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# Alloy selection for service in nitric acid

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A GUIDE TO THE USE OF  
NICKEL-CONTAINING ALLOYS  
N° 10075

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A GUIDE TO THE USE OF NICKEL-CONTAINING ALLOYS

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edited by Sandra Le Manchet, March 2020

# Alloy selection for service in nitric acid

## Introduction

Nitric acid (HNO<sub>3</sub>) is the second most important industrial acid after sulphuric. It is a strong oxidizer and a very corrosive acid. Even though most stainless steels do not resist 100% Nitric acid, they are resistant to corrosion by the 60% to 70% concentrations that result from ammonia/air oxidation processes, and the low-carbon or stabilized stainless steels play a major role in the production and handling of nitric acid over a wide range of temperatures and concentrations.

This publication examines the selection criteria for several stainless steels and nickel-bearing alloys in the production and handling of nitric acid and in its use, both in the production of ammonium nitrate fertilizers and as an acid mixture with hydrofluoric acid for descaling.

The Bibliography at the end of the publication contains references that will provide more detailed information on many of the specific subjects included in this publication.

*Table 1* lists many of the alloys that may be used for nitric acid service.

Table 1 Nominal composition of alloys used in Nitric Acid systems										
Alloy	UNS number <sup>a</sup>	Nominal composition, %							ASTM Spec. <sup>b</sup>	
		Ni	C	Cr	Mo	Cu	Fe	Other	Plate	Seamless tube and pipe
<b>Chromium-containing nickel alloys</b>										
825	N08825	42	0.03	21.5	3	2.25	30	Ti 0.9	B424	B163
G-30	N06030	Bal	0.02	29	5	1.5	15	(Cb + Ta) 1.0	B582	B622
690	N06690	Bal	0.03	29	-	-	9	-	B168	B167
C-22	N06022	Bal	0.01	21	13	-	4	W 3	B575	B622
C-276	N10276	58	0.01	15.5	16	-	5.5	W 3.5	B575	B622
<b>Ferritic stainless steels</b>										
430	S43000	-	0.08	17	-	-	Bal	-	A240	-
XM-27	S44627	-	0.05	26	1.2	-	Bal	Cb 0.12	A240	-
<b>Austenitic stainless steels</b>										
304	S30400	8	0.04	18	-	-	Bal	-	A240	A312
304L	S30403	8	0.02	18	-	-	Bal	-	A240	A312
304L NAG	S30403	11.5	0.01	18	-	-	Bal	-	A240	A312
321	S32100	8	0.04	18	-	-	Bal	Ti 0.40	A240	A312
347	S34700	8	0.04	18	-	-	Bal	Cb 0.50	A240	A312
316L	S31603	10	0.02	16.5	2.1	-	Bal	-	A240	A312
317L	S31703	12	0.02	18	3.1	-	Bal	-	A240	A312

Alloy	UNS number <sup>a</sup>	Nominal composition, %							ASTM Spec. <sup>b</sup>	
		Ni	C	Cr	Mo	Cu	Fe	Other	Plate	Seamless tube and pipe
<b>Austenitic stainless steels cont'd</b>										
310L NAG	S31002	20	0.01	25	-	-	Bal	-	-	A312
800	N08800	33	0.07	21	-	-	Bal	Al 0.3, Ti 0.3	A240	B407
20	N08020	33	0.02	19.5	2.2	3.2	Bal	Cb 0.40	A240	B729
4% Si	S30600	15	0.01	17.5	0.1	0.3	Bal	Si 4	A240	A312
5% Si	S30601	17.5	0.01	17.5	0.1	0.2	Bal	Si 5.3	A240	A312
5% Si	S32615	20	0.04	18	1	2	Bal	Si 5.3	A240	A312
6% Si	S38815	15	0.02	14	1	1	Bal	Si 6	A240	A312
<b>Duplex stainless steel</b>										
2304	S32304	4	0.02	23	0.3	-	Bal	-	A240	A790
2205	S32205	5	0.02	22	3.2	-	Bal	-	A240	A790
2507	S32750	7	0.02	25	4	-	Bal	-	A240	A790
329	S32900	3.5	0.04	25	1.5	-	Bal	-	A240	A790
7-Mo Plus	S32950	4	0.03	27.5	2	-	Bal	-	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.

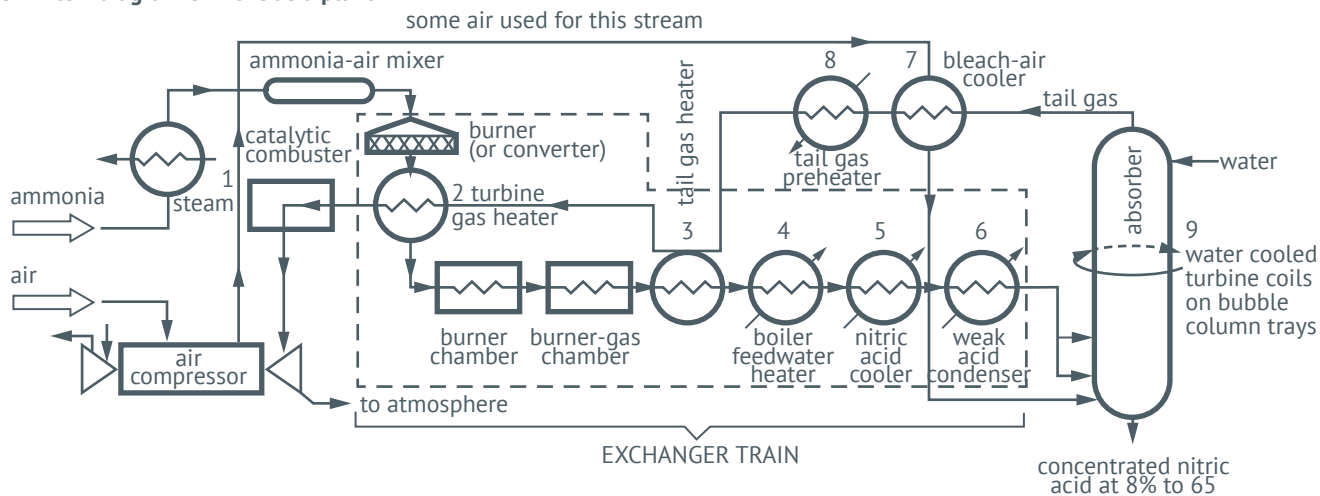
b - In ASTM specifications, most nickel alloys fall into the "B" specifications. However, due to a redefinition of a nickel alloy, a few alloys such as 800 and 20 are being reclassified as stainless steels and will be included in the "A" specifications. That work is still in progress.

## NITRIC ACID PRODUCTION

Nitric acid is almost always made by mixing gaseous ammonia with air, converting it to nitric oxide (NO) in a reactor over a platinum-rhodium catalyst at 800–950 °C (1470–1740 °F), and further oxidizing the NO to NO<sub>2</sub>. The nitric oxide is passed through an absorber column for

conversion to 60–65% HNO<sub>3</sub>, which is bleached with air and sent to storage. Off-gas from the bleaching operation is recycled to the absorber. Some details of the plant lay out may vary, but the basic design is imposed by the nature of the process. *Figure 1* is a schematic diagram of a typical plant.

**Figure 1** Flow diagram of nitric acid plant



The azeotrope of  $\text{HNO}_3$  and water at atmospheric pressure is 67%  $\text{HNO}_3$ . Higher concentrations of acid – 90% to 100% – are produced by distilling the dilute acid with a dehydrating agent, e.g., concentrated sulphuric acid, and condensing the fuming nitric acid vapours from the dehydration tower overhead.

## CORROSION BEHAVIOUR – MATERIALS SELECTION

Nitric acid is a powerful oxidizing agent as well as an acid. Metals and alloys which readily develop protective surface oxides (such as aluminum, titanium and the stainless steels) are generally resistant to nitric acid over a wide range of concentration.

### Stainless steels

Nitric acid is a very strong oxidizing medium, and therefore, chromium content plays an extremely important role in corrosion resistance of stainless steels and nickel alloys.

### Austenitic stainless steels

The most widely used grades of stainless steel for nitric acid are the low-carbon or stabilized austenitic grades: Type 304L (UNS S30403), Type 321 (S32100), and Type 347 (S34700).

They are resistant to corrosion over a wide range of temperatures and concentrations up to 60% nitric acid at the atmospheric boiling point. *Figure 2* shows an iso-corrosion diagram for Type 304L stainless steel in nitric acid.

Stainless steels with higher levels of carbon, such as Type 304 (S30400), that are not stabilized are subject

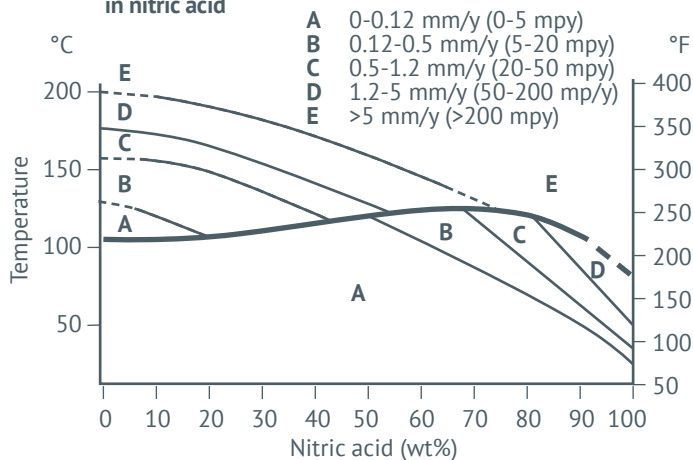
to intergranular attack in nitric acid at the heat-affected zone near welds as a result of sensitization due to the precipitation of chromium carbides at the grain boundaries.

Molybdenum additions, found in Types 316L (S31603), and 317L (S31703), are generally considered to improve the resistance of stainless steels to acid corrosion. However, in oxidizing acid, such as nitric acid, Type 304L generally performs better than the molybdenum grades because the molybdenum tends to promote the formation of sigma phase, which is less resistant to nitric acid attack. Except in mixed acids or contaminated nitric acid containing halides, Type 304L is preferred to Type 316L for nitric acid service based on both cost and corrosion resistance.

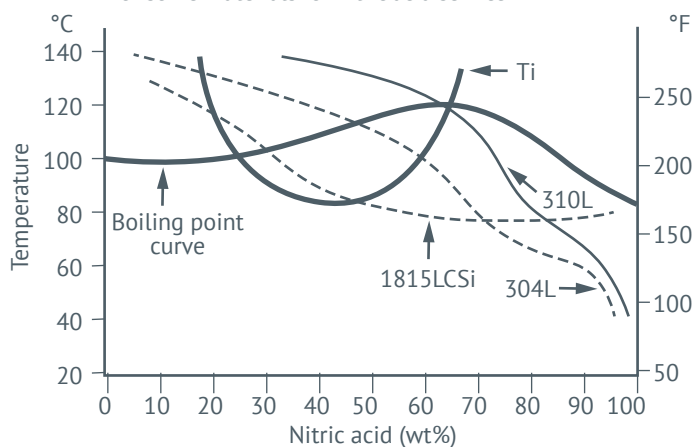
Selective corrosion along grain boundaries can occur when stainless steels are exposed to strong nitric acid at elevated temperatures. Type 304L can be optimized with extremely low carbon and low silicon, phosphorus, and sulphur residuals to be extremely resistant to intergranular corrosion after sensitization. This modified 304L is commonly called 304L Nitric Acid Grade (NAG).

For more severe conditions, the higher chromium of 310L (S31002) possesses even greater resistance than 304L to nitric acid concentrations above 60%, as shown in *Figure 3*. Again, the composition and microstructure are optimized, like 304L NAG, to resist intergranular corrosion at the heat affected zones near welds.

**Figure 2 Iso-corrosion diagram for AISI Type 304L stainless steel in nitric acid**



**Figure 3 Isocorrosion diagram of 0.1 mm/y (4mpy) for some materials for nitric acid service**



### Silicon-bearing austenitic stainless steels

Silicon is another element, in conjunction with chromium, that improves corrosion resistance in nitric acid.

A proprietary grade known as 1815LCSi (S30600) contains 4% silicon and is remarkably effective in resisting nitric acid >95%. *Figure 3* shows iso-corrosion rate curves of 0.1 mm/y (4 mpy) for Types 304L, 310L, and 1815LCSi in nitric acid. This alloy is used for piping systems and equipment involving highly concentrated nitric acid at temperatures up to the boiling point and is commonly used for 98% nitric acid transport tanker trucks and storage tanks.

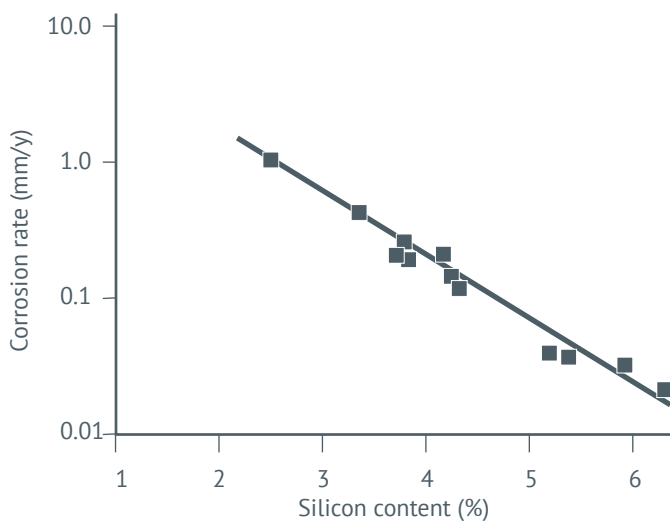
Other proprietary stainless steels containing 5% Si, such as S30601 and S32615, and a 6% Si alloy, S38815 have been developed for even more severe conditions in concentrated acid. *Figure 4* shows the beneficial effect of silicon on the corrosion resistance of austenitic stainless steels in boiling concentrated nitric acid.

### Duplex stainless steels

Duplex stainless steels possess a mixed microstructure containing approximately equal amounts of austenite and ferrite phase. This duplex structure results in higher strength as compared to austenitic grades.

Type 2304 (S32304) duplex stainless steel is being used successfully in nitric acid applications in chemical plants.

**Figure 4 Influence of silicon content on the corrosion of Cr/Ni steels in boiling highly concentrated nitric acid.**



Alloy selection for service in nitric acid

The temperature at which the corrosion rate in 65% nitric exceeds 0.12 mm/y (5 mpy) comparing various duplex steels against Type 304L and 316L is:

203 °C (397 °F) for Type 2304 (S32304)

221 °C (430 °F) for Type 2205 (S32205)

230 °C (446 °F) for Type 2507 (S32750)

212 °C (323 °F) for Type 304L and 316L

7-Mo PLUS® (S32950) has provided excellent service in nitric acid tube-side and shell-side cooler condensers operating at low to intermediate temperatures. In the Huey test, S32950 had a corrosion rate of about 0.17 mm/y (7 mpy) compared to Type 304L which had a corrosion rate of 0.25 mm/y (10 mpy). This alloy also offers useful resistance to chloride stress-corrosion cracking (SCC) making it a better candidate than Type 304L or 316L for nitric acid condenser/coolers cooled with chloride-containing waters.

A cautionary note – Ferrite in duplex alloys converts to the nonmagnetic sigma phase when exposed to temperatures in the sensitizing range and sigma phase is severely corroded by nitric acid. This mitigates against the use of welds and weld repairs of duplex alloys for nitric acid service if the welding or service conditions are such that substantial levels of sigma phase would be formed. Also, use of duplex is restricted to temperatures below 260 °C (500 °F) due to alpha prime precipitation.

### Ferritic stainless steels

Ferritic grades with 17% Cr or more, exemplified by Type 430 (S43000), were commonly used in nitric acid production and are still occasionally used. The corrosion resistance of Type 430 is generally good except in very strong acid. Its corrosion resistance is similar to Type 304. However, fusion welding reduces both the corrosion resistance and the ductility in the heat-affected zone. Because of welding problems ferritic stainless steels have, in general, been replaced by austenitic grades.

Superferritic stainless steels with high chromium contents, low interstitial content and low carbon levels, such as XM-27 (S44627) possess excellent resistance to hot nitric acid. However, due to welding difficulties noted for Type 430, they are generally only available in thin sections, but can be used for heat exchanger tubing.

### Higher alloyed stainless steels and nickel alloys

Higher alloy materials such as Alloy 20 (N08020), Alloy C-276 (N10276), Alloy C-22 (N06022), Alloy G-30 (N06030), Alloy 690 (N06690), Alloy 800 (N08800), and Alloy 825 (N08825) sometimes are used for specific applications in nitric acid environments, but the less expensive austenitic stainless steels are usually more economical and just as good. Some conditions in which higher alloys are useful include high velocity, mixed acids, or contaminated nitric acid.

Stainless steels are not recommended for mixtures of nitric and hydrochloric acid in which the chloride ion induces high corrosion rates and pitting of stainless steels. Nickel alloys, such as Alloy C-22 and Alloy G-30, exhibit low corrosion rates in nitric acid with hydrochloric acid concentrations below 10%.

Tubular equipment, such as acid coolers and cooler condensers are sometimes problem areas in nitric acid plants. The cooling media on the water side may contain chlorides and cause SCC in the austenitic stainless steels. Cooler condensers may present additional problems if the design allows condenser acid to migrate to warmer portions of the condenser where it can re-evaporate. Alloy 690 or G-30 may be useful.

### Other metals

Silicon cast iron F47003 (containing 14% silicon) possesses outstanding resistance to nitric acids above 45% concentrations to the atmospheric boiling point.

Aluminum alloys are useful only in concentrated nitric acid (93–100%) at ambient temperatures. Aluminum alloys 1100 (A91100) and 3003 (A93003) are frequently used for storage tanks of concentrated nitric acid >95%. Type 304L stainless steel is used for lower concentrations. The effect of nitric acid concentration on the corrosion rate of aluminum and stainless steel is shown in *Figure 5*.

Titanium is highly resistant to nitric acid below 25% and in the 65–90% range at the atmospheric boiling point, as shown in *Figure 3*. Type 304L possesses somewhat similar corrosion resistance to Titanium up to 60% acid. Above 60% acid, there are other high chromium and high silicon stainless steels which will provide greater corrosion resistance. Titanium is never used with red fuming nitric acid because a pyrophoric reaction can occur. In nitric acid solutions >90%, Titanium can be subject to stress-corrosion cracking.

Zirconium is better than titanium in 65–90% acid and finds application under the most severe conditions of concentration and temperature. Zirconium is also used to overcome vapor-phase corrosion, which can be severe in acid reboiler tubing. Zirconium can be subject to stress corrosion cracking in nitric acid in concentrations >70%.

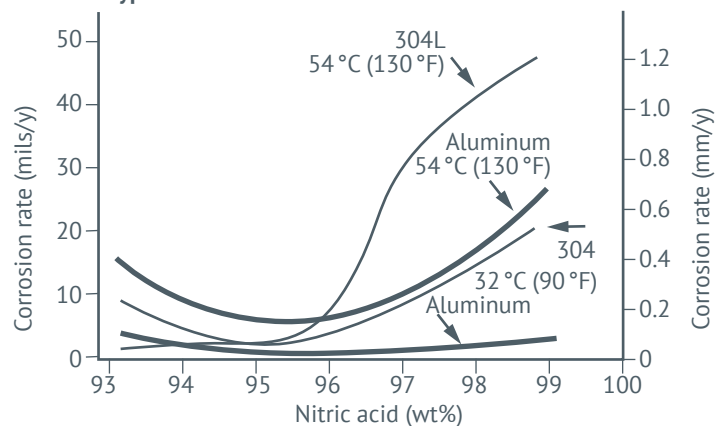
### Industrial applications for nitric acid

There are several major markets for nitric acid, all requiring facilities for storage and handling. It is good engineering practice to use Type 304L stainless steel for storage tanks, tank trucks, rail cars, piping, valves, and pumps.

Nitric acid is used in the production of acrylonitrile textile fibers (nylons), dyestuffs, and high explosives. Type 304L is widely used for production equipment in each of these. In nuclear fuel processing, Alloy 825 and Alloy 690 are used to handle solvents for dissolving fuel elements of uranium and uranium oxide together with their cladding elements. These solvents include nitric acid up to 45% HNO<sub>3</sub> at the boiling point, sulphuric acid, and caustic soda.

The largest industrial application for nitric acid is in the fertilizer industry, where it is used to produce ammonium nitrate and potassium nitrate. Type 304L stainless steel is the preferred material for mixers, evaporators, crystallizers, pumps, piping, and tanks. The nitrate is frequently stored in concentrated solutions of 83% or 92% at 85 °C. Alloy 800 or Type 329 stainless steel are sometimes used in heat exchangers where one might be concerned about SCC.

**Figure 5 Corrosion rate of aluminum A93003 and stainless steel Type 304 in concentrated nitric acid**



Mixtures of acids are frequently encountered in chemical and metallurgical processes. A mixture of nitric and hydrofluoric acids is used in the pickling of stainless steel to remove oxide films due to heat treating. Type 304L stainless steel is inadequate for pickling equipment with a corrosion rate typically about 25 mm/y (1000 mpy). Alloy 690 exhibits a corrosion rate of about 0.25 mm/y (10 mpy) and can be used for heating coils in this corrosive acid mixture.

The addition of nitric acid to sulphuric acid is beneficial for the corrosion resistance of the 18% chromium austenitic grades. For example, the corrosion rate for Type 304L in ambient 65% sulphuric acid is about 3 mm/y (120 mpy) but is reduced to <0.5 mm/y (<20 mpy) by the addition of about 5% nitric acid.

Figure 6 is a summary diagram to serve as a guide for alloy selection.

Table 2 shows equipment and suggested materials of construction in a nitric acid plant.

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

Figure 6 Nitric acid selection guide

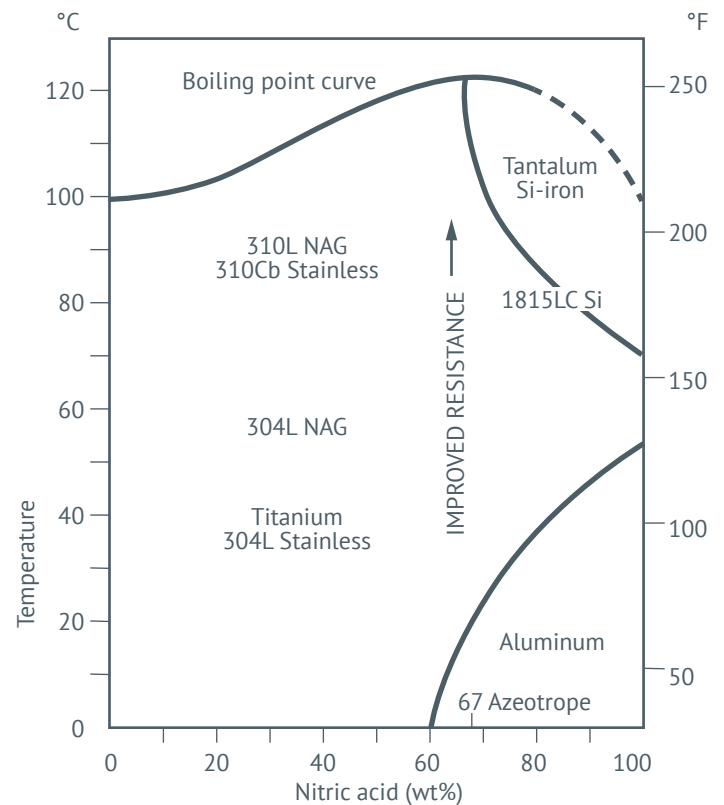


Table 2 Equipment and materials of construction for nitric acid

Specific equipment	Suggested materials of construction
Ammonia vaporizer	Carbon steel
Ammonia storage tanks	Carbon steel
Ammonia converter	Austenitic stainless steel, nickel alloys
Ammonia converter, cool end	347
Ammonia converter, hot end	Nickel alloys
Catalyst gauze	Platinum alloy
Catalyst support grid	Nickel alloys, highly alloyed stainless steels
NOx absorber	304L
Acid cooler / condenser	304L NAG, 304L, 329, titanium, zirconium 702
Acid concentrator	304L NAG, 7Mo Plus
Distillation column	14% Si cast iron
Concentrated acid cooler	High Si austenitic stainless steel, glass-lined steel
Concentrated acid condensers	Aluminum, glass/PFTE, high Si austenitic stainless steel, zirconium, niobium, tantalum
Acid mixing tank	304L
65% Acid storage tank	304L
Strong (>93%) acid storage tank	Aluminum alloys 3003 or 5056, glass-lined steel



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