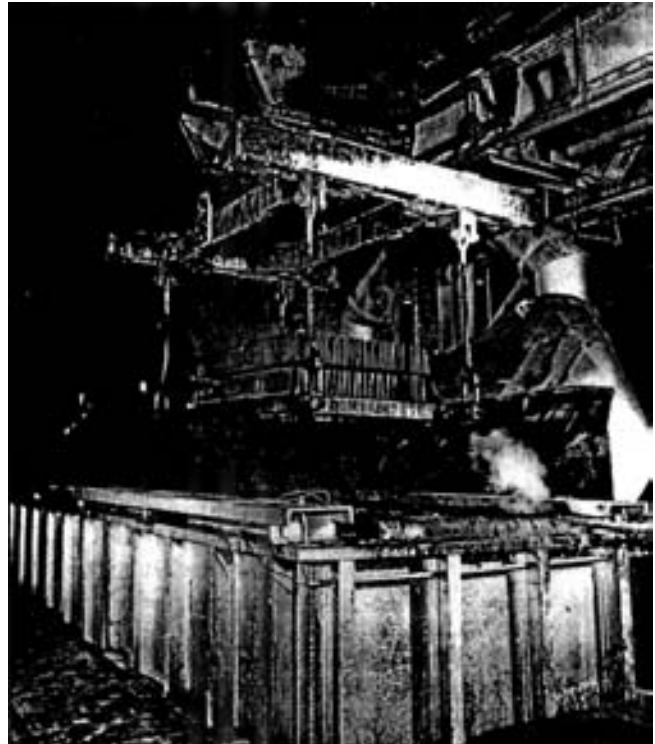
The reflux condenser off the top of a glass-lined reactor for the sulfonation of toluene and xylene utilizes HASTELLOY alloy B tubing to resist 98 percent sulfuric acid plus SO_2 and SO_3 at $150^\circ C$ ($300^\circ F$).

H. PICKLING

1. Iron and Steel

At one time, hot sulfuric acid solutions were widely used for pickling oxide scales from steel but, in some present applications, sulfuric acid has been replaced by other acids, particularly hydrochloric acid or a combination of acids. When sulfuric acid is used for pickling steel which has been hot rolled, forged or heat treated, acid concentrations are normally 5 to 15 percent by weight and temperatures from 60 to $93^\circ C$ (140 - $200^\circ F$). Inhibitors are often added to prevent too rapid an attack on the steel. Alloy 400 is one of the standard materials of construction for crates, racks, baskets, chains, hooks and other hardware holding the steel to be pickled. Alloy 400 is used for many of these applications because pickling conditions are particularly favorable to this alloy; the pickling reactions used up any oxygen that may be dissolved in the acid and the hydrogen evolved by reaction of the acid with steel tends to keep the solution in a reducing condition. In addition, the Alloy 400 crates, baskets and chains are galvanically protected by the steel parts with which they are in contact.

Caution should be observed in the use of Alloy 400 for pickling drums, either of continuous or batch types, which are not completely immersed in acid bath. In some cases, these drums have only the bottom portion immersed to pick up the acid and in others, the entire drum may be suspended above the bath and acid sprayed into it. In such installations, the exposed surfaces of the drum are covered with a thin layer of acid which becomes highly aerated. Furthermore, the drums may be only partly loaded, with the load constantly shifting, so that the actual area of contact between the drum and loading may be too small to provide galvanic protection. To provide satisfactory performance of Alloy 400, the drum should be immersed completely in the pickling acid, or if



"I" beam frames of MONEL alloy 400 support pickling racks, also constructed of MONEL alloy 400, which carry basic carbon and alloy steels through an 8-10 percent H_2SO_4 pickling solution. The "I" beam frames and rack base gave over 36 years of service.

(Photograph courtesy of Huntington Alloys, Inc.)

suspended partly or entirely above the acid surface, the pickling tank and drum should be enclosed with a sealed hood. Where this cannot be done, one of the alloys discussed below is a more suitable material of construction for the drums.

Because of changing economics and the oxidizing conditions sometimes encountered, the more highly alloyed stainless steels or nickel base alloys such as CARPENTER alloy 20 Cb-3, INCOLOY alloy 825, HASTELLOY alloy G and others are now often utilized to advantage. In some pickling applications, inhibitors or accelerators are added to control the operation. CARPENTER alloy 20 Cb-3 and Type 316 L stainless steel were indicated to have excellent corrosion for a sodium nitrate accelerated sulfuric acid pickling process as preparation for enameling.¹⁰⁶⁻¹⁰⁷

Table LXXXVIII shows corrosion test results in one of the mixed acid solutions used for the pickling of steel. The presence of a strong oxidizing agent, nitric acid, serves to passivate the stainless steels and many of the high nickel alloys. However, this same oxidizing agent caused excessive corrosion of the MONEL alloy 400 specimens.

2. Copper and Copper Alloys

Sulfuric acid solutions are used in the pickling of fabricated copper and copper alloy parts and in the continuous pickling of copper strip and sheet. In the processing of stamped or drawn copper alloy parts, these parts are often annealed and

pickled between draws. Acid concentrations and temperatures vary somewhat more than in steel pickling and depend upon the thickness of oxide film or scale to be removed. Concentrations may range from 5 to 20 percent and temperatures from atmospheric to 82°C (180°F). During pickling, the sulfuric acid solution dissolves copper from the product and gradually accumulates a copper sulfate content. Where ordinary immersion pickling processes are used and no oxidizing chemical is added to the solution, the copper sulfate usually remains in cuprous form and the solution is reducing in nature due to generation of hydrogen by the pickling reaction. The results of corrosion tests in the sulfuric acid pickling of copper and copper alloys are given in Tests 1, 2, 3 and 4 of Table LXXXIX.

It is the practice in some plants to use the same baskets or crates for holding brass parts through both annealing, usually at 593-650°C (1100-1200°F), and pickling cycles. INCONEL alloy 600 has given satisfactory service in this combined operation where resistance to sulfur attack from entrained acid in the furnace is needed. Other alloys such as Alloy 825 or CARPENTER 20 Cb-3 might also be considered for this service.

Types 316 or 316 L stainless steels are frequently utilized in the flash or bright pickling of brass parts where oxidizing salts such as dichromates or nitrates, or nitric acid are added to the sulfuric acid solutions. The results of plant corrosion tests in several types of bright pickling solutions are given in Table XC. It should be noted that Type 316 stainless steel was subject to crevice corrosion in two of the tests. It is suspected that unreported chlorides was present in these solutions. Precautions to minimize the chloride content of the solutions and avoiding crevices in the design of these tanks seems prudent.

Unfortunately, sensitized Type 316 stainless steel was not included in these tests, but experience has indicated that the low carbon grade, Type 316L, is necessary if welded construction is employed so as to avoid intergranular attack in

heat-affected zones of welds. Alloys such as CARPENTER 20 Cb-3, INCOLOY alloy 825, HASTELLOY alloy G and Alloy 904L could also be considered for this service if testing indicates that crevice corrosion is a problem with Type 316L stainless steel.

I. CHLORINE DRYING

Sulfuric acid is often utilized as a desiccant. One of these applications, involving the drying of gaseous chlorine, is particularly severe in regards to materials of construction. Table XCI shows the results of laboratory corrosion tests in dry chlorine and sulfuric acid saturated with either chlorine, nitrogen or air. Among the alloys tested, only HASTELLOY alloy C (now C-276) was resistant to excessive corrosion under all of the test conditions.

Plant corrosion tests have shown that HASTELLOY alloy C is extremely resistant to both wet and dry chlorine and chlorine in combination with sulfuric acid at temperatures up to 38°C (100°F) and, except for slight crevice corrosion, was not attacked at 82°C (180°F).^{109, 110} The results of plant corrosion

TABLE LXXXVIII
Plant Corrosion Test In Mixed Acid
Pickling Solution

Alloy	Corrosion Rate	
	mm/y	mpy
CARPENTER alloy 20 Cb-3	0.003	0.1
Type 316 stainless steel	0.003	0.1
INCOLOY alloy 825	0.01	0.3
Type 317 stainless steel	0.01	0.3
Type 329 stainless steel	0.01	0.3
INCOLOY alloy 800	0.04	1.5
Type 304 stainless steel	0.05	2.0*
Type 316 stainless steel	Intergranular Corrosion	
MONEL alloy 400	Corroded Away	

* Average of duplicate samples which corroded at 0.03 and 0.07 mm/y (1.3 and 2.7 mpy). This lack of reproducibility may indicate Type 304 stainless steel would be borderline for use in this solution.

Corrosive Media: 5-8 percent sulfuric, 8-12 percent nitric acid, up to 1.5 percent hydrofluoric acid, less than 1 percent phosphoric acid plus a detergent.

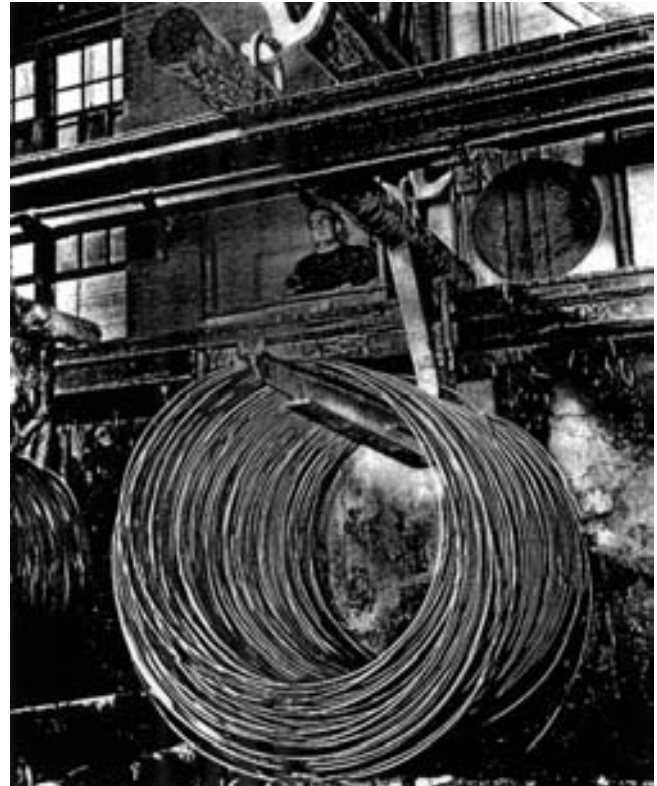
Temperature: 38°C (100°F)

Aeration: None

Agitation: Moderate

Duration: 101 days

Location of Specimens: Installed in basket at outlet carrying waste pickle liquor.



An INCOLOY alloy 825 pickling hook in use for pickling of wire rod. The pickling solution is 8-12 percent H₂SO₄ to which 300 pounds of salt have been added to the 3,000 gallon solution. This hook was in use for three years at the time the photograph was taken.

(Photograph courtesy of Huntington Alloys, Inc.)

tests shown in Table XCII, also indicate that a similar cast alloy, CHLORIMET alloy 3, showed extremely good corrosion resistance up to 38°C (100°F). Indeed, wrought HASTELLOY alloy C-276 is considered a standard material of construction for chlorine drying and ACI CW-12M-1 and CW-12M-2 alloys are utilized for cast valve and pump bodies.

Although Type 316 stainless steel is sometimes resistant to more concentrated sulfuric acid when chlorine is present to act as a strong oxidizing agent, experience has shown that this resistance does not extend to lower concentration of chlorine saturated sulfuric acid, nor to higher temperatures, or to wet chlorine.

TABLE LXXXIX
Plant Corrosion Tests in Pickling of Brass and Copper

Alloy	Corrosion Rate							
	Test 1		Test 2		Test 3		Test 4	
	mm/y	mpy	mm/y	mpy	mm/y	mpy	mm/y	mpy
Type 316 stainless steel	0.003 ^a	0.1 ^a	0.003	0.1	0.36	14	0.003	0.1
WORTHITE	0.01	0.3	–	–	0.05	2	0.003	0.1
DURIMET alloy 20	0.01	0.5	–	–	0.15	6	–	–
HASTELLOY alloy C	0.05	2.0	0.05	2.	–	–	–	–
MONEL alloy 400	0.91	36.0	0.13	5.	0.61	24	2.29	90
INCONEL alloy 600	1.40	55.0	1.17	46.	2.18	86	0.003	0.1
HASTELLOY alloy B	1.88 ^b	74.0 ^b	–	–	–	–	–	–
Nickel 200	Corroded away		–	–	1.32 ^c	52 ^c	2.18	86
Chemical Lead	–	–	–	–	0.13	5	0.08	3
Ni-Resist Type 1	–	–	–	–	–	–	15.75	620
Gray Cast Iron	–	–	–	–	–	–	39.12	1540
Carbon Steel	–	–	–	–	–	–	Corroded away	

^a Crevice corrosion to a maximum depth of 0.15mm (6 mils)

^b Perforated by localized corrosion. Original thickness of specimens 0.94mm (37 mils).

^c Pitted to a maximum depth of 0.23mm (9 mils).

Test 1: Immersed near center side of pickling tank in 5% sulfuric acid plus 0.5 oz. per gal. of copper as copper sulfate. solution heated and agitated with live steam. Temperature 80-85°C (175-185°F). Duration of test 30 days.

Test 2: Immersed in pickling tank in 19 to 28% sulfuric acid plus 2 to 4% copper sulfate, during flash pickling of brass pans. Temperature 60°C (140°F). Duration of test 41 days.

Test 3: Immersed in pickling tank during continuous pickling of oxidized copper sheet in 20% sulfuric acid plus up to 5% copper sulfate. Tank drained and refilled four times during test. Temperature 60-71°C (140-160°F). Duration of test 25 days.

Test 4: Exposed in spray pickling machine to spray of 10% sulfuric acid plus 2% copper sulfate. Aerated by spraying. Temperature 32°C (90°F). Duration of test 176 hours.

TABLE XC
Plant Corrosion Tests in Bright Pickling of Brass

Alloy	Corrosion Rate							
	Test 1		Test 2		Test 3		Test 4	
	mm/y	mpy	mm/y	mpy	mm/y	mpy	mm/y	mpy
Type 316 stainless steel	0.003	0.1	–	–	0.003 ^a	0.1 ^a	0.003 ^a	0.1 ^a
ALOYCO alloy 20	–	–	–	0.1	–	–	–	–
DURIMET alloy 20	–	–	–	–	0.003	0.1	0.003	0.1
WORTHITE	–	–	–	–	0.003	0.1	0.003	0.1
HASTELLOY alloy C	0.05	2	–	2	0.003	0.1	0.01	0.5
MONEL alloy 400	9.40	370	–	–	b	b	b	b
Chemical Lead	1.32	52	–	–	–	–	–	–
INCONEL alloy 600	b	b	0.01	0.5	0.01	0.4 ^a	0.01	0.4 ^a
Nickel 200	b	b	–	–	0.01	0.2 ^c	1.09	43 ^d
HASTELLOY alloy B	–	–	–	–	e	e	e	e

^a Perforated by crevice corrosion. Original thickness 0.79mm (31 mils).

^b Corroded away. Original thickness 0.79mm (31 mils).

^c Crevice corrosion to a depth of 0.25mm (10 mils).

^d Perforated by pitting on free surface and in crevice. Original thickness 0.79 (31 mils).

^e Corroded away. Original thickness 0.94mm (37 mils).

Test 1: Immersed 15 to 30 run (6 to 12 inches) below the minimum liquid level in pickling tank during pickling of brass in 7 to 8% sulfuric acid plus 0.8 to 0.9 oz. per gal. of sodium nitrate. Solution agitated with plunger. Temperature 69-74°C (155-165°F). Duration of test 13 days.

Test 2: Immersed in pickling tank during pickling of brass in 23% sulfuric acid and 18% nitric acid. Temperature 66-82°C (150-180°F). Duration of test 31 days.

Test 3: Immersed near center side of pickling tank during bright dipping of brass in 5% sulfuric acid plus 1.1 oz per gal. of sodium bichromate. Temperature 21-30°C (70-85°F). Duration of test 30 days.

Test 4: Immersed near center side of pickling tank during pickling of brass in 10% ferric sulfate solution plus 0.5% citric acid. Solution heated and agitated with live steam. Temperature 77-99°C (170-210°F). Duration of test 38 days.

TABLE XCI
Laboratory Corrosion Tests in Dry Chlorine and Sulfuric Acid—Gas Mixtures

Alloy	Corrosion Rate									
	Test 1		Test 2		Test 3		Test 4		Test 5	
	mm/y	mpy	mm/y	mpy	mm/y	mpy	mm/y	mpy	mm/y	mpy
HASTELLOY alloy C	nil ^a	nil	nil	nil	0.003	0.1	0.01	0.5	0.04	1.6
CHLORIMET alloy 3	nil	nil	nil	nil	—	—	0.03	1.2	0.10	3.9
Type 316 stainless steel	0.01	0.2	b	b	—	—	—	—	—	—
MONEL alloy 400	0.01 ^c	0.3 ^c	0.01	0.2	—	—	—	—	—	—
Carbon steel	0.01	0.2	0.33 ^d	13 ^d	—	—	—	—	—	—
Zirconium	nil	nil	b	b	corroded away		0.48 ^e	19 ^e	0.02 ^f	0.6 ^f
Titanium	Ignited ^g		Ignited ^g		nil	nil	nil	nil	nil	nil
Duriron	—	—	—	—	0.01	0.5	0.04 ^h	1.5 ^h	0.01 ⁱ	0.2 ⁱ
Durichlor	—	—	—	—	0.01	0.4	—	—	0.01 ^j	0.5 ^j
CARPENTER 20Cb	—	—	—	—	1.65	65	>2.03	>80	0.51 ^k	20 ^k
INCOLOY alloy 825	—	—	—	—	—	—	>1.52	>60	—	—
DURIMET alloy 20	—	—	—	—	—	—	—	—	—	—

Alloy	Corrosion Rate											
	Test 6		Test 7		Test 8		Test 9		Test 10		Test 11	
	mm/y	mpy	mm/y	mpy	mm/y	mpy	mm/y	mpy	mm/y	mpy	mm/y	mpy
HASTELLOY alloy C	0.09	3.4	0.05	2.0	0.01	0.3	0.02	0.6	nil	nil	0.02	0.6
CHLORIMET alloy 3	—	—	—	—	—	—	—	—	—	—	—	—
Type 316 stainless steel	4.45	175	9.63	379	13.36	526	nil	nil	0.01	0.2	0.01	0.2
MONEL alloy 400	11.81	465	0.01	0.3	0.15	5.9	0.84	33	0.66	26	0.69	27
Carbon steel	40.64	1600	5.08	200	75.69	2980	0.64	25	0.69	27	0.71	28
Zirconium	—	—	—	—	—	—	—	—	—	—	—	—
Titanium	—	—	—	—	—	—	—	—	—	—	—	—
Duriron	—	—	—	—	—	—	—	—	—	—	—	—
Durichlor	—	—	—	—	—	—	—	—	—	—	—	—
CARPENTER 20 Cb	—	—	—	—	—	—	—	—	—	—	—	—
INCOLOY alloy 825	—	—	—	—	—	—	—	—	—	—	—	—
DURIMET alloy 20	3.23	127	0.01	0.5	0.07	2.6	nil	nil	nil	nil	0.01	0.3

^a Nil is less than 0.00254 mm/y (<.01 mpy)

^b Zirconium specimens were destroyed and Type 316 stainless steel specimen was damaged when the titanium specimens ignited.

^c One MONEL alloy 400 specimen was damaged when the titanium specimens ignited.

^d Slight or shallow pitting attack. [Probably less than 0.0254 mm (1 mil).]

^e Both specimens perforated by pitting.

^f Pitted up to a depth of 0.46 mm (18 mils).

^g The titanium specimens apparently ignited upon exposure.

^h Pitted up to a depth of 1.57 mm (62 mils).

ⁱ Crevice corrosion up to a depth of 0.48 mm (19 mils).

^j Pitted up to a depth of 0.38 mm (15 mils).

^k Pitted up to a depth of 0.51 mm (20 mils).

Test 1: Dry chlorine gas at -18°C (0°F). Test duration 139 days. See Reference 109.

Test 2: Dry chlorine gas at 60°C (140°F). Test duration 36 days. See Reference 109.

Test 3: 40% sulfuric acid saturated with chlorine at ambient temperature. No aeration or agitation. Test duration 17 days.

Test 4: 45% sulfuric acid saturated with chlorine at 10°C (50°F). No aeration or agitation. Test duration 113 days.

Test 5: 45% sulfuric acid saturated with chlorine at 24°C (75°F), range 15-32°C (59-90°F). No aeration or agitation. Test duration 192 days.

Test 6: 50% sulfuric acid saturated with chlorine at ambient temperature. Chlorine bubbled through the solution for 8 hours continuously during the day and closed off to the atmosphere at night. Test duration 14 days. See Reference 110.

Test 7: 50% sulfuric acid saturated with nitrogen at ambient temperature. Nitrogen bubbled through the solution for 8 hours continuously during the day and closed off to the atmosphere at night. Test duration 14 days. See Reference 110.

Test 8: 50% sulfuric acid saturated with air at ambient temperature. Air bubbled through the solution for 8 hours continuously during the day and closed off to the atmosphere at night. Test duration 14 days. See Reference 110.

Test 9: 87% sulfuric acid saturated with chlorine at ambient temperature. Chlorine bubbled through the solution for 8 hours continuously during the day and closed off to the atmosphere at night. Test duration 14 days. See Reference 110.

Test 10: 87% sulfuric acid saturated with nitrogen at ambient temperature. Nitrogen bubbled through the solution for 8 hours continuously during the day and closed off to the atmosphere at night. Test duration 14 days. See Reference 110.

Test 11: 87% sulfuric acid saturated with air at ambient temperature. Air bubbled through the solution for 8 hours continuously during the day and closed off to the atmosphere at night. Test duration 14 days. See Reference 110.

TABLE XCII
Plant Corrosion Tests in Wet Chlorine Gas and Sulfuric Acid
Saturated with Chlorine

Alloy	Corrosion Rate																	
	Test 1		Test 2		Test 3		Test 4		Test 5		Test 6		Test 7		Test 8		Test 9	
	mm/y	mpy	mm/y	mpy	mm/y	mpy	mm/y	mpy	mm/y	mpy	mm/y	mpy	mm/y	mpy	mm/y	mpy	mm/y	mpy
HASTELLOY alloy C	0.01	0.4	0.003	0.1	nil ^a	nil ^a	nil	nil	nil	nil	0.02	0.8	0.02 ^b	0.9 ^b	0.15 ^c	6 ^c	0.13 ^d	5 ^d
HASTELLOY alloy C—as welded	0.01	0.2	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
HASTELLOY alloy C—welded and annealed	0.03	1.1	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Type 316 stainless steel	0.003	0.1	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Carpenter alloy 20Cb	0.08	3.1	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
MONEL alloy 400	>2.72 ^e	>107 ^e	—	—	—	—	>2.03 ^e	>80 ^e	—	—	—	—	—	—	—	—	—	—
Carbon Steel	>1.32 ^e	>52 ^e	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Titanium	0.05 ^c	1.9 ^c	>0.99 ^e	>39 ^e	nil	nil	nil	nil	nil	nil	nil	nil	nil	nil	nil	nil	nil	nil
Zirconium	—	—	—	—	0.51	20	>2.03 ^e	>80 ^e	0.51	20	>2.29 ^e	>90 ^e	>1.09 ^e	>43 ^e	1.27 ^f	50 ^f	>0.76 ^e	>30 ^e
CHLORIMET alloy 3	—	—	—	—	0.01 ^b	0.5 ^b	0.01	0.4	0.02	0.6	0.28	11	0.23 ^b	9 ^b	0.51 ^f	20 ^f	1.37 ^d	54 ^d

- a. Nil is less than 0.00254 mm/y (<0.1 mpy)
- b. Incipient crevice corrosion observed; less than 0.0254 mm (<1 mil)
- c. Crevice corrosion (depth unknown)
- d. Perforated by pitting
- e. Corroded away. Rate calculated as if entirely consumed in exposure period
- f. Samples suffered severe pitting (depth unknown)

Test 1: 87 percent sulfuric acid saturated with chlorine (essentially 95 percent chlorine, 5 percent air), flowing at a velocity of 110 meters per minute (6 feet per second). Temperature 21°C (70°F). Test duration 79 days

Test 2: Partially dry chlorine gas with entrained 87 percent sulfuric acid flowing at 220 meters per minute (12 feet per second). Temperature 21°C (70°F). Test duration 300 days.

Tests 3 through 9: Conducted in most of the various wet chlorine environments found in caustic-chlorine plants. Into corrosion test spools were exposed in the vapor space above the anolyte in chlorine cells, in the gas stream in collection headers, partly in the gas and partly in the condensed water and organic sludge which accumulates in collection headers, and in various sections of gas coolers.

Test	Temperature		Test duration (days)
	°C	°F	
3	10	50	139
4	16	60	73
5	38	100	133
6	77	170	67
7	82	180	137
8	88	190	18
9	88	190	202

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PART VI - APPENDIX
1. Nominal Composition of Nickel-Containing Alloys in Use or Corrosion Tested
in Sulfuric Acid and Related Compounds

Alloys	Composition, %								
	Ni	Fe	Cr	Mo	Cu	C	Si	Mn	Other
WROUGHT ALLOYS									
Stainless Steels—Austenitic									
AISI Type 216	6.0	Balance	19.5	—	—	0.08 Max	1.0 Max	8.0	N 0.25-0.50
AISI Type 216L	6.0	Balance	19.5	—	—	0.03 Max	1.0 Max	8.0	N 0.25-0.50
AISI Type 302	9.0	Balance	18.0	—	—	0.15 Max	1.0 Max	2.0 Max	
AISI Type 304	9.5	Balance	18.5	—	—	0.08 Max	1.0 Max	1.5	
AISI Type 304 L	10.0	Balance	18.5	—	—	0.03 Max	1.0 Max	1.3	
AISI Type 304 H	9.5	Balance	19.0	—	—	0.04 to 0.10	1.0 Max	2.0 Max	
AISI Type 309	13.5	Balance	23.0	—	—	0.20 Max	1.0 Max	2.0 Max	
AISI Type 310	20.0	Balance	25.0	—	—	0.25 Max	1.0 Max	2.0 Max	
AISI Type 316	13.0	Balance	17.0	2.25	—	0.08 Max	1.0 Max	1.7	
AISI Type 316L	13.0	Balance	17.0	2.25	—	0.03 Max	1.0 Max	1.8	
AISI Type 317	14.0	Balance	19.0	3.25	—	0.08 Max	1.0 Max	2.0 Max	
AISI Type 317L	14.0	Balance	19.0	3.25	—	0.03 Max	1.0 Max	2.0 Max	
AISI Type 321	11.0	Balance	18.0	—	—	0.08 Max	1.0 Max	2.0 Max	Ti 5XC Min
AISI Type 347	11.0	Balance	18.0	—	—	0.06 Max	1.0 Max	2.0 Max	Cb + Ta 1 OXC Min
NITRONIC alloy 32	1.5	Balance	18.0	—	—	0.15 Max	1.0 Max	12.5	N 0.20-0.45
NITRONIC alloy 33	3.0	Balance	18.0	—	—	0.08 Max	1.0 Max	13.0	N 0.20-0.40
NITRONIC alloy 50	12.5	Balance	22.0	2.25	—	0.06 Max	1.0 Max	5.0	N 0.20-0.40, Cb & V 0.10-0.30
NITRONIC alloy 60	8.5	Balance	17.0	—	—	0.10 Max	4.0	8.0	N0.08-0.18
Stainless Steels—Duplex and Precipitation Hardening									
AISI Type 329	4.5	Balance	27.5	1.5	—	0.10 Max	1.0 Max	2.0 Max	
FERRALUM	5.5	Balance	25.0	3.5	3.0	0.06	1.0 Max	1.0 Max	
UNS S15700	7.0	Balance	15.0	2.5	—	0.09 Max	1.0 Max	1.0 Max	Al 1.1
UNS S17400	4.0	Balance	16.5	—	4.0	0.07 Max	1.0 Max	1.0 Max	Cb + Ta 0.3
UNS S17700	7.0	Balance	17.0	—	—	0.09 Max	1.0 Max	1.0 Max	Al 1.1
UNS S35000	4.0	Balance	17.0	3.0	—	0.08 Max	1.0 Max	1.0 Max	N 0.1
UNS S45000	6.0	Balance	15.0	0.75	1.5	0.05 Max	1.0 Max	1.0 Max	Cb 8XC Min
Iron-Base Nickel-Chromium Molybdenum Alloys									
HASTELLOY alloy M-532	26.0	42.0	22.0	5.0	—	0.05 Max	1.0 Max	2.5 Max	Ti 4XC Min
JESSOP alloy JS-700	25.0	46.0	21.0	4.5	—	0.03	0.5	1.7	Cb 0.30
JESSOP alloy JS-777	25.0	44.0	21.0	4.5	2.2	0.04 Max	1.0 Max	2.0 Max	Cb 8XC Min
Alloy 904L	25.5	45.0	21.0	4.7	1.5	0.02	1.0 Max	2.0 Max	
Iron-Base Nickel-Chromium-Copper-Molybdenum Alloys									
CARPENTER alloy 20Cb ¹	29.0	43.0	20.0	2.0 Min	3.0 Min	0.07 Max	1.0	0.8	Cb 0.7
CARPENTER alloy 20Cb-3	34.0	39.0	20.0	2.5	3.3	0.07 Max	0.6	0.8	Cb + Ta 0.6
CARPENTER alloy 20Mo-6	33.0	33.0	24.0	5.7	3.2	0.025 Max	0.4	0.4	Cb 0.2
Nickel-Base Chromium-Iron Molybdenum-Copper Alloys									
INCOLOY alloy 825	42.0	30.0	21.5	3.0	2.2	0.03	0.02	0.05	Al 0.1, Ti 0.9
HASTELLOY alloy G	45.0	19.5	22.2	6.5	2.0	0.03	0.35	1.3	W 0.5, Cb + Ta 2.12
HASTELLOY alloy G-3	44.0	19.5	22.2	7.0	1.9	0.015 Max	0.4	0.8	Cb + Ta 0.3 W 1.5 Max, Co 5.0 Max
Nickel-Copper Alloys									
MONEL alloy 400	66.5	1.2	—	—	31.5	0.2	0.2	1.0	
MONEL alloy K-500	65.0	1.0	—	—	29.5	0.1	0.2	0.8	Al 2.7, Ti 0.6
Nickel-Base Molybdenum									
Chromium-Iron Alloys									
HASTELLOY alloy C ²	54.0	5.0	15.5	16.0	—	0.08 Max	1.0 Max	1.0 Max	Co 2.5 Max, W 4.0, V 0.4 Max
HASTELLOY alloy C-276	54.0	5.0	15.5	16.0	—	0.02 Max	0.05 Max	1.0 Max	Co 2.5 Max, W 4.0, V 0.4 Max
HASTELLOY alloy C-4	61.0	3.0 Max	16.0	15.5	—	0.015 Max	0.08 Max	1.0 Max	Co 2.0 Max, Ti 0.7 Max
INCONEL alloy 625	61.0	5.0 Max	21.5	9.0	—	0.1 Max	0.5 Max	0.5 Max	Cb + Ta 3.6
Nickel-Base Molybdenum Alloys									
HASTELLOY alloy B ¹	61.0	5.0	1.0 Max	28.0	—	0.05 Max	1.0 Max	1.0 Max	Co 2.5 Max, V 0.3, P 0.025 Max, S 0.03 Max
HASTELLOY alloy B-2	67.0	2.0 Max	1.0 Max	28.0	—	0.02 Max	0.1 Max	1.0 Max	Cc 1.0 Max, P 0.04 Max, S 0.03 Max
Iron-Nickel-Chromium Alloys									
INCOLOY alloy 800	32.5	46.0	21.0	—	0.4	0.05	0.5	0.8	Al 0.4, Ti 0.4
INCOLOY alloy 804	41.0	25.4	29.5	—	0.2	0.05	0.4	0.8	Al 0.3, Ti 0.6
Nickel-Chromium Alloys									
INCONEL alloy 600	76.0	8.0	15.5	—	0.2	0.08	0.2	0.5	
INCONEL alloy 601	60.5	14.1	23.0	—	0.5	0.05	0.2	0.5	Al 1.4

APPENDIX (Continued)

5. Sulfuric Acid Specific Gravity of Aqueous Sulfuric Acid Solution:

AT $\frac{20^\circ}{4^\circ}$ C.

Be.	Sp. gr.	Per cent H ₂ SO ₄	G. per liter	Lbs. per cu. ft.	Lbs. per gal.	Be.	Sp. gr.	Percent H ₂ SO ₄	G. per liter	Lbs. per cu. ft.	Lbs. per gal.
0.7	1.0051	1	10.05	0.6275	0.0839	41.8	1.4049	51	716.5	44.73	5.979
1.7	1.0118	2	20.24	1.263	0.1689	42.5	1.4148	52	735.7	45.93	6.140
2.6	1.0184	3	30.55	1.907	0.2550	43.2	1.4248	53	755.1	47.14	6.302
3.5	1.0250	4	41.00	2.560	0.3422	44.0	1.4350	54	774.9	48.37	6.467
4.5	1.0317	5	51.59	3.220	0.4305	44.7	1.4453	55	794.9	49.62	6.634
5.4	1.0385	6	62.31	3.890	0.5200	45.4	1.4557	56	815.2	50.89	6.803
6.3	1.0453	7	73.17	4.568	0.6106	46.1	1.4662	57	835.7	52.17	6.974
7.2	1.0522	8	84.18	5.255	0.7025	46.8	1.4768	58	856.5	53.47	7.148
8.1	1.0591	9	95.32	5.950	0.7955	47.5	1.4875	59	877.6	54.79	7.324
9.0	1.0661	10	106.6	6.655	0.8897	48.2	1.4983	60	899.0	56.12	7.502
9.9	1.0731	11	118.0	7.369	0.9851	48.9	1.5091	61	920.6	57.47	7.682
10.8	1.0802	12	129.6	8.092	1.082	49.6	1.5200	62	942.4	58.83	7.865
11.7	1.0874	13	141.4	8.825	1.180	50.3	1.5310	63	964.5	60.21	8.049
12.5	1.0947	14	153.3	9.567	1.279	51.0	1.5421	64	986.9	61.61	8.236
13.4	1.1020	15	165.3	10.32	1.379	51.7	1.5533	65	1010	63.03	8.426
14.3	1.1094	16	177.5	11.08	1.481	52.3	1.5646	66	1033	64.46	8.618
15.2	1.1168	17	189.9	11.85	1.584	53.0	1.5760	67	1056	65.92	8.812
16.0	1.1243	18	202.4	12.63	1.689	53.7	1.5874	68	1079	67.39	9.008
16.9	1.1318	19	215.0	13.42	1.795	54.3	1.5989	69	1103	68.87	9.207
17.7	1.1394	20	227.9	14.23	1.902	55.0	1.6105	70	1127	70.38	9.408
18.6	1.1471	21	240.9	15.04	2.010	55.6	1.6221	71	1152	71.90	9.611
19.4	1.1548	22	254.1	15.86	2.120	56.3	1.6338	72	1176	73.44	9.817
20.3	1.1626	23	267.4	16.69	2.231	56.9	1.6456	73	1201	74.99	10.02
21.1	1.1704	24	280.9	17.54	2.344	57.5	1.6574	74	1226	76.57	10.24
21.9	1.1783	25	294.6	18.39	2.458	58.1	1.6692	75	1252	78.15	10.45
22.8	1.1862	26	308.4	19.25	2.574	58.7	1.6810	76	1278	79.75	10.66
23.6	1.1942	27	322.4	20.13	2.691	59.3	1.6927	77	1303	81.37	10.88
24.4	1.2023	28	336.6	21.02	2.809	59.9	1.7043	78	1329	82.99	11.09
25.2	1.2104	29	351.0	21.91	2.929	60.5	1.7158	79	1355	84.62	11.31
26.0	1.2185	30	365.6	22.82	3.051	61.1	1.7272	80	1382	86.26	11.53
26.8	1.2267	31	380.3	23.74	3.173	61.6	1.7383	81	1408	87.90	11.75
27.6	1.2349	32	395.2	24.67	3.298	62.1	1.7491	82	1434	89.54	11.97
28.4	1.2432	33	410.3	25.61	3.424	62.6	1.7594	83	1460	91.16	12.19
29.1	1.2515	34	425.5	26.56	3.551	63.0	1.7693	84	1486	92.78	12.40
29.9	1.2599	35	441.0	27.53	3.680	63.5	1.7786	85	1512	94.38	12.62
30.7	1.2684	36	456.6	28.51	3.811	63.9	1.7872	86	1537	95.95	12.83
31.4	1.2769	37	472.5	29.49	3.943	64.2	1.7951	87	1562	97.49	13.03
32.2	1.2855	38	488.5	30.49	4.077	64.5	1.8022	88	1586	99.01	13.23
33.0	1.2941	39	504.7	31.51	4.212	64.8	1.8087	89	1610	100.5	13.42
33.7	1.3028	40	521.1	32.53	4.349	65.1	1.8144	90	1633	101.9	13.63
34.5	1.3116	41	537.8	33.57	4.488	65.3	1.8195	91	1656	103.4	13.82
35.2	1.3205	42	554.6	34.62	4.628	65.5	1.8240	92	1678	104.8	14.00
35.9	1.3294	43	571.6	35.69	4.770	65.7	1.8279	93	1700	106.1	14.19
36.7	1.3384	44	588.9	36.76	4.914	65.8	1.8312	94	1721	107.5	14.36
37.4	1.3476	45	606.4	37.86	5.061	65.9	1.8337	95	1742	108.7	14.54
38.1	1.3569	46	624.2	38.97	5.209	66.0	1.8355	96	1762	110.0	14.70
38.9	1.3663	47	642.2	40.09	5.359	66.0	1.8364	97	1781	111.2	14.87
39.6	1.3758	48	660.4	41.23	5.511	66.0	1.8361	98	1799	112.3	15.02
40.3	1.3854	49	678.8	42.38	5.665	65.9	1.8342	99	1816	113.4	15.15
41.1	1.3951	50	697.6	43.55	5.821	65.8	1.8305	100	1831	114.3	15.28

APPENDIX (Continued)

6. Density and Composition of Fuming Sulfuric Acid

Actual H ₂ SO ₄ %	Specific gravity	Equiv. H ₂ SO ₄ %	Weight, lb./cu. ft.	Weight, lb. per U.S. gal.	Comb. H ₂ O, %	Free SO ₃ , %	Total SO ₃ , %	SO ₃ , lb./cu. ft.
100	1.839	100.00	114.70	15.33	18.37	0	81.63	93.63
99	1.845	100.22	115.07	15.38	18.19	1	81.81	94.14
98	1.851	100.45	115.33	15.41	18.00	2	82.00	94.57
97	1.855	100.67	115.70	15.46	17.82	3	82.13	95.08
96	1.858	100.89	115.88	15.49	17.64	4	82.36	95.44
95	1.862	101.13	116.13	15.52	17.45	5	82.55	95.87
94	1.865	101.35	116.32	15.55	17.27	6	82.73	96.23
93	1.869	101.58	116.57	15.58	17.08	7	82.92	96.66
92	1.873	101.80	116.82	15.61	16.90	8	83.10	97.12
91	1.877	102.02	117.07	15.64	16.72	9	83.28	97.50
90	1.880	102.25	117.26	15.67	16.57	10	83.47	97.88
89	1.884	102.47	117.51	15.70	16.35	11	83.65	98.30
88	1.887	102.71	117.69	15.73	16.17	12	83.83	98.66
87	1.891	102.92	117.94	15.76	15.98	13	84.02	99.09
86	1.895	103.15	118.19	15.79	15.80	14	84.20	99.52
85	1.899	103.38	118.44	15.82	15.61	15	84.39	99.95
84	1.902	103.60	118.63	15.86	15.43	16	84.57	100.33
83	1.905	103.82	118.81	15.89	15.25	17	84.75	100.69
82	1.909	104.05	119.06	15.92	15.06	18	84.94	101.13
81	1.911	104.28	119.28	15.95	14.88	19	85.12	101.45
80	1.915	104.50	119.50	15.98	14.70	20	85.30	101.93
79	1.920	104.73	119.75	16.01	14.51	21	85.49	102.37
78	1.923	104.95	119.94	16.04	14.33	22	85.67	102.75
77	1.927	105.18	120.19	16.07	14.14	23	85.86	103.20
76	1.931	105.40	120.44	16.10	13.96	24	86.04	103.63
75	1.934	105.62	120.62	16.12	13.78	25	86.22	104.00
74	1.939	105.85	120.94	16.16	13.59	26	86.41	104.50
73	1.943	106.08	121.18	16.19	13.41	27	86.59	104.93
72	1.946	106.29	121.37	16.22	13.28	28	86.72	105.31
71	1.949	106.53	121.56	16.25	13.04	29	86.96	105.71
70	1.952	106.75	121.75	16.28	12.86	30	87.14	106.09
69	1.955	106.97	121.93	16.30	12.68	31	87.32	106.47
68	1.958	107.20	122.12	16.33	12.49	32	87.51	106.87
67	1.961	107.42	122.31	16.35	12.31	33	87.69	107.25
66	1.965	107.65	122.56	16.38	12.12	34	87.88	107.71
65	1.968	107.87	122.74	16.40	11.94	35	88.06	108.08
64	1.972	108.10	122.99	16.43	11.76	36	88.24	108.53
63	1.976	108.33	123.24	16.46	11.57	37	88.43	108.98
62	1.979	108.55	123.43	16.50	11.39	38	88.61	109.37
61	1.981	108.77	123.55	16.52	11.21	39	88.79	109.70
60	1.983	109.00	123.74	16.54	11.02	40	88.98	110.10
59	1.985	109.22	123.80	16.55	10.84	41	89.16	110.38
58	1.987	109.45	123.93	16.56	10.65	42	89.35	110.83
57	1.989	109.68	124.05	16.58	10.47	43	89.53	111.06
56	1.991	109.90	124.18	16.60	10.29	44	89.71	111.40
55	1.993	110.13	124.30	16.62	10.10	45	89.90	111.75
50	2.001	111.25	124.80	16.68	9.18	50	90.72	113.34
40	2.102	113.50	131.10	17.53	7.35	60	92.65	121.46
30	1.982	115.75	123.62	16.50	5.51	70	94.49	116.81
20	1.949	118.00	121.56	16.25	3.67	80	96.33	117.10
10	1.911	120.25	119.19	15.92	1.84	90	98.16	117.00
0	1.857	122.50	115.83	15.50	0.00	100	100.00	115.83

7. Trademarks

Trademarks

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