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# **Alloy selection for service in sulphuric acid**

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A GUIDE TO THE USE OF  
NICKEL-CONTAINING ALLOYS  
N° 10057

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A GUIDE TO THE USE OF NICKEL-CONTAINING ALLOYS

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# Alloy selection for service in sulphuric acid

## Introduction

Commercial concentrated sulphuric acid is one of the most important heavy industrial chemicals. Worldwide consumption is more than 200m tonnes/year. It is sold primarily as 93%, 96% and 98.5% H<sub>2</sub>SO<sub>4</sub>, although the range of “concentrated sulphuric acid” nominally covers the range from 70% to 99+%. Lower acidities, in the range 25-70%, are considered to be “intermediate”, or “dilute” when <25%. Corrosion characteristics of these three ranges of concentration are quite different, only the concentrated product exhibiting the nature of a strongly oxidising acid.

This publication describes the behaviour of nickel-containing alloys and the specific nature of their reactivity with both high and low concentrations, considered separately. The behaviour of other metals commonly used in the manufacture or handling of this acid are also discussed. *Table 1* lists the main nickel-containing alloys and their UNS number considered in this introductory publication. It is not possible to mention all alloys used in sulphuric acid here. A more detailed discussion of all aspects of materials selection for sulphuric acid is available elsewhere.<sup>1</sup>

**Table 1 Nominal composition of nickel-containing alloys most are used in sulphuric acid systems**

		Nominal composition, %						ASTM Spec. <sup>b</sup>	
Alloy	UNS number <sup>a</sup>	Ni	C	Cr	Mo	Cu	Fe	Plate	Seamless tube and pipe
<b>Group I – Commercially pure (C.P.) nickel and nickel-copper alloys</b>									
200	N02200	99.5	0.08	-	-	-	0.2	B162	B161
400	N04400	66.5	0.2	-	-	-	1.2	B127	B165
<b>Group II - Chromium-containing nickel alloys</b>									
600	N06600	76	0.08	15.5	-	-	8	B168	B167
825	N08825	42	0.03	21.5	3	2.25	30	B424	B163
625	N06625	61	0.05	21.5	9	-	2.5	B443	B444
31	N08031	31	0.02	27	6.5	1.2	15	B582	B622
G-30	N06030	42	0.01	29.5	5	1.8	15	B582	B622
C-22/622	N06022	56	0.01	21.5	13.5	-	4	B575	B622
C-4	N06455	66	0.01	16	15	-	5.5	B575	B622
C-276	N10276	58	0.01	15.5	16	-	5.5	B575	B622
59	N06059	60	0.01	23	15.5	-	0.7	B575	B622
686	N06686	56	0.01	21	16	-	2.5	B575	B622
C-2000	N06200	57	0.01	23	16	-	1.5	B575	B622
<b>Group III - Nickel-molybdenum alloys</b>									
B-2	N10665	70.5	0.01		28	-	-	B333	B622
B-3	N10675	63	0.005	2	30	-	2	B333	B622
B-4	N10629	66	0.01	1	28	-	4	B333	B622

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		Nominal composition, %						ASTM Spec. <sup>b</sup>	
Alloy	UNS number <sup>a</sup>	Ni	C	Cr	Mo	Cu	Fe	Plate	Seamless tube and pipe
<b>Austenitic stainless steels</b>									
304	S30400	8	0.04	18	-	-	Bal	A240	A312
304L	S30403	8	0.02	18	-	-	Bal	A240	A312
316	S31600	10	0.04	16.5	2.1	-	Bal	A240	A312
316L	S31603	10	0.02	16.5	2.1	-	Bal	A240	A312
CF8M	J92900	10	0.04	19	2.3	-	Bal	-	-
310	S31000	21	0.05	25	-	-	Bal	A240	A312
20	N08020	33	0.02	19.5	2.2	3.2	Bal	A240	B729
CN7M	N08007	29	0.04	20	2.3	3.5	Bal	-	-
904L	N08904	24	0.01	20	4.5	1.5	Bal	A240	A312
6%Mo <sup>c</sup>	S31254	18	0.01	20	6.2	0.7	Bal	A240	A312
6%Mo <sup>c</sup>	N08367	24	0.01	21	6.2	-	Bal	A240	A312
6%Mo <sup>c</sup>	N08926	25	0.01	20.5	6.2	1	Bal	A240	A312
7%Mo	S32654	22	0.01	24	7.3	0.5	Bal	A240	A312
4% Si <sup>d</sup>	S30600	15	0.01	17.5	0.1	0.3	Bal	A240	A312
5% Si <sup>d</sup>	S30601	17.5	0.01	17.5	0.1	0.2	Bal	A240	A312
5% Si <sup>d</sup>	S32615	20	0.04	18	1	2	Bal	A240	A312
6% Si <sup>d</sup>	S38815	15	0.02	14	1	1	Bal	A240	A312
<b>Duplex stainless steel</b>									
2205	S32205	5	0.02	22	3.2	-	Bal	A240	A790
255	S32550	5.5	0.02	25	3.5	2	Bal	A240	A790
7-Mo Plus	S32950	4	0.03	27.5	2	-	Bal	A240	A790
CD4MCu	J93370	5	0.2	25	2	3	Bal	-	-

a - UNS numbers beginning with an "N" indicate a nickel alloy, but the definition of a nickel alloy is different than that used by ASTM.

b - in ASTM specifications, most nickel alloys fall into the "B" specifications. However, due to a redefinition of a nickel alloy, a few alloys such as 800 and 20 are being reclassified as stainless steels, and will be included in the "A" specifications. That work is still in progress.

c - the 6%Mo alloys are a series of stainless steels, many of which are proprietary, all with roughly 6%Mo content and roughly equivalent in performance.

d - the austenitic stainless steels with high Si are proprietary and were developed from nitric acid grades for use in strong sulphuric acid.

The corrosion behaviour of alloys suitable for equipment used in the manufacture of concentrated sulphuric acid and in its storage and handling is described. This is followed by similar information on materials in contact with dilute and intermediate strength acid and an introduction to the effects of common contaminants.

This publication does not cover concentrations in excess of 99% H<sub>2</sub>SO<sub>4</sub> such as anhydrous, fuming sulphuric acid (i.e., "oleum") or sulphuric acid mixed with other acids, such as nitric acid. A more complete treatment of the use of materials in contact with sulphuric acid of all strengths, in mixtures and in the presence of contaminants can be found elsewhere.<sup>1</sup>

## Sulphuric acid manufacture

The first step in the manufacturing process is the production of sulphur dioxide ( $\text{SO}_2$ ) by oxidation of an available feedstock. *Figure 1*, a simplified flow diagram, presents three alternative routes for the generation of  $\text{SO}_2$ . The first of these is combustion of sulphur; the second is recovery of  $\text{SO}_2$  from metallurgical processes, such as roasting of pyrites and other sulphide ores. The third alternative route is regeneration from spent acid. Because such acid tends to be contaminated, this process sequence customarily begins with thermal degeneration, followed by scrubbing of the resultant sulphur dioxide prior to cooling and drying.

A catalytic converter that is used to form sulphur trioxide ( $\text{SO}_3$ ) from the  $\text{SO}_2$  represents the most important part of the

sulphuric acid plant.  $\text{SO}_2$  at about  $425^\circ\text{C}$  ( $800^\circ\text{F}$ ) reacts with excess air in the presence of vanadium pentoxide catalyst during several passes through the catalyst beds inside the converter. Since the reaction is highly exothermic, the gases are passed through gas to gas heat exchangers after each pass through the catalyst bed. The  $\text{SO}_3$  (the anhydride of sulphuric acid) then enters the absorbing towers where it reacts to form sulphuric acid. About 35% of the heat generated during the process serves to raise the temperature of the sulphuric acid produced. It has been found that, in the temperature range  $155\text{--}190^\circ\text{C}$  ( $310\text{--}370^\circ\text{F}$ ) relatively low corrosion rates prevail for stainless steels such as Type 304 (S30400) and Type 310 (S31000), for duplex stainless steels such as Alloy 2205 (S32205) and for the high-silicon modified 5.5% Si stainless steels.

**Figure 1** Diagram of sulphuric acid production showing three possible feedstocks

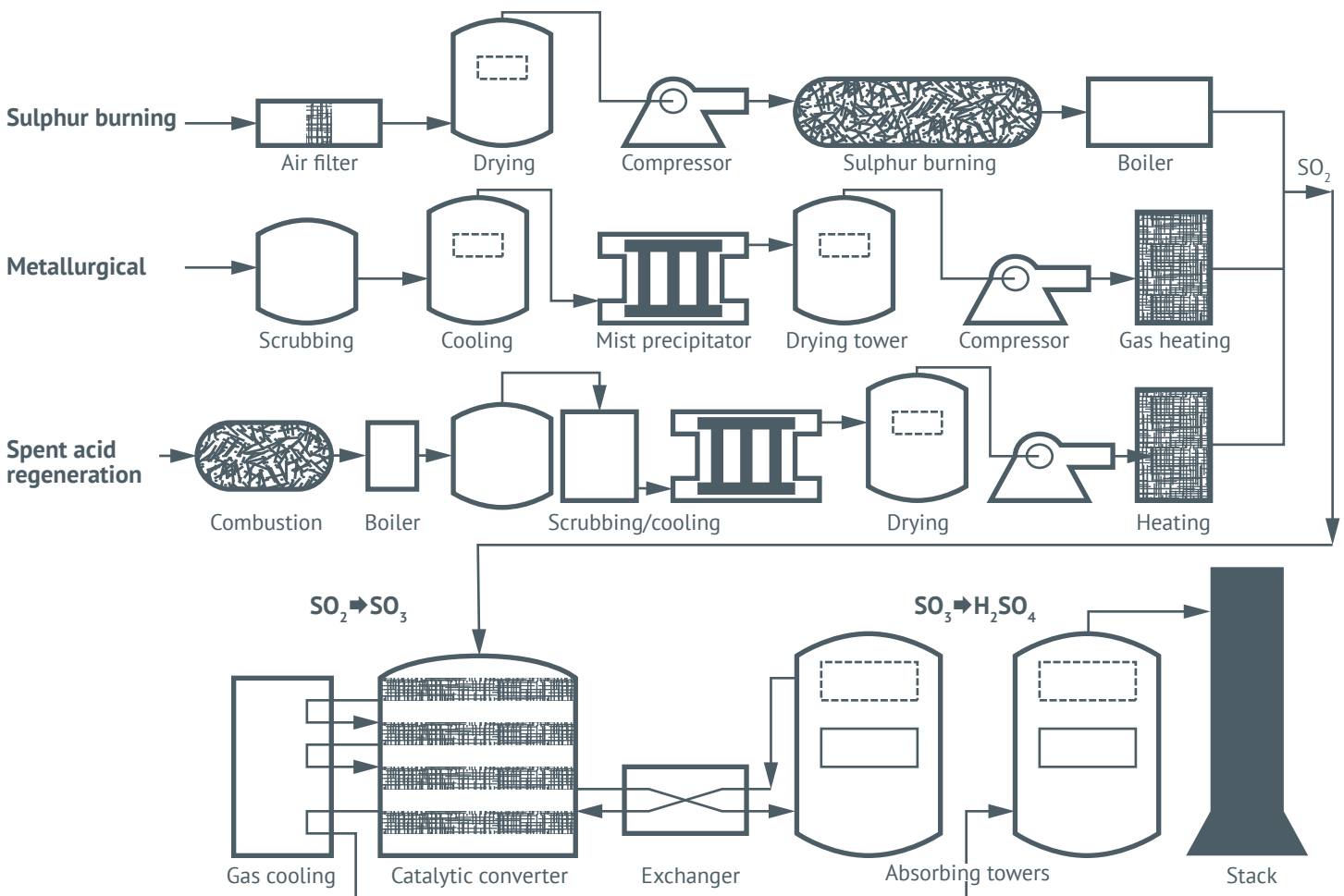




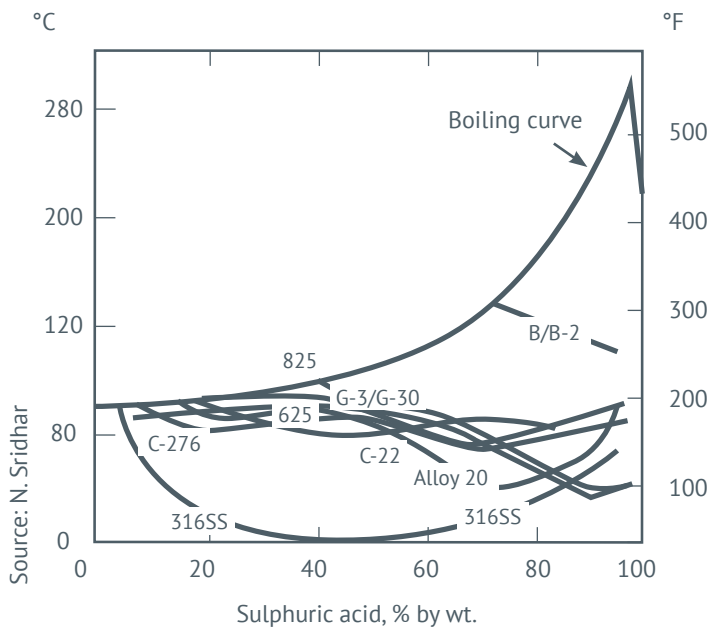
Figure 2 shows the iso-corrosion curves for some of the nickel-containing alloys.

Stainless steel has replaced carbon steel and cast iron as the preferred material of construction for converters and acid coolers. New alloys and the use of anodic protection have increased resistance to corrosion by hot acid. In general, Type 304L (S30403) is specified for the shell and internals of the converter. Drying towers and acid pump tanks are made from high silicon austenitic stainless steel as an alternative to the traditional brick-lined carbon steel which is still in use. Acid piping and coolers are made from high silicon stainless steel, or from anodically protected Type 316 (S31600) stainless steel. Silicon-containing austenitic stainless steels work well at acid temperatures higher than those for which anodically protected Type 316 is recommended.

## CORROSION BEHAVIOUR – CONCENTRATED SULPHURIC ACID

NACE standard practice SP0391 provides details of the materials of construction to be used in the storage and handling of concentrated sulphuric acid at ambient temperature.<sup>2</sup> This standard also addresses some of the engineering practices that ensure trouble-free operation.

**Figure 2 Iso-corrosion curves for some stainless steels and nickel alloys in reagent grade sulphuric acid – 0.5 mm/y (20 mpy)**



Source: N. Sridhar

Alloy selection for service in sulphuric acid

### Carbon steels

Cold concentrated  $H_2SO_4$  is only slightly corrosive to steel and cast iron, due to the rapid formation of a ferrous sulphate ( $FeSO_4$ ) film. However, even moderate flow rates, ( $>0.6$  m/s;  $>2$  ft/s) or fluid impingement, can cause the removal of the protective film and allow corrosion to proceed. Dilution also tends to solubilise  $FeSO_4$ . Elevated temperatures greater than about  $40^\circ C$  ( $105^\circ F$ ) will also destroy the film and permit corrosion. In the case of any of these changed conditions, higher alloys would typically be substituted to cope with the now corrosive conditions. Also, the use of carbon steel may be limited by the iron specification in the product acid.

### Cast irons

Grey cast iron will resist higher velocities (up to around  $1.8$  m/s,  $6$  ft/s) than steel because of a locking effect of the graphite flakes on the ferrous sulphate. Ductile (nodular) cast iron is less effective. The austenitic high-nickel cast irons offer no significant advantage but 14% silicon cast iron has excellent resistance up to 100% acid at the boiling point, with corrosion rates less than  $0.12$  mm/y ( $5$  mpy) over the range of concentrations. The high-silicon cast iron resistance is due to the formation of a silica-rich film, although it will not tolerate free  $SO_3$ .

### Stainless steels

Although martensitic and ferritic stainless steels find no application, conventional austenitic grades are routinely employed in strong  $H_2SO_4$ , e.g., for nozzle liners, piping, etc., where flow conditions render carbon steel unsuitable. The resistance of the 18-8 grades can be enhanced by anodic protection, e.g., for Type 316L (S31603) acid coolers.

Types 304 and 304L and the molybdenum-bearing grades, Types 316 and 316L, are generally resistant to strong sulphuric acid at ambient temperature and, unlike carbon steel and cast iron, resist erosion-corrosion. Corrosion resistance of these grades is good up to about  $6$  m/s ( $20$  ft/s) in the absence of abrasive particles (although normal design would be limited to about  $2-3$  m/s [ $6.5-10$  ft/s]).

Unprotected Type 316 is somewhat less resistant than Type 304 in hot acid above about 93% because of the ease of oxidation of the molybdenum component. Table 2 provides typical corrosion rates in 99% sulphuric acid at a

temperature of 105-115 °C (220-240 °F) in an absorption tower environment. At flow rates of 1.5 m/s (5 ft/s) or more, the corrosion rate for Type 316 increases to more than 7 times that of the molybdenum-free grade, Type 304. The standard cast form of Type 316, CF8M (S92900) is appropriate for shut-off valves.

Table 2 Corrosion rates in absorption tower environment with 99% sulphuric acid at 105-115 °C (220-240 °F).		
Alloy	Corrosion Rate	
	mm/y	mpy
304	0.02	0.8
316	0.06	2.2
310	0.01	0.4
5.5% Si	0.005	0.2
904L	0.17	6.8
20Cb-3	0.08	3.2
C-276	0.32	12.6
B-2	2.3	91

High silicon austenitic stainless steel, UNS S30600, containing 4% Si was originally developed for use in concentrated nitric acid. More recently alloys of approximately 18% Cr, 16% Ni, 5-6% Si have been produced for use in concentrated sulphuric acid. Alloys with nominally 5% Si, such as UNS S30601 and S32615 and a 6% Si alloy, UNS S38815 are used in hot, concentrated acid and compete with anodically-protected 300 stainless steels for use in towers, coolers and piping.

### Anodic Protection

Anodic protection is effective for Type 304, 316 and other stainless steels and can extend the temperature of application in all strong acid solutions. It can ensure that the stainless steel remains in a stable, passive condition, effectively non-corroding, at temperatures and acid strengths at which it would otherwise be in an active or active/passive corroding condition. The electrical-current requirements to apply anodic protection increase as acid strength decreases or as acid temperature increases.

In laboratory tests, a rate of 0.75 mm/y (29 mpy) for freely corroding Type 316 in 93% acid (plus 4 ppm iron and 800 ppm SO<sub>2</sub>) at 70 °C (158 °F) was reduced to less than 0.05 mm/y (2 mpy) by anodic protection.<sup>3</sup> At 100 °C (212 °F), the corrosion

rate is reduced from about 5 mm/y (200 mpy) to less than 0.05 mm/y (2 mpy).<sup>2</sup> Type 316L shell and tube coolers have been routinely anodically protected. The limiting temperature for unprotected coolers is about 75 °C (167 °F) while anodically protected coolers are used as high as 125 °C (257 °F).<sup>4</sup>

### Specialty alloys

A number of special alloys have been developed, mostly as casting alloys but some are available in wrought form. They were largely developed for concentrated acid contaminated with nitrates or sulphides but also offer improved resistance with increased temperatures and/or in the case of erosion-corrosion or abrasion.

One of the original alloys of this type was designated "alloy 20", which now has a number of modern variants, e.g. alloy 20Cb-3 (N08020). These alloys are used in concentrated sulphuric acid primarily to resist velocity or turbulence. The cast form, CN7M (N08807) is used for throttling valves and pumps to withstand turbulent flow and erosion. Titanium-stabilised Alloy 825 (N08825) has substantially the same resistance as Alloy 20 in concentrated acid. Other variants such as Alloy 904L (N08904) resist concentrated sulphuric acid to about 50 °C (122 °F).

There are a number of duplex grades such as 7-Mo Plus (S32950) and Alloy 255 (S32550) that have good resistance to concentrated sulphuric acid, e.g. in 98% acid up to about 150 °C (300 °F). Duplex castings such as CD4MCu (J93370) are also resistant to turbulent concentrated acid.

### Nickel and its alloys

Most chromium-free, high-nickel alloys (e.g., Alloys of the 200, 400 and 500 series) find no application in this oxidising acid.

The nickel-based alloy with the best resistance is the Ni-Mo Alloy B-2 (N10665) and derivatives thereof. This type of alloy is resistant to 70% acid up to the atmospheric boiling point and 99+% H<sub>2</sub>SO<sub>4</sub> to about 120 °C (250 °F) in the absence of oxidising contaminants. The acid must be a pure grade, however, such as "water-white" or "electrolytic", because traces of ferric ion contamination or of nitric acid formed in the air oxidation of feedstocks will attack these chromium-free grades.

The Ni-Cr-Mo grades, based on the original Alloy C and typified by Type C-276 (N10276) are resistant to about 90 °C (195 °F) in the 93-98% range (with <40 ppm chloride) and lesser concentrations above 70% to about 50 °C (120 °F).

### Other metals

Titanium and zirconium and their alloys are not resistant to concentrated acid.

In the absence of fluoride contamination, tantalum has a reasonable resistance in concentrated acid. It is, however, subject to initially high corrosion rates and very susceptible to absorbing hydrogen with the attendant embrittlement.

Niobium is resistant to concentrated acid under oxidising conditions, e.g. if oxidising ions are present. It is also resistant at all concentrations up to 95% at room temperature. In concentrated acid, niobium can embrittle.

## CORROSION BEHAVIOUR – DILUTE AND INTERMEDIATE CONCENTRATIONS

Pure dilute sulphuric acid is rarely encountered, it nearly always contains contaminants of various types and concentrations. From 5% to 25%,  $H_2SO_4$  is a classical reducing acid, its maximum hydrogen ion (proton) content occurring at about 25 wt% concentration. From 25% to 70%, the acid gains in oxidising capacity. Over the entire range corrosion characteristics are, however, determined almost entirely by the nature and concentration of the contaminants present.

The various alloys interact with sulphuric acid in a complex manner. A single process may involve not only a wide range of sulphuric acid concentrations but also the presence of such contaminants as ferric and cupric ions, nitrates, chlorides, ammonia, sulphur dioxide and metallic oxides. These variables exert significant influence not only on the oxidising capacity of sulphuric acid solutions but also on the performance of stainless steels and nickel-bearing alloys in contact with them.

### Carbon steels and cast irons

With the exception of the high-silicon cast irons, all conventional steels and irons are non-resistant to the full range of weak acid.

### Stainless steels

Martensitic and ferritic grades have almost no application in dilute acid.

At moderately elevated temperatures, austenitic grades are limited first by concentration. For example, “breakaway corrosion” (i.e., loss of passivation) with a corrosion rate  $>0.12\text{mm/y}$  ( $>5\text{ mpy}$ ) occurs in 0.25%  $H_2SO_4$  well below 60 °C (140 °F) for molybdenum-free grades, such as Type 304, but about 90 °C (190 °F) in 0.5% acid for Type 316.

Under aerated conditions, however, Type 304 will resist 15% acid at ambient temperatures. Type 316 will resist 10% acid under de-aerated conditions, and 30% acid under aerated conditions at room temperature. Corrosion rates under these conditions can be drastically reduced by the presence of oxidising contaminants such as cupric, ferric or nitrate ions (which enhance passivation) while corrosion is initiated or increased by reducing species such as chlorides or fluorides.

Either stabilised or low-carbon grades must always be used for welded construction because acid in these concentration ranges is specific for intergranular corrosion of sensitised stainless steel.

Certain duplex grades such as 7-Mo Plus (S32950) can resist 5% acid to the boiling point and up to 40% at ambient temperatures. The ferrite phase in duplex alloys, in general, is potentially subject to selective attack in these weak concentrations.

Superaustenitic grades of 4% Mo (e.g. Alloy 904L), 6% Mo (e.g. UNS S31254, UNS N08367) and the copper-bearing Alloy 20 offer gradually increasing resistance to intermediate concentrations. In 5% acid at 80 °C (176 °F) both Alloy 904L and Alloy 20 showed  $<0.025\text{ mm/y}$  ( $<1\text{ mpy}$ ) in one test, in another Alloy 20 corroded at  $2.3\text{ mm/y}$  (90 mpy) suggesting that these alloys are borderline at this temperature.<sup>1</sup>

In the presence of severe chloride contamination, even more highly alloyed grades such as Alloy 31 (N08031) or 7% Mo alloys such as UNS S32654 are now available.

### Nickel and its alloys

Nickel-copper alloys such as Alloy 400 (N04400) can resist boiling 5% sulphuric acid (which rapidly loses any dissolved



oxygen) but very high rates of attack are encountered below the boiling point. At and above 25%, where the acid becomes increasingly oxidising in nature, both Alloy 400 and Alloy 200 (N02200) show increasing corrosion rates.

The Ni-Mo alloys (e.g., Alloy B-2) show good resistance, even in the presence of dissolved oxygen, to about 50 °C (122 °F) and again at the boiling point where the oxygen is removed by ebullition. Even traces of oxidising contaminants will, however, cause very severe attack.

Of the Cr-bearing alloys, Alloy 600 (N06600) has no practical application. The Ni-Cr-Mo grades, Alloy C types, can be useful. Alloy C-276 for example, corrodes at less than 0.12 mm/y (5 mpy) up to 75 °C (165 °F) in 25% sulphuric acid and up to 50 °C (122 °F) at up to 70%. In practical applications, trace amounts of oxidising ions can greatly enhance resistance.

### **Copper and its alloys**

With rare exceptions in which the acid is kept in a reducing condition, copper-based alloys cannot be used in weak sulphuric acid. The corrosion is autocatalytic, the accretion of dissolved copper providing increasing levels of cupric ions which are themselves oxidising contaminants.

### **Lead**

Lead, often in the form of lining on a steel vessel, used to be the standard material for handling weak and intermediate strength acid. Resistance is due to the formation of insoluble lead sulphate films, which are susceptible to mechanical damage, erosion, abrasion, etc., with attendant higher rates of attack. Unless the protective film is disturbed by mechanical effects, corrosion rates are below 0.12 mm/y (5 mpy) up to 50% acid at the atmospheric boiling point and to about 120 °C (250 °F) in the 50-70% range.

In many modern industrialised countries, lead has fallen into disuse because of poor mechanical properties (susceptibility to 'static fatigue' in free-standing or loose-lined construction) the severe shortage of skilled craftsmen ('lead burners') and because of health and toxicity considerations. Nevertheless, it is still offered as an automatically applied lining (e.g., in Germany). In other parts of the world it is still being used where its corrosion resistance is deemed acceptable.

### **Other metals**

Titanium and its alloys are quite readily attacked by dilute mineral acids, in the absence of oxidising contaminants and are not usually employed.

Zirconium will nominally resist up to 70% acid at the boiling point, above which catastrophic "breakaway" corrosion occurs. Welds may, however, suffer preferential attack as low as 50-60 °C (140 °F). Contaminants in chemical processes can lower the critical concentration closer to 60% and, in the presence of ferric or cupric ions, pyrophoric corrosion products (a potential hazard for fire or explosion) may form.

In the absence of fluoride contamination, tantalum resists 0-70% sulphuric acid to the atmospheric boiling point. In fact, reboilers for 70% acid in concentrators are commonly fabricated from tantalum.

## **CORROSION BEHAVIOUR – EFFECT OF CONTAMINANTS**

Small amounts of contaminants, present in the nominally pure acid, can have a strong influence on the corrosion performance of many alloys.

### **Chloride ions**

Halides in sulphuric acid make it difficult to achieve and maintain passivity on stainless steels and higher nickel alloys. In 10M (approx. 64% acid) at room temperature pre-passivated Type 316 could remain passive indefinitely. In the presence of 5 ppm chlorides passivity is lost and active corrosion occurs. Chlorides increase attack on stainless steels in the passive state but have an inhibiting effect on them when they are actively corroding. If an oxidising agent, such as nitric acid, is present together with chlorides, pitting or crevice corrosion may occur and corrosion rates may increase.

### **Fluoride ions**

Contamination of sulphuric acid by fluoride ions is common and many materials are attacked by even small quantities of fluorides in acid solution. Fluoride contamination should be avoided if plant equipment contains glass, tantalum, zirconium or silicon-containing alloys. The 5% silicon-containing austenitic stainless steels now being used in strong acid applications rely on a silica-rich surface to resist acid attack and this protective film can be attacked by fluorides.

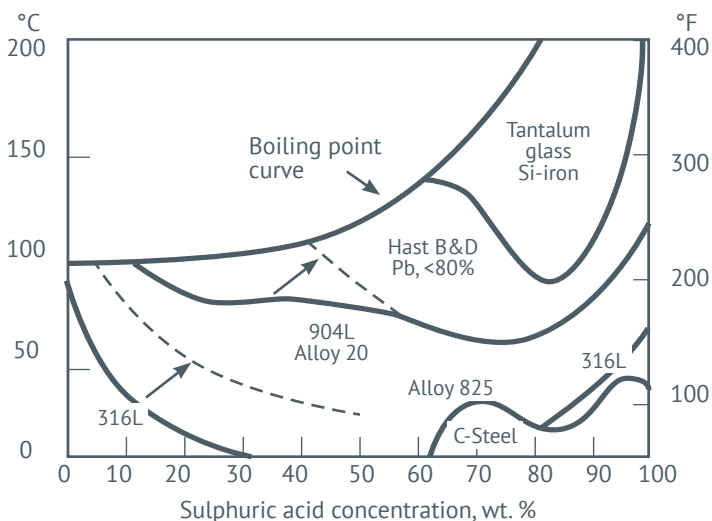
## Oxidising ions

The most common oxidant in strong sulphuric acid is nitric acid, formed from nitrogen in air during the manufacturing process or from recovery of nitration acids. Passivation of Type 304 begins in 70% acid at 60 °C (140 °F) when the nitric acid concentration is about 700 ppm (300 ppm for Type 316). When Type 304 is activated in anhydrous mixed acids above about 50 °C (122 °F), however, nitric acid additions increase corrosion. *Figure 3* shows the iso-corrosion data for selected alloys and the beneficial effects of the presence of oxidising metal salts.

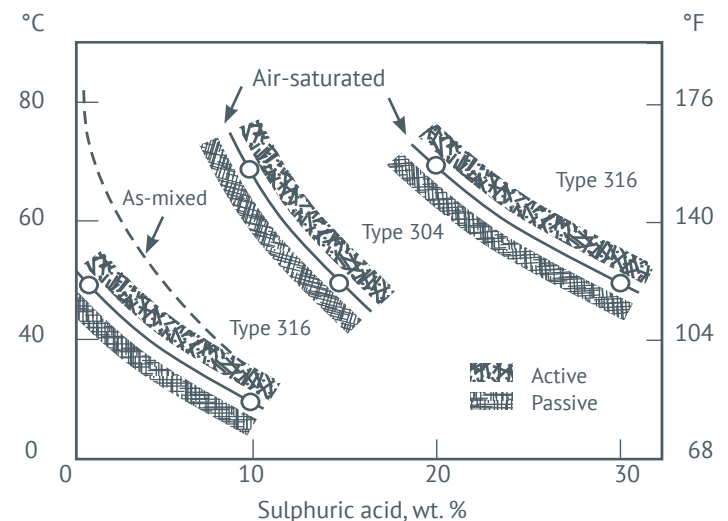
The presence of air in dilute sulphuric acid can have a similar beneficial effect by passivating stainless steels, *Figure 4*.

Other oxidising cations, such as ferric or cupric can drastically reduce corrosion in concentrated acid and even in less concentrated acid at elevated temperatures. It is, however, unwise to rely on passivation by oxidants to reduce corrosion, as crevices (in which an adequate concentration of inhibitor is difficult to maintain) are almost always present in equipment, and the oxidants may be inadvertently reduced, e.g. by organic contaminants.

**Figure 3** 0.5 mm/y (20 mpy) Iso-corrosion curves for selected alloys showing effect of oxidising salts (dotted lines)



**Figure 4** Active passive regions for types 304 and 316 stainless steel



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