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Alloy selection in wet-process phosphoric acid

A GUIDE TO THE USE OF
NICKEL-CONTAINING ALLOYS

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First edition by C.M. Schillmoller, 2nd edition update by Geir Moe with contribution by Sandra LeManchet

Alloy selection in wet-process phosphoric acid

Introduction

Phosphoric acid is a major industrial chemical. It follows sulfuric and nitric acids in importance and tonnage produced. Phosphoric acid is supplied commercially as merchant grade, technical grade, superphosphoric acid grade, and food grade. Merchant grade is 40–60% acid concentration and may contain chloride and fluoride ions. Technical grade is defined as >85% acid concentration. Superphosphoric acid is 105% acid concentration. Food grade is 75–85% acid concentration and contains <15 ppm chloride and <1 ppm fluoride.

Phosphoric acid is utilized in nearly every major industry. In the chemical industry it is used in the manufacture of phosphates. In the electronics industry it is used in the preparation of semiconductors and printed circuit boards. Pure phosphoric acid is used in the food industry as an acidulant in cola-type beverages and in jams and jellies. It

is used to remove mineral deposits from process equipment and boilers. Its major use is the production of fertilizer for agriculture and a mineral supplement in animal feed.

It is a moderately strong inorganic acid, that is stronger than acetic but weaker than sulfuric acid and hydrochloric acid. It may be produced directly by absorption of phosphorous pentoxide (P_2O_5) in water (in which case there are few contaminants) or as a contaminated product from the digestion of phosphate rock with sulfuric acid, which contains impurities, such as fluorides and chlorides that markedly increase its corrosivity. Oxidizing compounds, such as ferric and cupric salts, may also be present to influence corrosion.

Table 1 lists many alloys that may be considered for phosphoric acid service.

Table 1 Nominal composition of some alloys used in phosphoric acid systems

		Nominal composition, %							ASTM Spec. ^b	
Alloy	UNS number ^a	Ni	C	Cr	Mo	Cu	Fe	Other	Plate	Seamless tube and pipe
Chromium-containing nickel alloys										
825	N08825	42	0.03	21.5	3	2.25	30	0.9Ti	B424	B163
G-3	N06985	Bal	0.01	21.5	6.5	2	19	-	B582	B622
G-30	N06030	Bal	0.02	29	5	1.5	15	2.5W, 1Nb	B582	B622
G-35	N06035	Bal	0.02	33	8.1	0.1	1	-	B575	B622
690	N06690	59	0.02	28	-	-	9	-	B168	B167
625	N06625	61	0.05	21.5	6.5	1.2	15	3.6Nb	B582	B622
C276	N10276	58	0.01	15.5	16	-	5.5	3.6W	B575	B622
C4	N06455	66	0.01	16	16	-	5.5	-	B575	B622
C22/622	N06022	56	0.01	21.5	13.5	-	4	3W	B575	B622
C2000	N06200	57	0.01	23	16	1.6	1.5	-	B575	B622
686	N06686	56	0.01	21	16	-	2.5	3.5W	B575	B622

		Nominal composition, %							ASTM Spec. ^b	
Alloy	UNS number ^a	Ni	C	Cr	Mo	Cu	Fe	Other	Plate	Seamless tube and pipe
Austenitic stainless steels										
304L	S30403	8.1	0.02	18.1	-	-	Bal	-	A240	A312
CF8	J92600	8.1	0.04	18.1	-	-	Bal	-	-	-
316L	S31603	10.1	0.02	16.5	2.1	-	Bal	-	A240	A312
CF8M	J92900	10.1	0.04	19.1	2.3	-	Bal	-	-	-
317L	S31703	11.1	0.02	18.1	3.1	-	Bal	-	A240	A312
317LM	S31725	14.1	0.02	18.1	4.1	-	Bal	-	A240	A312
317LN	S31753	11.1	0.02	18.1	3.1	-	Bal	0.15N	A240	-
317LMN	S31726	14.7	0.02	17.5	4.1	-	Bal	0.15N	A240	A312
20	N08020	33	0.02	19.5	2.2	3.2	Bal	0.4Nb	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
28	N08028	31	0.01	27	3.5	1	Bal	-	B709	B668
	N08026	34	0.01	23	5.2	2.2	Bal	0.12N	B463	B729
6%Mo ^c	S31254	18	0.01	20	6.2	0.7	Bal	0.20N	A240	A312
6%Mo ^c	N08367	24	0.01	21	6.2	-	Bal	0.22N	A240	A312
6%Mo ^c	N08926	25	0.01	20.5	6.2	1	Bal	0.20N	A240	A312
31	N08031	31	0.02	27	6.2	1.2	Bal	0.20N	B625	B622
7%Mo	S31277	27	0.01	21.5	7	1	Bal	-	A240	A312
7%Mo	S32654	22	0.01	24	7.3	0.5	Bal	0.50N, 3.5Mn	A240	A312
Duplex stainless steels										
2202	S32202	22.5	0.02	22	0.3	-	Bal	0.21N, 1.3Mn	A240	A790
2205	S32205	5	0.02	22	3.2	-	Bal		A240	A790
CD4MCu	J93370	5	0.02	25	2	3	Bal	-	-	-
255	S32550 ^d	5.5	0.02	25	3.5	2	Bal	0.22N	A240	A790
	S32520 ^d	7	0.02	25	3.5	1.7	Bal	0.24N	A240	A790
2507	S32750 ^d	7	0.02	25	4	-	Bal	0.25N	A240	A790
	S32760 ^d	7	0.02	25	3.5	.07	Bal	0.7W, 0.22N	A240	A790

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 Alloy 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 equivalent performance.

d - these alloys are known as super duplex, some are proprietary, all with roughly equivalent performance.

CORROSION IN PURE AND CONTAMINATED PHOSPHORIC ACID

Pure phosphoric acid is much less corrosive than sulfuric acid. The corrosion resistance in pure phosphoric acid varies with the type of stainless steel and improves with higher alloy content. *Figure 1* delineates the zones where various alloys can be considered. Type 316L (S31603) is extensively used in the phosphoric acid industry for acid storage, handling and transport of pure acid.

However, about 90% of phosphoric acid production in the United States is by the wet-process, the most common wet-process is the dihydrate process.

In the wet-process, phosphate rock is crushed and reacted with a sulfuric/phosphoric acid mixture to form dilute, impure phosphoric acid (H_3PO_4). Acid produced in this manner has a significant amount of impurities originating in the phosphate rock. Some of the process impurities that have pronounced effects on corrosion are chlorides, fluorides (largely as fluorosilicic acid), sulfuric acid, and oxidizing cations (e.g., ferric and cupric ions).

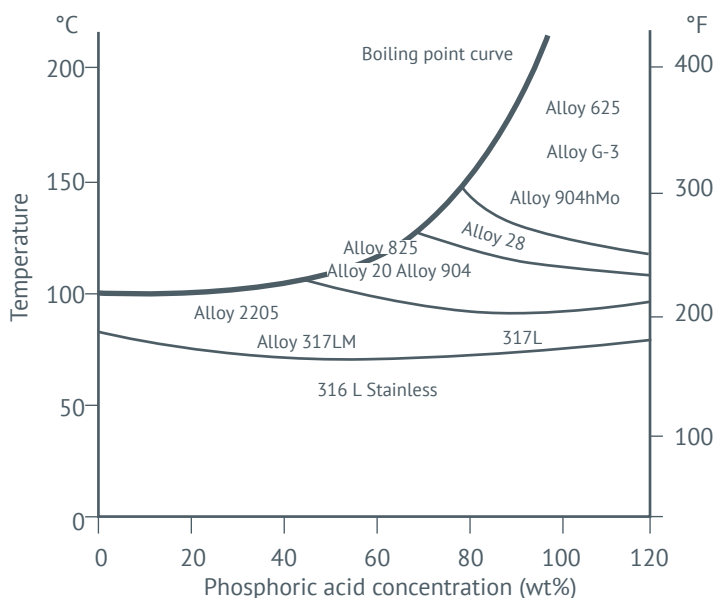
Chloride contamination significantly increases corrosion of Type 316L stainless steel and requires more highly alloyed stainless and nickel-rich alloys for many applications. Free

fluorides also substantially increase the corrosivity of the phosphoric acid. Fortunately, fluoride ions form strong complexes with silicon, whereby the content of free fluoride is decreased through the formation of fluorosilicates.

Thus, when considering alloy selection in phosphoric acid manufacture, utilizing the wet-process, one must analyse the corrosiveness of phosphoric acid, sulfuric acid and the influence of fluorine, silica, aluminium, iron, magnesium, manganese, calcium and sodium. It is obvious that these impurities can make the corrosion process very complicated and some tend to protect the stainless steels because of scale formation or beneficial oxidizing behaviour while others create strong localized attack. Further, the influence of temperature when in excess of 65 °C (150 °F) can be substantial, as well as the effects of solution velocity, especially when dealing with abrasive conditions.

As the phosphoric acid is concentrated compounds of sodium, calcium and silicates precipitate, reducing corrosion, but impair heat transfer. Residual fluorine aggravates the corrosion at higher concentrations and temperatures. Iron, aluminium and magnesium, if present, form complexes with the free residual fluorine and thereby reduce its corrosiveness. Often magnesium is purposely added in the production of superphosphoric acid and has proven beneficial as an inhibitor.

Figure 1 Areas of applicability for various alloys in phosphoric acid



Sulfuric acid

Because its corrosion characteristics change radically with its concentration sulfuric acid presents considerable problems in many processes. Concentrated, cold sulfuric acid can be stored in carbon steel for piping, valves and pumps where the design velocity with carbon steel should not exceed 3 feet per second. Heat of dilution can raise local temperatures to levels beyond the capabilities of Alloy 20 (N08020); therefore, for acidulation of phosphate rock the sulfuric acid is frequently pre-diluted by mixing with recirculated phosphoric acid of intermediate concentration. Alloy 20, Type 904L (N08904), Alloy 825 (N08825) and Alloy G-3 (N06985) are frequently used for equipment as they can solve most problems.

Cupric and ferric ions in solution inhibit the corrosion of stainless steels in sulfuric acid. The effect of copper content is obvious in the improved corrosion resistance of the

aforementioned alloys. Additional details about sulfuric acid corrosion can be found in the Nickel Institute publication 'Alloy selection for Sulfuric Acid Service (10 057)'.

CORROSION OF STAINLESS STEELS AND NICKEL-BASE ALLOYS

Ferritic stainless steels

Low-chromium ferritic grades with 11-13% chromium, such as Type 409, and Type 410 find no application in phosphoric acid service. The 17% chromium grades, such as Type 430 also show very high rates of corrosion in all concentrations of phosphoric acid at room temperature. Thus, ferritic stainless steels find no application in phosphoric acid service.

Austenitic, super austenitic and duplex stainless steels in pure acid

The conventional "18-8" type of stainless steels are the workhorse materials for service in pure phosphoric acid. Type 304L (S30403) shows good general corrosion resistance up to 80% acid below 74 °C (167 °F). Type 316L is extensively used in the phosphoric acid industry for acid storage, handling and transport. Type 317L (S31703) behaves similarly to Type 316L.

Alloy 20 shows no better corrosion resistance than Type 316L up to 60% pure phosphoric acid at boiling temperatures. Between 70% and 90% acid, Alloy S31277 shows improved resistance over Types 316L, 317L, and Alloy 825 below the boiling point.

Type 255 (S32550) exhibits corrosion resistance similar to Type 317L in pure phosphoric acid, as shown in the isocorrosion diagram in *Figure 2*, but may be useful in contaminated phosphoric acid because of its greater resistance to chloride.

Contaminated wet-process acid

There are several contaminants that affect the corrosion of stainless steels and nickel-base alloys in phosphoric acid. Their effects on corrosivity can be quite complex. The major contaminants are fluoride, chloride, sulfate, ferric ion, silicon, aluminum, magnesium, calcium and sodium. These contaminants can be divided into two classes based on whether they increase or inhibit corrosion in wet process acid. Fluoride, chloride, sulfate, and iron may stimulate corrosion. Aluminum, silicon, magnesium, calcium and sodium may counter the aggressive impurities and tend to inhibit corrosion. If sufficient amounts of the second group are present relative to the first, it is possible that corrosion may be completely prevented. This of course would depend on the nature of the precipitate deposited on the metal surface.

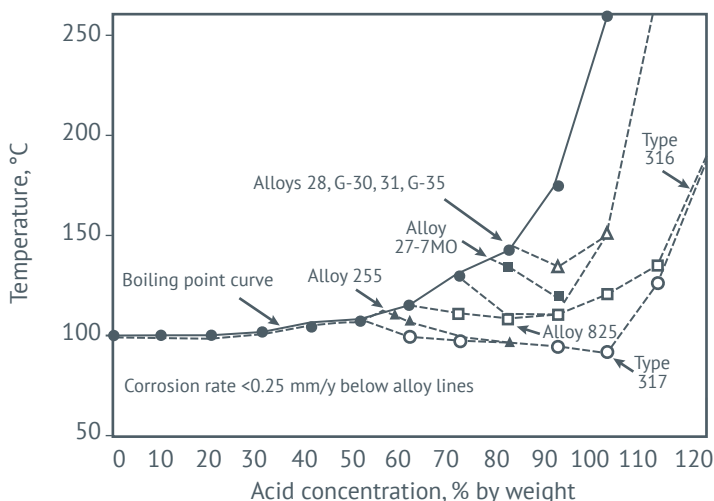
Silicon, aluminum and magnesium form strong complexes with fluoride, which reduces the concentration of free fluoride ions in the phosphoric acid solution, with attendant reductions in corrosion rate.

On the other hand, silica (SiO_2), as suspended quartz, would tend to accelerate attack by increasing erosion-corrosion of the metals.

Calcium and sodium may help decrease the risk of corrosion by precipitating sulfates and fluorosilicates, unfortunately these elements can impair heat transfer in heat exchangers when deposited as scales.

Iron, present as ferric ion, causes the acid to be strongly oxidizing in nature. This would help facilitate the formation of passive films on the stainless steels and nickel alloys. On the other hand, ferric ion can be detrimental when fluoride and chloride are present. Fluoride and chloride destroy the passivity of the stainless steel, causing it to be active. The reduction of ferric ions sustains corrosion of the active stainless steel at a high rate.

Figure 2 Isocorrosion diagram for various alloys in phosphoric acid¹⁰



304L is very susceptible to pitting and crevice corrosion from contamination by either chlorides or fluorides, and in the active state, will rapidly corrode with the release of hydrogen gas in as little as 15 ppm chloride. This may produce flammable explosive hydrogen/air mixtures. Because of poor service experience Type 304L has been very little used for handling, storage or manufacturing of contaminated phosphoric acid. Table 2 shows the effect of chlorides on corrosion of Types 304L and 316L in contaminated phosphoric acid.

Table 2 Effect of chloride on corrosion of Type 304 and 316 in 75% phosphoric acid*		
	Corrosion rate, mm/y (mpy)	
Chlorides, ppm	304	316
8	0.04 (1.4)	
15	0.28 (11.0)	
23	12.9 (508) ^a	
198	27.5 (1081)	0.03 (1.2)
* Temperature was 29.4-37.8 °C (85-100 °F) for 23 h		
^a Hydrogen gas evolved, and acid turned green		

At even higher chloride contents 316L shows a rapidly increasing corrosion rate, Figure 3.

The detrimental effect of chlorides and fluoride also occurs with the high-alloy stainless steels as shown in Figure 4. Figure 4 shows the result of laboratory test using a synthetically produced "Florida Acid".⁶ Of these stainless steels, the Alloy 28 (N08028) shows the highest resistance when exposed to the combined effects of chloride and fluoride contaminated phosphoric acid. Alloy 28 was originally developed for use in the manufacture of phosphoric acid. This observation is supported by actual plant equipment service experience.

Laboratory corrosion tests performed in solution of $30\%P_2O_5 + 2\%H_2SO_4 + 1.5\%H_2SiF_6 + 0.35\%Fe^{3+} + 0.26\%Al^{3+} + 1000 \text{ ppm } Cl^-$ at temperatures of 80 °C (176 °F) and 110 °C (230 °F) with and without additions of hydrofluoric acid of 0.2% and 0.4% are shown in Figures 5 and 6.⁷ Figure 5 shows if there is no hydrofluoric acid contamination, all materials present a corrosion rate below 0.2 mm/yr, which is a common threshold for material selection. A 0.2%

hydrofluoric acid addition shows a marked increase in the corrosion susceptibility of 904L, while alloys S32520, 28 and 31 (N08031) show rather stable corrosion rates. At 110 °C, 904L is strongly susceptible to corrosion even if there is no hydrofluoric acid contamination (Figure 6). Alloys S32520, 28, 31 and G-30 exhibit stable corrosion resistance in the absence of HF contamination, and corrosion rates under 0.2 mm/y in the presence of HF contamination, except for S32520 in 0.4% HF.

Additional tests were conducted with an increased concentration of sulfuric acid (8% instead of 2%). At 80 °C, alloys 28 and 31 presented a good corrosion resistance. However, at 110 °C, none of the tested alloys performed well.

Figure 3 Effect of chlorides on corrosion of Type 316 in 85% phosphoric acid¹⁰

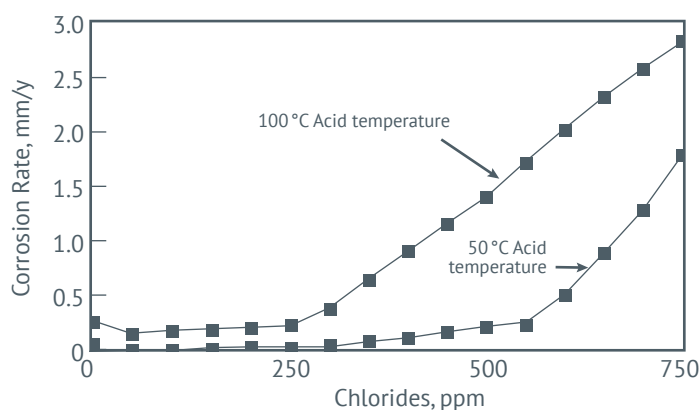
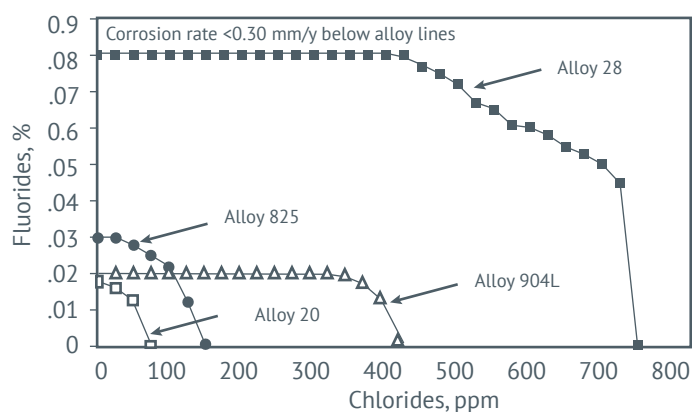


Figure 4 Effect of chloride and free fluoride on corrosion resistance of various alloys in synthetic "Florida acid" (70% $H_3PO_4 + 4\% H_2SO_4 + 0.45\%Fe^{3+}$) at 100 °C (212 °F)¹⁰



Similarly, Figure 7 also shows the effect of chloride on the corrosion resistance of various stainless steels. The data illustrates the threshold chloride concentration (i.e., the critical chloride concentration that would result in accelerated corrosion on the alloys) plotted versus various super stainless steels. Type 317L stainless steel is included for purposes of comparison. The super duplex Type 255 shows good corrosion resistance relative to 317L, when chloride is present, in contrast to its relative performance in pure phosphoric acid as shown in Figure 2. Although other super stainless steels, such as S31254, N08926, N08367, S32654, N08026, and S31277, were not evaluated in these tests, they could be expected to also lie between Type 904L and Alloy 28, thus they may be useful in contaminated phosphoric acid because of their higher molybdenum content.

Figure 5 Corrosion rates at 80 °C (176 °F) in 30% P₂O₅ + 2% H₂SO₄ + 1.5% H₂SiF₆ + 0.35% Fe³⁺ + 0.26% Al³⁺ + 1000 ppm Cl⁻ with and without HF addition ⁷

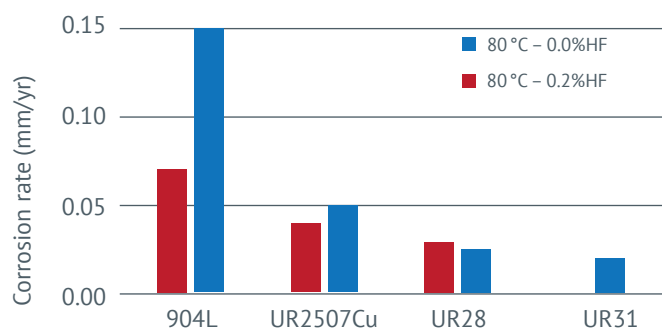
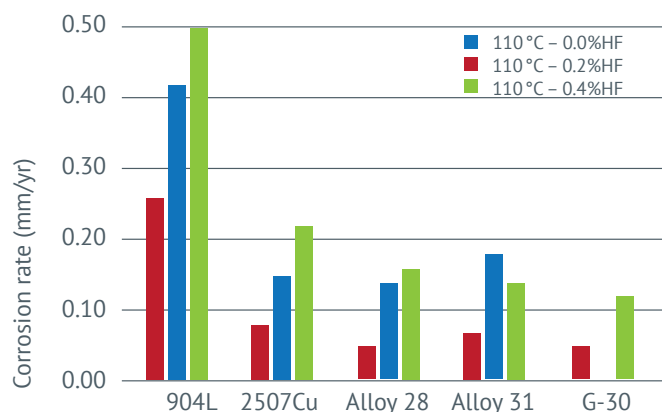


Figure 6 Corrosion rates at 110 °C (230 °F) in 30% P₂O₅ + 2% H₂SO₄ + 1.5% H₂SiF₆ + 0.35% Fe³⁺ + 0.26% Al³⁺ + 1000 ppm Cl⁻ with and without HF addition ⁷



Nickel-base alloys

The nickel-based alloys comprise two groups those with and without chromium. Only those with chromium demonstrate passivation.

Chromium-free alloys

Pure nickel alloys such as alloys 200 (N02200) and 201 (N02201), the nickel-copper alloy 400 (N04400), and the nickel-molybdenum alloy B-2 (N10665) have no practical applications in phosphoric acid experiencing high rates of corrosion in aerated solutions or those contaminated with oxidizing ions (e.g., Fe³⁺, Cu²⁺, etc.).

Figure 7 Threshold chloride limit for various stainless steels at 80 °C in 41% H₃PO₄ (30% P₂O₅) + 2% H₂SO₄ + 1.38% F⁻ + 1.5% H₂SiF₆ + 0.35% Fe³⁺ + 0.26% Al³⁺ + 0.2% HF ⁸

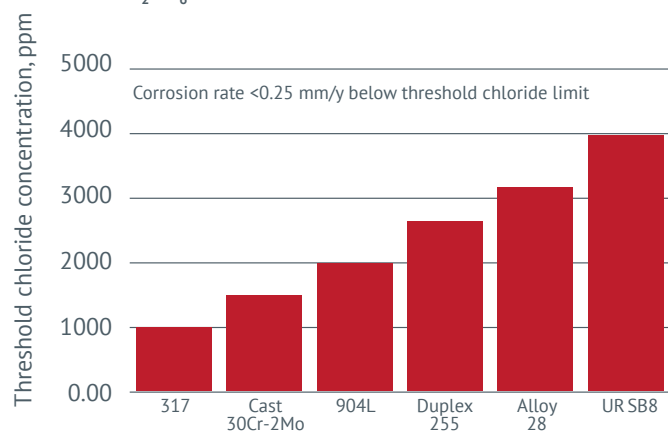
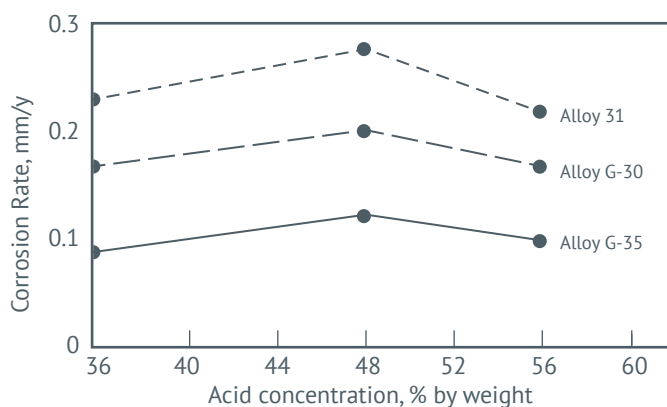


Figure 8 Corrosion of alloys G-35, G-30 and 31 in wet-process phosphoric acid at 121 °C (250 °F) ¹⁰



Chromium-bearing nickel-base alloys

The basic nickel-chromium alloy 600 (N06600) is of limited use in phosphoric acid and is not generally used.

Nickel-rich G-type alloys – A family of chromium-bearing nickel-rich alloys has been developed specifically for wet-process phosphoric acid service where chloride and fluoride contamination are present. This family can be called G-Type which comprises alloys G-3, G-30 (N06030), and G-35 (N06035), which show excellent corrosion resistance in wet-process phosphoric acid.

The high-chromium alloys G-30 and 690 (N06690), approximately 30% Cr, are very resistant, even though the latter alloy contains no molybdenum. Molybdenum has little influence as shown in *Table 3* by the higher corrosion rates of the Ni-Cr-Mo alloys, 625 (N06625), C22 (N06022) and C276 (N01276). The good resistance of the Alloy G-30 is consistent with its reported service performance.⁶

		Industrial Grade	
Alloy	Reagent-grade	Wet-process A	Wet-process B
G-30	0.13 (5)	0.46 (18)	0.15 (6)
690	0.13 (5)	0.51 (20)	0.18 (7)
625	0.30 (12)	0.91 (36)	0.30 (12)
C22	0.30 (12)	0.85 (33)	0.28 (11)
C276	0.39 (15)	1.90 (74)	0.72 (28)
825	-	13.97 (550)	0.64 (25)
Type 316	0.76 (30)	28.96 (1140)	1.70 (67)

The order of resistance between the G-type alloys and Alloy 28 appears to vary with the specific phosphate ore processed, which is to say that the kind and concentration of contaminants varies in an unpredictable manner in various geographic locations. Alloy G-35 showed somewhat better corrosion resistance than Alloys G-30 or 31 in wet-process phosphoric acid at 121 °C (250 °F), which suggests the alloy may offer better performance in evaporator tubing applications, *Figure 8*.

Other laboratory data shows Alloy 31 is comparable to alloy G-30 in pure phosphoric acid and slightly superior to Alloy 59 (N06059) in pure and contaminated phosphoric acid, *Table 4*.⁶

Test Environment	Temperature	Alloy 28	Alloy G-30	Alloy 31	Alloy 59
72% H ₃ PO ₄	116 °C (241 °F)	1.2 (47)	0.10 (4)		
	120 °C (248 °F)			0.08 (3)	0.13 (5)
75% H ₃ PO ₄	116 °C (241 °F)	1.4 (55)	0.20 (8)		
	120 °C (248 °F)			0.05 (2)	0.15 (6)
72% H ₃ PO ₄ +4.5% H ₂ SO ₄ +0.9% H ₂ SiF ₆ +1.5% Fe ₂ O ₃ +400 ppm Cl-	120 °C (248 °F)			0.78 (31)	0.99 (39)

C-type family – This family of alloys includes alloys C4 (N06455), C276, C22, C2000 (N06200), 59, and 686 (N06686) are similar in composition and corrosion characteristics. *Table 3* and *4* show they possess no performance advantage over Alloys G-30 and 31 in pure or contaminated phosphoric acid. In fact, C-Type alloys often show less resistance than the alloy G-30 under wet-process conditions. They also exhibit active/passive behavior near the boiling point and should not be used under these conditions. Consequently, they are used infrequently.

Cast alloy

Silicon cast iron F47003 (containing 14% silicon) possesses excellent resistance to hot phosphoric acid. Demonstrating a corrosion rate in 85% acid, of only 0.03 mm/y (1.3 mpy) at 75 °C (167 °F) and 0.17 mm/y (6.8 mpy) at 100 °C (212 °F).

The cast alloys CF8 (J92600), CF8M (J92900) and CN7M (N08007) are very resistant to erosion effects up to about 2.4-3.7 m/s (8-12 ft/s). Duplex casting CD4MCu (J93370) shows even greater erosion-corrosion resistance up to 4.9-6.1 m/s (16-20 ft/s) in 40% acid at room temperature. All of these cast alloys have been used in pumps, valves and agitator blades in phosphoric acid service.

Abrasion and velocity effects

Whenever pH conditions drop below 4.5, corrosion of carbon steel becomes severe. In the presence of velocity effects and abrasion from gypsum sludge and sand particles, the

otherwise protective corrosion product film is removed leading to accelerated attack. Rubber-lined steel and/or carbon brick are extensively utilized for equipment, with alloys such as Type 316L stainless, Type 904L and Alloy 20 for piping, shafts, agitators, and cast CN7M for pumps and valves. Where needed higher nickel alloys such as Alloy 28 and Alloy G-3 are utilized, as well as hardfacing materials.

Duplex stainless steels, such as Type 2205 (S32205) and 255 have given good performance from a standpoint of corrosion as well as abrasion resistance. These high strength duplex stainless steels have a hardness over 200 Brinell. Alloys with a hardness of 140 Brinell or below are generally susceptible to high wear rates.

Selection of alloys

With the many differences in feedstock and rock impurities, as well as the many process differences and various methods of controlling fluorine, metallic constituents and precipitates, it is impossible to generalize alloy selection to cover all the variations in conditions. Only general comments will be presented.

Much of a wet-process acid system is constructed of steel with a rubber lining to resist acid corrosion. Sometimes it is augmented with acid-resisting brick in locations where impingement and abrasion are a factor. The rubber lining is applied to the many large vessels such as clarifiers, thickener tanks, reactors, separation chambers, fume ducts and transfer piping. Frequently also the rakes, shafts, agitator blades,

impellers and valve bodies are rubber covered. Even though much progress has been made in the installation methods and quality of the liners, maintenance is required on a regular basis.

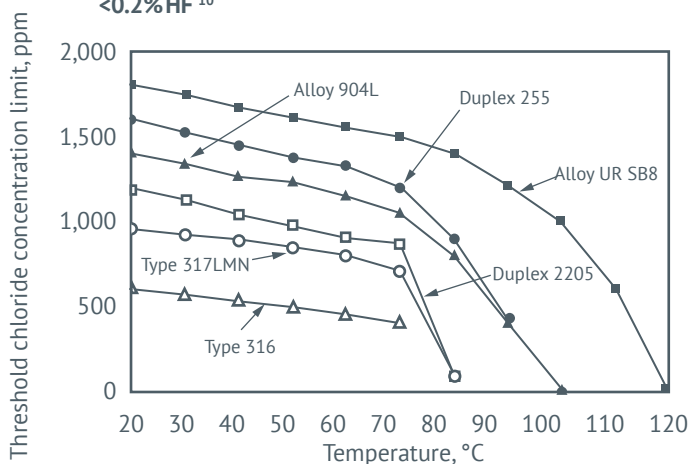
For critical components, high velocity components and parts where the temperature is too high for rubber, alloys are utilized. Much of this is Type 316L stainless steel; mostly for applications below 65-82 °C (150-180 °F). Type 317L stainless is specified for applications where severe pitting of Type 316L has been experienced.

Storage and transport

Type 316L stainless steel is routinely used to store phosphoric acid⁴. This has been validated by measuring the corrosion resistance of 316L in 54% P_2O_5 with various amounts of chlorides – 500 ppm up to 3500 ppm. The test temperature was set to 50 °C (122 °F) to consider a possible increase in the wall temperature due to the sun. The corrosion rate of 316L remained very low up to 1500 ppm chlorides, for which a corrosion rate higher than 1 mm/yr was measured. Therefore, 316L is suitable unless there is a risk of significant chloride contamination. The duplex stainless steels 2202 (S32202), 2205 and S32520 were found to be resistant up to at least 3500 ppm chlorides at 50 °C.⁷

Type 316L stainless steel is suggested for handling superphosphoric acid of 105% phosphoric acid (76% P_2O_5) concentration at 60-95 °C (140-205 °F). In some instances, more highly alloyed materials such as Types 255 and 317L have been used.

Figure 9 Chloride concentration limits suggest for various stainless steels used in transportation of industrial grade phosphoric acid (75% H_3PO_4) containing <4% H_2SO_4 , <1% F and <0.2% HF¹⁰



In cargo vessels, the Code requires tanks handling phosphoric acid to be Type 316L. For superphosphoric acid, Types 317L, 317LN (S31753) or 2205 is used. The duplex Type 2205 has higher strength than the fully austenitic grades and has a coefficient of thermal expansion more closely matching that of the steel vessel.⁵

Chloride concentration limits suggested for various stainless steels used in the transportation of industrial-grade phosphoric acid are shown in Figure 9.⁸ Note that the threshold or critical chloride concentration decreases as the temperature increases and that the higher alloyed super stainless steels are more resistant than the lower alloyed stainless steels. This is consistent with service performance of stainless steels in acid chloride environments.

Agitators and pumps

The main central agitator and agitator paddles used for mixing sulfuric acid-recycle acid with phosphate rock must resist severe abrasion due to gypsum as well as general corrosion due to temperature and sulfuric acid. Type 316 agitators typically corrode after only a few months. They have been replaced with higher-alloy materials, such as 904L, 825, Alloy 28, 255, 31 and G-30.

Agitators or mixers were studied in a corrosion test program using the Rhone-Poulenc (dihydrate) and Nissan (hemihydrate) processes in India.³ The primary difference in the phosphate rock digestion processes is the higher operating temperatures in the Nissan process and, thus, more corrosive conditions. Neither Type 904L nor coatings gave satisfactory service. Potential mixer materials were exposed to 37% H_3PO_4 (27% P_2O_5), 34% solids, and 8% sulfate at 80 °C (176 °F) and 95 °C (203 °F). The results showed that 904L is adequate for the lower-temperature Rhone-Poulenc process, but not for the more aggressive, higher-temperature Nissan process. Alloys 31 and G-30 were tested for an additional 12 months as full mixer blades. Both alloys showed acceptable performance, but alloy 31 was selected due to its lower cost.

For sulfuric acid handling, and the higher concentrations of phosphoric acid (over 45% concentration) Alloy 20 and Alloy 825 have been frequently used in the USA, while in Europe Type 904L and Alloy 28 have been the more predominant selections. For pumps and valves the cast version of Alloy 20 (ACI CN7M) has been the most common. Since the slurries can be corrosive as well as abrasive the duplex stainless steels have made strong inroads, such as CD MCu₄ and more recently Type 255.

Pumps are utilized to transfer phosphoric acid mixtures from reactor vessels to the filters. They are also subjected to very severe abrasion and must usually be replaced annually. In one plant Alloy 825 pumps failed after two years due to impeller erosion. After 18 months of service Alloy 28 did not show any visible corrosion.¹

Evaporators

The three levels of concentration most frequently encountered are from 28% clarified acid to 40%, from 40% to 54% and from 54% to super acid 70% P_2O_5 . The first two steps are often done single or in parallel stages. The first stage is usually not very

corrosive and can be handled with Type 316L stainless steel or Alloy 20 or Type 904L. The other two evaporator stages can be substantially more corrosive as temperatures are higher, respectively 120 °C (250 °F) and 175 °C (350 °F) approximately, and the stronger influence of fluorine and chlorides.

To resist the extreme corrosion conditions in this part of the process, heat exchangers are generally made of impervious graphite tube-and-shell or block exchangers. Type 904L has experienced very severe corrosion in this area, with rates as high as 1 mm/y (40 mpy) and in one case failed in six months. Alloy 28, Alloy G-3 and G-30 have been used in this application from 41% to 75% H_3PO_4 (30-54% P_2O_5).¹

In a plant in the Mediterranean Basin, corrosion problems were reported in the elbows exposed to vapors of 75% H_3PO_4 (54% P_2O_5), 1.45% H_2SO_4 , 0.22% fluoride and 300 ppm chloride at 90 °C (194 °F). The elbows in the vapor recirculation system were originally rubber-lined steel. Maintenance of the rubber lining was very difficult and costly. Two vapor elbows were placed in service using Alloys 31 and G-30. The elbows were washed with cold seawater once per week to remove heavy deposits. After one year of testing, inspections showed pitting and underdeposit corrosion on both alloys. The alloy 59 welds in alloy 31 showed no corrosion, while the G-30 welds in alloy G-30 had extensive attack. After two years, alloy 31 needed only minor repairs, while alloy G-30 required extensive repairs. The operator concluded that both alloys 31 and G-30 were better than the rubber lining, but alloy 31 had the better overall performance and was less expensive.³

Phosphate fertilizers

In the manufacture of triple superphosphate good performance can be expected from Type 904L, Alloy 825 and Alloy 28, while Type 316L stainless is standard in various handling operations. Dicalcium phosphate fertilizers can mostly be manufactured in Type 316L equipment. The mono-ammonium phosphate used in the USA can be quite corrosive, while the disalt ammonium phosphate used in Europe is alkaline and not especially difficult to handle.²

Readers seeking more information on any of the subjects covered by this publication should refer to the References.

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