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SOLVING CORROSION PROBLEMS  
IN WET PROCESS PHOSPHORIC ACID PLANTS

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ABSTRACT

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Corrosion of materials of construction is a serious problem for design, engineering, operation and maintenance personnel in the fertilizer industry. The trend to higher concentrations and temperatures, and the necessity of using closed loop recirculating systems to meet stringent pollution control requirements, have substantially increased the severity of the corrosive environment.

Guidelines will be presented in alloy selection in phosphoric acid and sulfuric acid systems. The corrosion process is very much complicated by the presence of metallic impurities, chlorides and free fluorine, some of which protect stainless steels because of scale formation or beneficial oxidizing behavior, while others substantially aggravate the corrosivity of the phosphoric acid.

A number of applications and problems due to corrosion and the abrasive action of rock slurries will be discussed, with emphasis on Florida phosphate rock conditions. Materials of construction, both metallics and non-metallics, will be cited for use in agitator shaft assemblies in digesters, filter section, slurry pumps, piping, valves and concentrator units. Where operating conditions are too severe for Type 316L and the duplex stainless steels, the Cr-Ni-Mo and Ni-Cr-Mo alloys are capable of providing reliable solutions and have the potential for significantly reducing maintenance costs.

## INTRODUCTION

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Sufficient advantage does not seem to have been taken of new cost-effective alloys which substantially contribute to reduction in capital investment, provide higher efficiency and increase operating capabilities. It is important to understand the limitations of the various materials available to ensure their proper performance, if needed with certain process manipulations.

Today's plants frequently must be able to cope with phosphate rock supply from several locations with different corrosive properties. Limited water availability and severe control on effluent disposal demand recirculation of process streams with resultant acid and chloride build-up in the system. Demand for reductions in energy consumption force us into more efficient, larger size units with a corresponding demand for higher equipment reliability.

The bulk of all phosphoric acid production today is by the wet process. This term is here specifically intended as referring to digestion or acidulation of phosphate rock with sulfuric acid, even though nitric acid and hydrochloric acid have been used for attack of rock. The type of calcium sulfate produced in the reaction further characterizes the process as dihydrate, hemihydrate, or anhydrite. The wet process is the most severe from the point of view of corrosion. The manufacturing process includes the production of superphosphate and ammonium phosphate-based fertilizers.

## GENERAL ALLOY SELECTION CONSIDERATIONS

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The industry traditionally has been conservative in its choice of alloys, adhering to long-time proven metallurgy with as basic choices Type 316L stainless steel, Alloy 904L and Alloy 20Cb-3. High nickel alloys were utilized when the former selections proved inadequate. Operating parameters and environmental factors have an important impact on alloy performance, in particular the effect of pH, temperature and the presence of chlorides, fluorides and oxygen. Seemingly unimportant variables such as the presence of aluminum, iron, magnesium, silica, calcium, and sodium can change the corrosion picture completely.

As it is not possible to review all suitable materials, a selection was made of several austenitic stainless steels, two duplex stainless steels, and a number of molybdenum-bearing nickel-chromium alloys. Their chemical composition, tradenames and suppliers are shown in Table 1, as well as the generic name that will be utilized in the text and figures.

The authors plan to present information via simplified charts. These alone cannot be used for selecting materials of construction. However, concise and condensed information is valuable in that it presents a bird's eye view of the situation and can be used for screening purposes, and by ranking the expected alloy performance the number of materials to be tested or considered can be minimized.

### AVOIDING FAILURES OF STAINLESS STEELS

Our industrial progress has been greatly dependent on the availability of AISI 304 and 316 types of stainless steels for the majority of our applications. They are readily available, easy to fabricate and proven in performance; they have served us very well. Frequently, in contrast to the behavior of carbon steel and high-nickel alloys, the mode of corrosion of stainless steel is insidious; attack can occur very rapidly and is mostly of a very localized nature. Over 70% of equipment failures encountered with stainless steels in the chemical, petroleum and other process industries are due to intergranular corrosion, stress corrosion cracking or localized attack in the form of pitting, under-deposit and crevice corrosion.

The presence of stress, mostly in the heat affected zone adjacent to welds, will accelerate intergranular corrosion on stainless steel. Titanium or columbium are frequently added to the alloy to tie up the carbon as a stable carbide and avoid harmful precipitation. Alternately, the low carbon (0.03% C max.) variety can be used without fear of intergranular corrosion developing in service subsequent to welding. For cast structures such as pumps and valves, a high-temperature heat treatment above 1800°F followed by quench cooling is commonly used to prevent intergranular corrosion.

Chloride stress corrosion cracking can occur at temperatures above 150 F. The stainless steels with 8% to 12% nickel content are particularly prone to this mode of attack. Alloys with no nickel, those with 22% Ni and over, and the duplex stainless steels are highly resistant to CSCC and have given excellent performance in the chemical industry.

The resistance of alloys to pitting and crevice corrosion is enhanced by the addition of chromium and molybdenum. An empirical formula is frequently used to rank the resistance of alloys; the pitting index is equal to the  $\%Cr + 3.3 \times \%Mo + 16 \times \%N$ . The higher the index the more resistant the alloy. For example in seawater with a chloride content of 20,000 ppm and a pH of 7.8, we find that alloys with a pitting index of 38 or above are resistant to crevice corrosion and under-deposit attack.

Figure 1 was developed to predict the usefulness of various alloys under strongly oxidizing (Scale A), intermediate (Scale B) and reducing (Scale C) conditions in acid brine solutions. This so-called "redox" potential, the pH, the chloride content and the temperature control the susceptibility of stainless steels to pitting, with high rates of attack to be expected at higher temperatures and under oxidizing conditions, and more moderate rates when reducing or intermediate conditions prevail.

As can be appreciated, the chloride level under acid conditions is extremely important in determining the alloy selection amongst the stainless steels. In recent years, because of recirculating effluent water being used for wash waters, there has been a substantial build-up of chlorides in the system. In some processes it is possible to make the system more alkaline and reduce the corrosivity.

#### SULFURIC ACID

The corrosive characteristics of sulfuric acid are well known. In the dehydrate process it is used either in concentrated form (93% or 98% H<sub>2</sub>SO<sub>4</sub>) or diluted (55% or 70% H<sub>2</sub>SO<sub>4</sub>). Figure 2 delineates the zones where the various alloys find economic use. While concentrated, cold sulfuric acid can be stored in carbon steel tanks, one may like to use Type 316 stainless steel for piping, since the design velocity for carbon steel or cast iron cannot exceed 3 feet per second. Alloy 20 is the preferred selection for valves and pumps.

Heat of dilution can raise local temperatures to levels close to boiling, beyond the capabilities of Alloy 20. Therefore, for acidulation of phosphate rock the sulfuric acid is frequently pre-diluted by mixing with recirculated phosphoric acid of intermediate concentration. Alloy G-3, Alloy C-276, karbate and teflon have been used for critical parts at the acid mixing and acid addition locations.

The presence of impurities in sulfuric acid strongly affect the performance of alloys. For example, cupric and ferric ions in solution or the presence of some nitric acid, inhibits the corrosion of stainless steels in sulfuric acid. The dashed lines in Figure 2 show the inhibiting effect of metal sulfate salts, thereby substantially extending the range of operation.

Alloy 20, Alloy 904, Alloy 825 and Alloy G-3 can handle the full range of sulfuric acid concentrations up to 150°F. They are frequently used for heaters, agitators, mixing equipment and instrumentation as they have substantial tolerance to impurities in sulfuric acid, and provide good performance in mixtures of sulfuric and phosphoric acids.

## PHOSPHORIC ACID

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Pure phosphoric acid is much less corrosive than sulfuric acid. Type 316, 317 and 317LM stainless steels can be used over the full range of concentrations up to 200 °F. Beyond this temperature, and at the higher concentrations, corrosion rates on most metals become substantial. Figure 3 delineates the zones where various alloys should be considered. Again cupric and ferric ions in solution inhibit the corrosion of the stainless steels. Halides increase acid corrosion.

Impurities, aeration, velocity and abrasion, as well as the manufacturing process, affect the corrosion characteristics in different ways. Any phosphoric acid obtained from sulfuric acid acidulation will contain free sulfuric and fluosilicic acids and traces of HF and HCl acids.

The fluoride content of the acid is very critical. Free HF, released by the heat of reaction in the digestion of phosphate rock and in the acid concentration processes, adds considerably to any corrosion problem. Fortunately, fluoride ions form strong complexes with silicon whereby the content of free fluoride is decreased through the formation of fluorosilicates. The corrosion of fluorides can also be inhibited by addition of aluminum.

Chlorides in the acid, originating from the rock and/or the wash water contamination, increase the rate of corrosion and pitting tendencies of most alloys. Caution has to be exerted when using Type 316 stainless steel above 300 ppm chlorides, as this is generally considered the useful limit.

Under abrasive or high velocity conditions, adding hardness and strength to the alloy is only useful if the conditions of adequate corrosion resistance have first been satisfied. The duplex stainless steels such as CD4MCu and cast versions of Alloy 2205 and Alloy 255 frequently have given good performance.

## WET PROCESS ACID MANUFACTURE

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More than 95% of the phosphoric acid is produced by a wet process that consist in attacking natural phosphate rock by sulfuric acid. These processes generate a lot of complex corrosion problems. The 3 major steps are:

- (1) acidulation of natural phosphates,
- (2) filtration of the slurry, and
- (3) concentration of the acid.

Alloy considerations for the above will be discussed and examples cited. Figure 4 shows a simplified flow diagram to identify the equipment and the process steps under consideration. While the corrosive conditions to be described will be mainly directly applicable to impurities contained in Florida rock, the same line of thinking and steps to be considered in upgrading in alloy selections, can be directly utilized with phosphate rock deposits elsewhere.

The non-metallics play an important role in the material to be selected, and it is recognized that first-cost economics frequently favor concrete lined with acid brick or rubber-coated steel for vessels and piping, shafts and agitators. It is the writers' aim in this article to narrow-down the choice to readily available corrosion-resisting alloys, that can be considered for critical components to provide reliability, and reduce maintenance and shutdown.

#### ATTACK OF PHOSPHATE ROCKS

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Concentrated sulfuric acid is used together with recycle acid from the filter to react with the phosphate rock, fed into the reactor as a slurry. A mixture of hydrated calcium sulfate crystals in suspension in liquid phosphoric acid of about 30% P<sub>2</sub>O<sub>5</sub> (40% H<sub>3</sub>PO<sub>4</sub>) is obtained. Secondary reactions with calcium fluoride and silica take place. Operating temperatures are 175 to 190 °F. The rock contains 3 percent fluorides, 200 ppm chlorides, 1% to 2% aluminum and iron, and 0.3% to 1% magnesium. Between 2% and 3% excess sulfuric acid is maintained in the mixture, which has a high abrasive capacity. Figure 5 shows a sketch of the isothermal reactor.

Even though the Fe<sup>+++</sup> and Al<sup>+++</sup> favor passivation of the stainless steels, the presence of halides make conditions too severe for Type 316L or 317L. Alloy 904L, Alloy 825 and Alloy 20 are common selections in the reactor system, but have proven inadequate for the acid addition piping, the main agitator, pumps and vapor phase conditions.

ACID ADDITION PIPING. The cold concentrated sulfuric acid can be handled in carbon steel or ductile iron provided flow velocities are kept at 3 ft/sec. Higher velocities will result in failures at elbows. Type 316L stainless has no such restrictions and is considered the safer selection for the piping from the sulfuric acid storage tank to the reactor. The pipe section inside the reactor where the concentrated acid is introduced into the acid slurry mixture, is exposed to temperatures close to the boiling point, because of the heat of dilution.

Problem solution: Alloy C-276 and teflon piping are the only suitable materials at the concentrated acid entry location. Silicon iron which is highly resistant to sulfuric acid dilution conditions, is appreciably affected by the presence of hydrofluoric acid.

MAIN AGITATOR AND DRAFT TUBE. Rubber-coated steel was subject to frequent repairs; Alloy 904L and Alloy 20 proved inadequate because of the severe abrasive action and elevated temperature of the corrosive slurry.

Problem solution: To resist the combined effects of corrosion and abrasion a superior corrosion-resistant alloy is required such as Alloy 904hMo or Alloy G-3/G-30. These alloys should be suitable in most cases for the shafting, the agitator blades and the draft tube. One company had rubber-coated the 904L shaft and used duplex Alloy 255 for the agitator blades, with reasonably good service.

It has been known that some phosphate rocks, high in halides and containing oxidizing metal salts as well as chlorates, can even corrode Alloy 904hMo and Alloy G-3. Figure 1 suggests the use of Alloy 625 or C-276 in this case.

PUMPS. Under the severe corrosive conditions described and with the abrasive action of the acid slurry, cast alloys such as CD4MCu and Alloy 2205 have frequently proven inadequate for the filter feed pumps.

Problem solution: the cast versions of Alloy 28, Alloy 904hMo and Alloy G have been used successfully in this application. Alternately, the cast version of Alloy 255 duplex stainless steel can be considered. The proper choice of pumps is vital to the success of the phosphate plant.

#### FILTRATION OF THE 30% P2O5 SLURRY

The phosphoric acid and by-product gypsum are separated on a horizontal vacuum table filter with wet cake discharge and 2 or 3 countercurrent washes. Filtrate pumps remove the filtrates from the separator. The cake is discharged to a gypsum slurry tank. Fig. 6 shows a diagram of the operation.

This stage of the industrial phosphoric acid production is much less corrosive, chiefly because the temperature is only 120 °F, instead of the 185°F prevailing in the reactor. The Type 316L and 317L grades have provided fair to good service. There should be concern however about under-deposit and crevice corrosion, when high concentrations of chlorides and fluorides are present. Also erosion has been a problem.

FILTER PLATES. The chloride content in the slurry is about 400 ppm and crevice corrosion is being experienced in stagnant areas of the rotating filter. Also, a number of filter plates have cracked due to cyclical strains suffered by the filter on account of its shape and rotation.

Problem solution: The duplex stainless steel Alloy 2205 has substantial better pitting and crevice corrosion resistance than Type 316 stainless steel, and with a yield strength twice that of Type 316, it also offers good resistance to erosion and to corrosion fatigue. If experience indicates that the resistance of Alloy 2205 to crevice corrosion is inadequate, then either Alloy 255 or Alloy 904 should be considered for the filter plates.

PUMPS. The duplex stainless steels (Alloy 2205, CD4MCu and Alloy 255), because of their good corrosion and erosion resistance, are also very suitable for filtrate and gypsum slurry pump applications in this service.

#### CONCENTRATION OF THE ACID

The three levels of concentration most frequently encountered are from 28 % clarified acid to 40% P2O5, from 40% to 54% P2O5 and from 54% to 70% P2O5 superacid. The first two steps are often done singly or in parallel stages. Concentration is generally performed under partial vacuum.

The first stage is usually not very corrosive and can be handled with either Type 316L, Alloy 904 or Alloy 20. The other two evaporator stages can be substantially more corrosive because the temperatures are higher, and because of the stronger influence of fluorine and chlorides. The evaporator bodies are frequently rubber-lined. Circulation is performed by a very large pump with a high rotating speed. Figure 7 shows a typical forced circulation evaporator. Fluorine scrubbing is often applied prior to evaporation to super acid.

EVAPORATOR HEATER. Two graphite tubed heat exchangers are scheduled for replacement. Concentration is from 30% to 54% P2O5. Acid temperature is 185°F; the heat is supplied by steam at 285 °F. Alloy skin temperatures reach 245°F. The chloride content is 1000 ppm.

Problem solution: Replacing graphite by alloy tubes permit longer runs without cleaning, higher velocities and it eliminates breakages of brittle tubes. There is a choice in selection: Alloy 28, Alloy 904hMo and Alloy G-3, with a progression of slightly increasing cost and somewhat better performance.



While Alloy 28 has many successful heater applications, the effects of chlorides and fluorides can be very pronounced, making it necessary to control the corrosion by adjusting the redox potential through addition of Mg, Mn and/or Si.

When higher levels of chlorides are being encountered (2000 ppm and over), and more elevated temperatures (270 °F), it appears desirable to specify Alloy G-30. Alloy G-30 has been recently developed and is a 30%Cr-5%Mo modification of G-3, with better corrosion and pitting resistance in phosphoric acids than G-3. It is offered at a comparable price.

EXCHANGERS FOR 70% P2O5 SUPER ACID. Because of the higher temperatures and higher concentrations being encountered the choice has essentially narrowed down to Alloy G-30 and Alloy 625. There have been a number of successful applications in the U.S. and Europe in Alloy G-3 and Alloy 625.

COST ANALYSIS FOR EVAPORATOR HEATERS. In a recent study Haynes International compared the fabricated cost for a heat exchanger containing 359 tubes of different alloys, 1.5" OD x .083" wall x 18' length. The evaporator was designed for a circulation rate of 10,000 gpm and an acid-feed rate of 100 to 125 gpm. Cost ratios were expressed relative to 316L = 1. They were:

for Alloy 904L:	1.8	for Alloy 28:	2.3
Alloy 904hMo:	2.3	Alloy 825:	2.3
Alloy G-30:	2.5	Alloy 625:	2.9

RECIRCULATION PUMPS. An in-line forced circulation pump made of Alloy 20 suffered early failure in evaporator service handling 54% P2O5, which contained chlorides and fluorides. The pump was attacked by gypsum particles that had not been retained by the filter. It was replaced with Alloy 255 duplex stainless to resist the corrosion as well as abrasion action. Again poor performance was experienced.

Problem solution: Since the recommendation for heat exchanger tubulars in this application is Alloy 904hMo or Alloy G-3, one must select for the pump an equivalent or better corrosion resistant alloy. The duplex stainless steel Alloy 255 cannot resist the abrasive conditions because it has inadequate corrosion resistance for the application. A cast version of Alloy 904hMo (Alloy IN-862) or cast Alloy 625 would be expected to give excellent service here. An alternate selection would be Lewmet 25 (29Cr-38Ni-4.5Mo-3Cu) which has given good performance in axial flow propeller pumps for forced circulating evaporators. Lewmet 25 has a pitting index of 44, similar to Alloy G-3, and offers good strength and hardness.

FLUORINE RECOVERY SYSTEM. The fluorine scrubbers are invariably rubber-lined. The strength of the solution is 15% to 25%  $H_2SiF_6$ . The tower is separated from the phosphoric acid concentration unit. A problem was encountered with the materials for the sprays inside the scrubbing towers, piping and nozzles. In some designs Monel alloy 400 (UNS N04400) has performed well, while in others it severely corroded.

Problem solution: Alloy 400 and 70-30 copper-nickel are satisfactory, provided a separator is used to prevent P2O5 entrainment. When the P2O5 in the solution exceeds 0.14% there is rapid attack on Alloy 400. In systems where all concentration vapors are passed through the fluorine scrubber, there is sufficient P2O5 entrainment to reach 1% to 2% concentration in the fluosilicic acid solution, and it is recommended to use Alloy G-30 or Alloy C-276. Also non-metallics such as teflon and Kynar pipe can be utilized.

#### MISCELLANEOUS ALLOY APPLICATIONS

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The following problems and questions were raised during a PHOSPHATE FERTILIZER INDUSTRY WORKSHOP held by the Nickel Development Institute in Lakeland, Florida on 17 November, 1988. This Materials Engineering Workshop dealt with many aspects of alloy selection, the effects of impurities in phosphoric and sulfuric acid solutions, abrasion and velocity effects, fabrication and welding guidelines, and numerous day-to-day maintenance problems being experienced in the industry. A number of these will be cited.

Question 1. What are some of the problems with welding duplex stainless steels, Alloy 2205 and Alloy 255?

Answer: Autogenous welds frequently result in over 80% ferrite with low ductility. In order to obtain a duplex structure in the desired 40-60% ferrite/austenite range, the material should be heat-treated at 2000 to 2100 °F, followed by a fast cool to avoid sigma and chi phases and 885 °F embrittlement. Alternately, one can use filler metals with 8-10% nickel content versus the 5-6% Ni in the alloy, and obtain 40-60% ferrite and good ductility without heat treatment. Our guide for welding duplex stainless steels is as follows: 350 °F max interpass; high heat input preferred; avoid moisture in the coating and hydrogen in weld; avoid high base metal dilution; use nickel-enhanced welding rods.

Question 2. What are generally considered the upper temperature limits of the non-metallics in phosphoric acid?

Answer: 150 °F seems the upper temperature for rubber-lined equipment, while karbate has been used in boiling phosphoric acid. A summary of published findings is shown in Table 2.

Question 3. At what concentrations do free fluorides start increasing the corrosion rates of stainless steels, and how much silicon addition is needed for inhibition?

Answer: Free fluoride concentrations in excess of 2000 ppm substantially increase the rate of attack on Type 316L stainless in 30% P2O5. Fig. 8 indicates that a Si/F ratio of 2 will suppress the influence of free fluorides. Aluminum will also suppress the corrosion by fluorides, but is not as effective as silicon. Fig. 9 shows that the reactor problem is related to the combined effects of free fluorides and excess H2SO4, which should be kept as low as possible.

Question 4. Do cast alloys have the same chemical compositions as the corresponding wrought alloys? And how do I make sure to get a quality casting?

Answer: The composition of cast grades differs from the wrought equivalent to improve fluidity in the mold, reduce shrinkage, and minimize hot tears and cracks. It is therefore desirable to specify the American Casting Inst. designations as shown in Table 3, to get the proper composition. Mechanical properties and quality is assured by specifying ASTM A743/743M and asking for 0.03% C max. ASTM A744/744M can be used with the higher carbon grades, since it does include post weld heat treatment after repair. For best performance the molybdenum-containing alloys will require a solution anneal at 2000-2050 °F.

Question 5. Is the addition of an oxidizing substance always beneficial in improving the performance of a stainless steel?

Answer: In many cases, the addition of trivalent iron or manganese has been beneficial in extending the performance of Type 316L and the specialty stainless steels, as it shifts the electrochemical (redox) potential to passivity. It has been frequently used in phosphoric acid and sulfuric acid systems when corrosion is accelerated by temperature or by the presence of 200-300 ppm of chlorides (refer Fig. 2). Also nitric acid has been used as an oxidizing substance.

Special caution is recommended, since in recent years, because of recirculation of waterwash, the chloride levels encountered may have increased to 700 - 2000 ppm. If the oxidizing substances shift the system from Scale C to Scale B (refer Fig. 1), the stainless steels will become much more susceptible to pitting and crevice corrosion.

Question 6. Stainless steel and rubber-covered impellers of exhaust fans handling gases from the digesters have suffered repeated failures. What alloy should be considered?

Answer: The gases probably contain moisture, P2O5 entrainment and fluorides. Temperatures are 160-175 °F. High tip speeds, vibration and centrifugal stresses contribute to

the failures. Good performance would be expected from Alloy 625 because of its good corrosion resistance, strength and excellent fatigue properties. Alternately, the exhaust fan can be installed after the scrubber, instead of ahead of it. The temperature would be lower, probably 120°F, and the corrosive conditions much less severe. Type 316L stainless steel would be suitable under these conditions.

Question 7. Hot cracking failures and preferential corrosion in the heat affected zone has been experienced with Alloy 904L and Alloy 904hMo under severe corrosive conditions.

Answer: It is important to use the right welding filler metal. It should achieve 2% to 8% ferrite in the weld deposit to minimize cracking as the weld metal cools. Heat input should be kept low to prevent the formation of detrimental intermetallic chi and sigma phases. Further, segregation of alloying elements during solidification of the weld metal can result in molybdenum depleted zones, more susceptible to corrosive attack than the base metal.

The solution has been to upgrade to a filler metal with a higher Mo content, sufficient Cr to maintain a level of corrosion resistance equal to the base metal, and sufficient Ni to minimize the depletion effect. SMAW welding rods Hastelloy G-3 and Inconel 112 (Alloy 625) are frequently used for the welding of respectively 904L and 904hMo. Proper filler metal selection and good joint preparation will enhance the properties of the weld deposit.

Question 8. For the acid coolers in the sulfuric acid plant we are considering Type 316 stainless steel tubing. Is this the right alloy selection?

Answer: Type 316 can be used, provided it is placed under anodic protection. This is a strong oxidizing environment for which non molybdenum-containing alloys are preferred. There is a very narrow concentration zone where Type 304 stainless steel can be considered. Improved reliability can be obtained with Type 309 and Type 310 stainless steels, because of their higher chromium content. In recent years several high-silicon stainless steels have been developed, designated here as 18/18Si, that have given excellent corrosion resistance. Fig. 10 shows the limits of usefulness of these alloys and the narrow "window" in the acid absorption-cooling cycle. The new 18/18Si alloy is also very suitable for the absorption tower and piping system.

Question 9. Are there any other new developments in alloy choice and fabrication methods that should be considered by the phosphate industry?

Answer: Great progress has been made with the newer duplex stainless steels 2205, 2507 and 255 which have almost entirely replaced Type 329 stainless steel and CD4MCu.

They have a corrosion resistance superior to Type 316L and Type 317L, with twice the yield strength and very good erosion and abrasion resistance.

The Cr-Ni-Mo alloys meet the need for good resistance to oxidizing as well as reducing conditions. The 20Cr/25Ni/6Mo alloys are now readily available in tube, pipe, sheet and plate under various trade names such as 904hMo, AL-6XN, and 25-6Mo. In phosphoric acid they offer a corrosion resistance superior to the duplex alloys as well as to Alloy 904L, Alloy 20 and Alloy 825, and they are very cost-effective.

For the most severe applications consider the Ni-Cr-Mo alloys. In addition to Alloy G-3, Alloy 625 and Alloy C-276 there are now two new materials: Alloy G-30 and C-22. The modifications are very helpful in phosphoric acid systems, since they are more capable in handling halides as well as oxidizing impurities. Also they offer a higher pitting and crevice corrosion resistance. G-30 especially should be attractive as it has excellent properties at a reasonable price (refer page 9, comparing cost of evaporator heaters).

Much work has been carried out in making alloy clad steel and alloy liners in carbon steel vessels, ducts and piping more economical. Various techniques such as "wall papering" (sheet lining), co-extrusion and weld-overlay have substantially reduced the relative cost of solid alloy fabrication versus carbon steel with rubber and neoprene liners. Also various hard-facing materials are available for building up worn parts of agitators and pump impellers.

#### CONCLUSION

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Traditionally, corrosion resistant alloys beyond Type 316L were used as a last resort when protective coatings, plastics and rubberlined steel components proved to be inadequate. Presently specialty stainless steels and nickel-base alloys are increasingly applied in the phosphoric acid industry, whose aim it is to provide high reliability and cut back on unscheduled shutdowns and maintenance. Increased safety and reduction in air and water pollution are additional advantages.

Of interest is a 1984 EPRI study which shows cost comparisons for sheet lining and roll-bonded Alloy 625 and C-276, for solid Alloy 904L and Type 316L and for non-metallic linings for absorbers and ducting in flue gas scrubbers. Their findings included the cost of fabrication and maintenance over 30 years, are summarized in Fig. 11. Specialty alloys should no longer be considered as "exotic".

The performance of alloys depend to a large extent on an understanding and control of the impurities contained in the phosphate rock. Knowing when to use Type 316L, Type 317L and Type 317LM stainless steels and when not to, is crucial. The Cr-Ni-Mo and Ni-Cr-Mo have consistently offered reliable performance, since they work well in oxidizing as well as reducing media. Figures 1, 2 and 3 "rank" these alloys.

Obviously, in every system there is a relation between the desired redox potential and the minimum pitting index. The figures provided in this article are intended as a guide. Only experience and exposure of test coupons will confirm the desired, minimum alloy selection to resist the corrosive effects of the phosphate system.

Unfortunately, in many of the applications one has to superimpose the effects of erosion and abrasion. Providing hardness and strength is insufficient, unless conditions of adequate corrosion resistance have first been satisfied. Alternately, a higher level of corrosion resistance must be offered for agitators and mixers than for the vessel walls.

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**TABLE 1**  
**Some Stainless Steels and Nickel-Chromium Alloys Used**  
**in the Phosphate Industry**

Generic name	316L	317LM	2205	904 Stainless Steels	904NiMo	28	20	825	G-3 Nickel-Chromium-Molybdenum Alloys	C-276 Nickel-Chromium-Molybdenum Alloys	625 Inconel
UNS DESIGNATION	S31603	S31725	S31803	N08904	N08925	N08028	N08020	N08825	N06985	N10276	N06625
Tradenames and comparable products			SAF 2205	904L 2PK65, JS700	254SMo AL-6X	Sanicro 28	Carpenter 20Cr-3	Incoloy 825	Hastelloy G-3	Hastelloy C-276	Inconel 625
Chemical composition (nominal analysis, %)											
C max.	0.03	0.03	0.03	0.02	0.02	0.02	0.03	0.025	0.015	0.015	0.10
Cr	17.5	18.0	22.0	20.5	20.5	27.0	20.0	21.0	22.0	16.0	21.5
Ni	13.5	13.0	5.0	25.0	25.0	31.0	37.5	42.0	48.0	57.0	61.0
Mo	2.75	4.5	3.0	4.7	6.0	3.5	2.5	3.0	7.0	16.0	9.0
Cu	—	—	—	1.5	1.0	1.0	3.5	2.5	2.0	—	—
N	—	0.14	0.15	—	0.12	—	—	—	—	—	—
Cb/Ta	—	—	—	—	—	—	0.3	—	0.3	—	—
Others	—	—	—	—	—	—	Cb	Al, Ti	Co	Ti	Al, Ti, Co
Pitting Index	26	32	32	36	40	38	28	31	43	N/A	51
Tradenames:	Carpenter; Carpenters Technology Hastelloy G-3 and C-276; Cabot Corporation 904L; Uddeholm 254SMo; Avesta										
Tradenames:	2PK65 and Sanicro 28; Sandvik AL-6X; Allegheny Ludlum JS 700; Jessop Steel Inconel 625 and Incoloy 825; Inco Alloys International										

**Guide to Cost of Stainless Steels and  
Nickel-Chromium Alloys**

FORM	S31603	S31725	S31803	N08904	N08925	N08028	N08020	N08825	N06985	N10276	N06625
Plate	1.0	1.4	1.4	2.0	2.6	2.6	2.8	2.8	4.0	6.8	5.9
Tube (sm/s)	1.0	1.2	1.2	1.6	2.2	1.8	—	2.2	3.5	5.0	4.3
(w/d)	0.5	0.6	0.6	1.3	—	—	1.8	1.8	2.1	3.8	3.3



Table 2

TEMPERATURE LIMITS OF NON-METALLICS IN 85% IMPURE PHOSPHORIC ACID	
Teflon	up to 500 <sup>o</sup> F
PVC	140
Polyethylene	120
Saran	150
Karbate	Boiling
Soft rubber	150
Hard rubber	160
Butyl rubber	150
Neoprene	160
Haveg 41	250
Penton	250
Carbon & Graphite	500 plus
Durcon	200

Table 3

COMPARABLE CAST AND WROUGHT ALLOYS	
<u>WROUGHT</u>	<u>CAST</u>
TYPE 316L SS	ACI CF-3M
TYPE 317 SS	ACI CG-8M
CARPENTER* alloy 20Cb-3	ACI CN-7M
INCOLOY* alloy 825	
JESSOP JS700, 904L	
ALLOY 904hMo	IN-862
ALLEGHENY LUDLUM* AL-6X	
HASTELLOY* alloy-G	Remelt Alloy G Cast Alloy 625
* Tradenames	

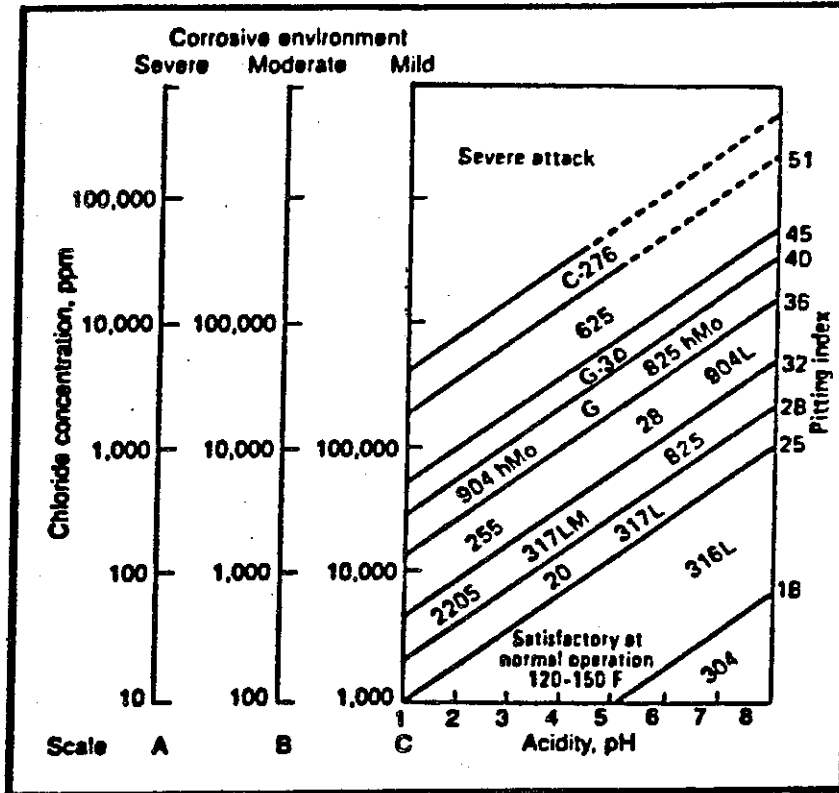


FIGURE 1.  
 Susceptibility of corrosion resisting alloys to pitting and crevice corrosion in a warm acid brine. Scale A represents a highly oxidizing medium, Scale B intermediate, and Scale C a strongly reducing medium.

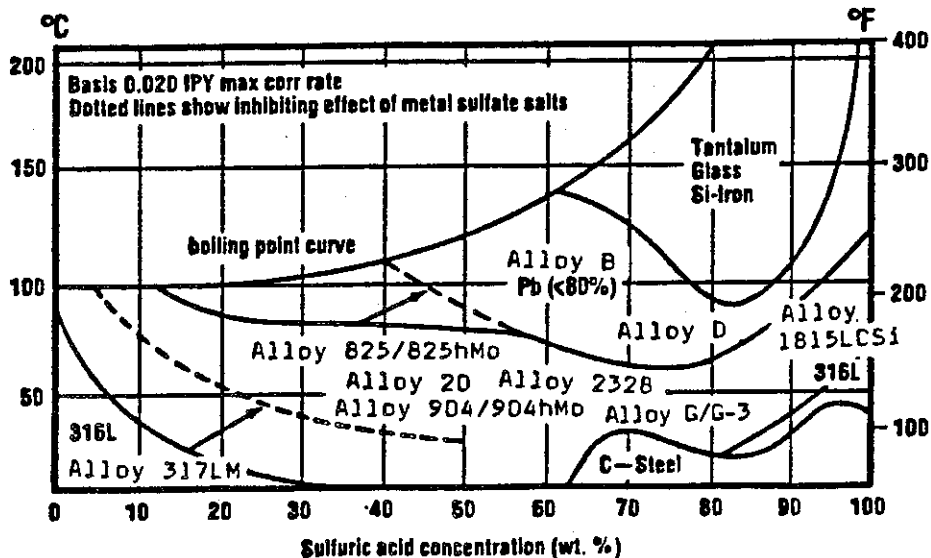


Figure 2. Sulfuric acid—alloy selection chart

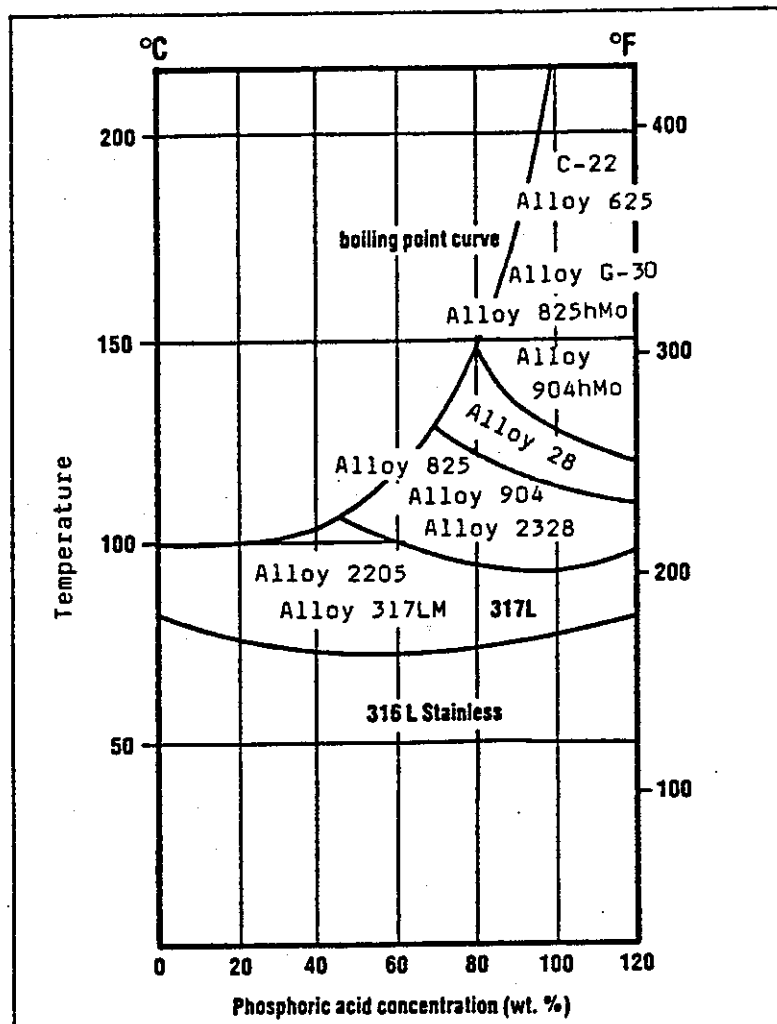


Fig.3 Phosphoric acid—alloy selection guide

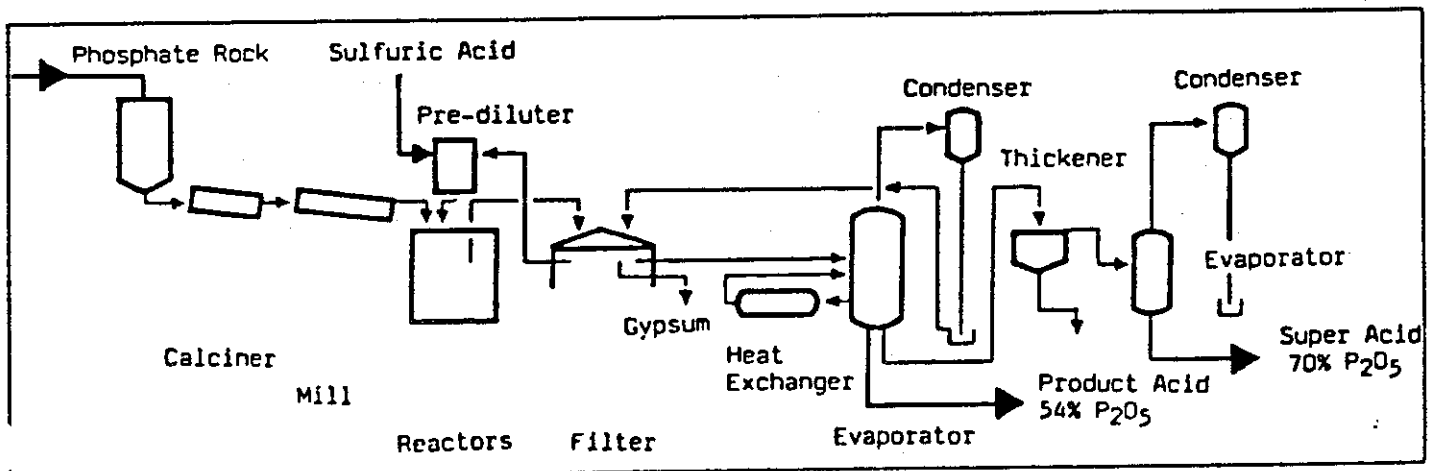


FIGURE 4  
Flowsheet for the Manufacture of Phosphoric Acid by the "Wet" Method

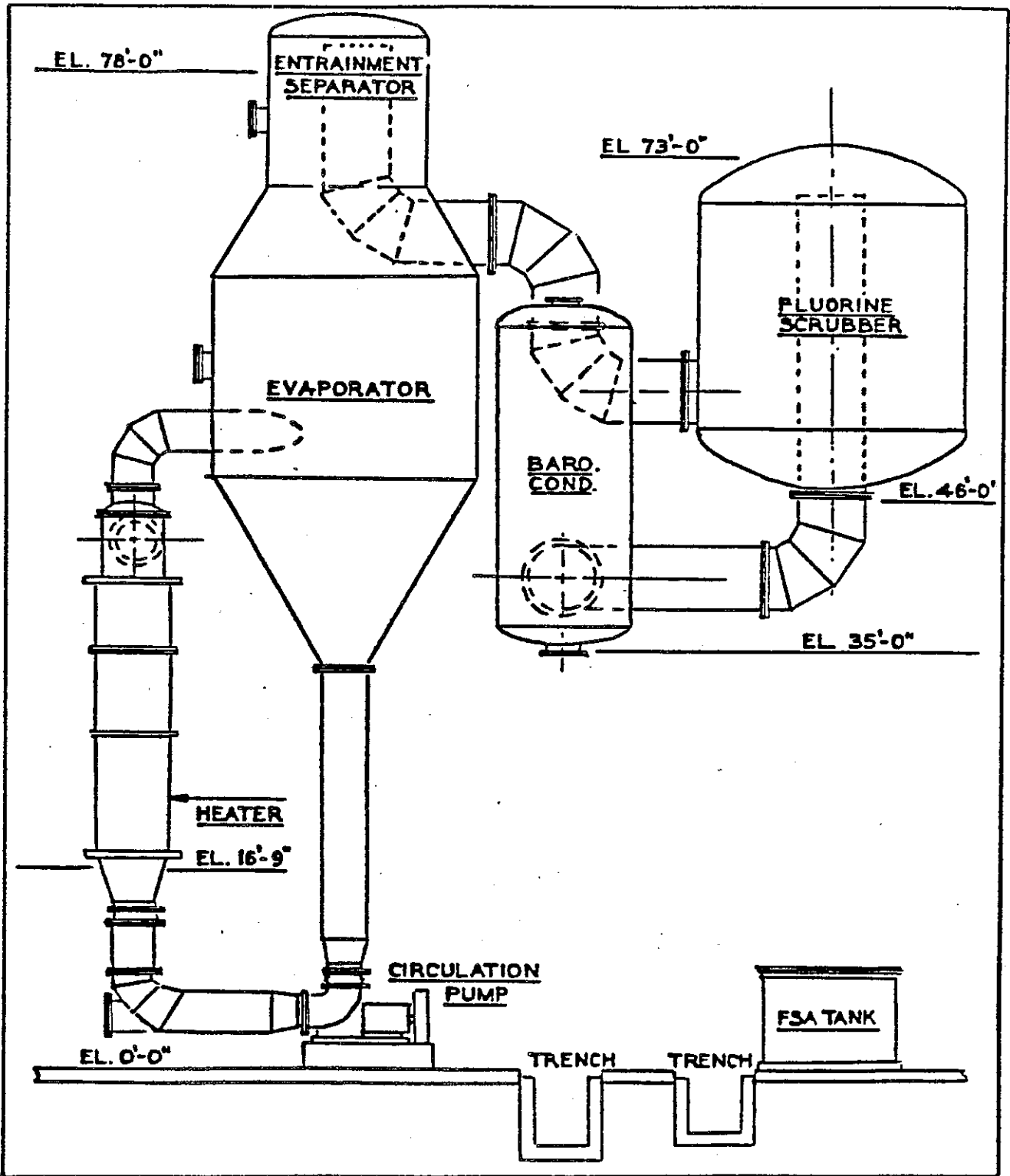


Figure 7. Forced Circulation Evaporator

Fig. 8 - Inhibition of fluorides by silicon and aluminum

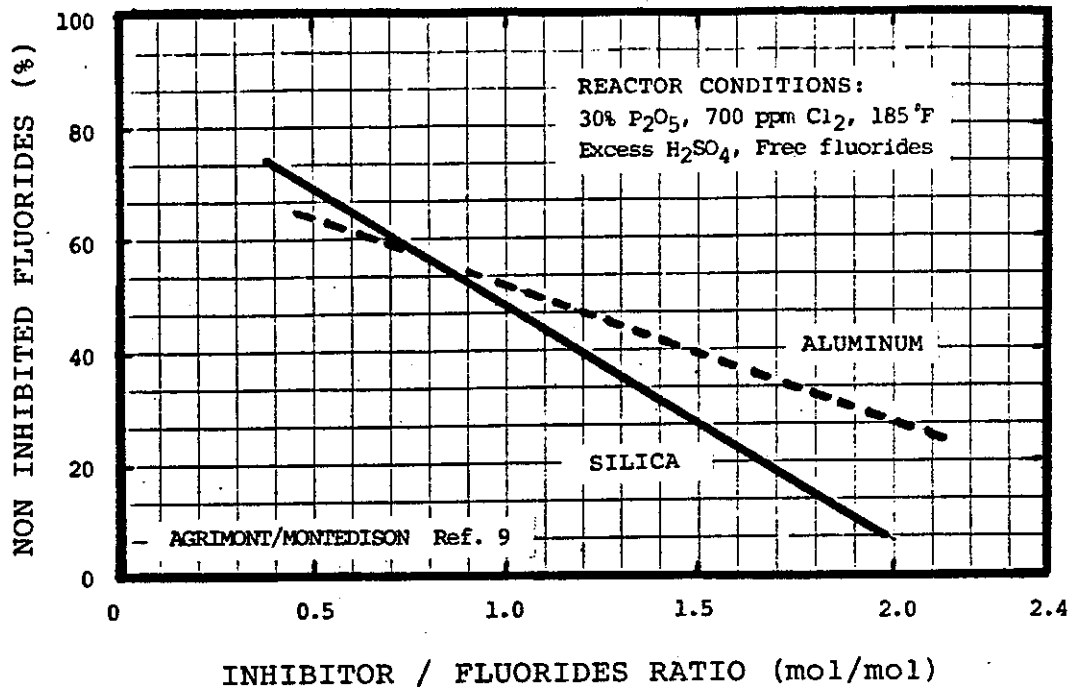
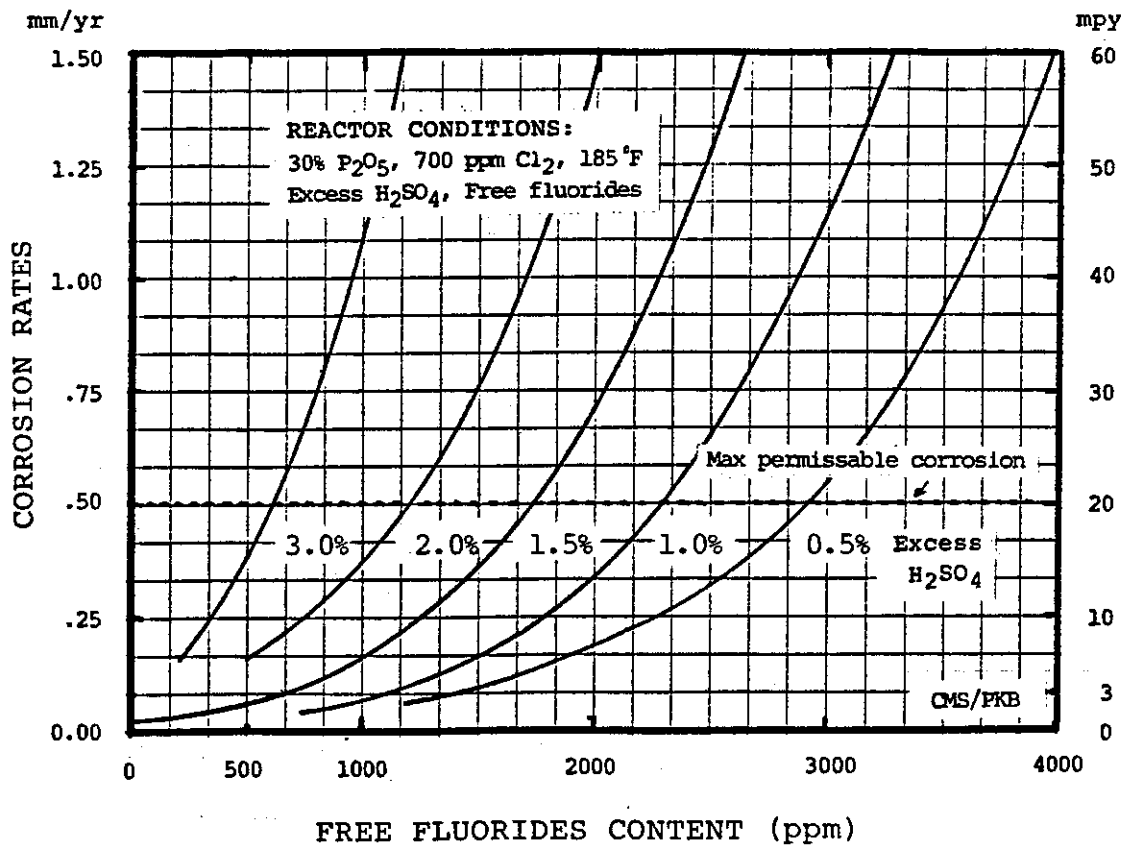


Fig. 9 - The effect of free fluorine and excess sulfuric acid on the corrosion rate of AISI Type 316L in the reactor



CORROSION RATES IN ABSORPTION TOWER ENVIRONMENT WITH 99% SULFURIC ACID AT 220 - 240°F					
Alloy	Corrosion Rate (mpy)	Composition %			
		Cr	Ni	Mo	Si
Type 304L	0.8	18	8	-	-
Type 316L	2.2	17	12	2.5	-
Type 310	0.4	25	20	-	-
Type 18/18Si	0.2	18	18	-	5.5
Alloy 904L	6.8	20	25	4.5	-
Alloy 20Cb-3	3.2	20	34	2.5	-
Alloy C-276	12.6	15	57	16	-
Alloy B-2	.91	-	70	28	-

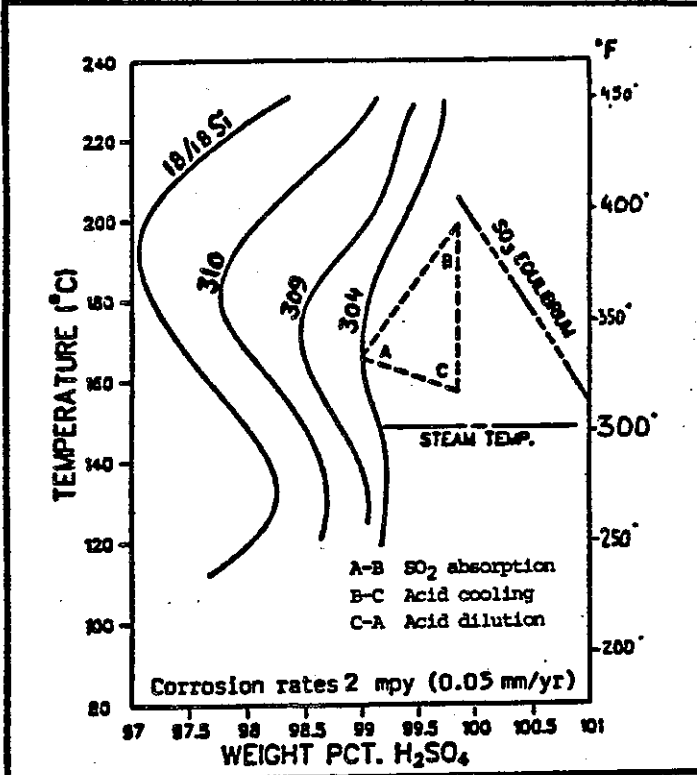


Figure 10 - Comparative iso-corrosion curves of various stainless steels in highly concentrated sulfuric acid.

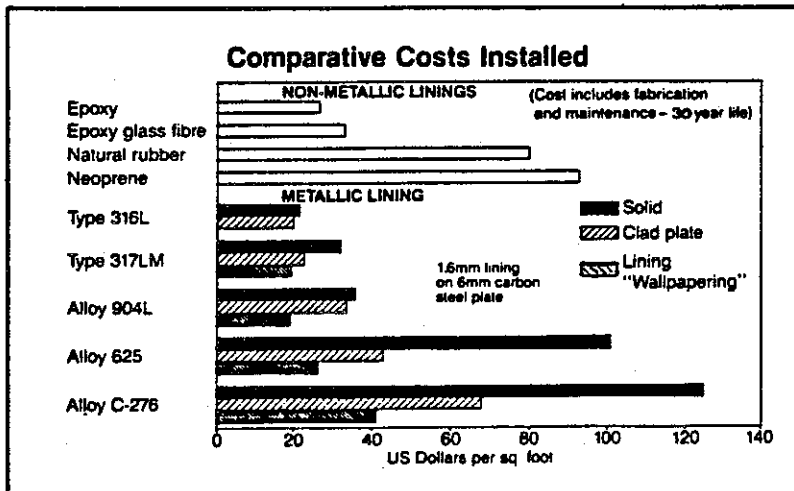


Figure 11 - Comparative installed costs