

HASTELLOY® alloy G-30 and FERRALIUM® alloy 255
The Cost Effective Answers to Corrosion/Erosion
Problems in Wet Phosphoric Acid Production

by

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Abstract

A recent trend in the manufacture of phosphoric acid has been to steadily increase the concentration of the final product. This has involved the use of higher temperatures for processing. This has also led to increased production rates in certain cases. More stringent pollution control requirements have further necessitated the use of closed loop recirculating systems increasing the severity of these corrosive environments.

Many corrosion-resistant materials of construction, both metallics and non-metallics, are used in phosphoric acid plants. Since corrosive conditions vary widely in different parts, the selection for the most cost effective material for a particular component becomes very important. Some of the corrosive/erosive areas are digesters or attack tanks, the associated agitator shaft assembly, the filter section, the recirculating slurry pumps, piping, valves and the concentrator units.

This paper presents data on two alloys: one is relatively new, a high chromium-nickel-base alloy, known as HASTELLOY alloy G-30; while the other is a high chromium, super duplex stainless steel known as FERRALIUM alloy 255. Some laboratory tests data are presented as well as, field tests data, economic comparisons to various other materials of construction and some applications history. The data show that these two alloys are not only providing reliable solutions to the corrosion/erosion problems during wet phosphoric acid manufacture, but have the potential for significantly reducing maintenance costs, hence providing the lowest uniform annual cost.

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INTRODUCTION

Wet phosphoric acid manufacturing consists of a series of operations with severe corrosion/erosion problems. Erosive environments are created by the presence of particulate matters from phosphate rock and gypsum solids, moving at high velocities caused by process, agitation and turbulence. Even though pure phosphoric acid is significantly less corrosive than sulfuric acid, wet process acid can vary widely in its corrosivity. This is primarily a function of the source of phosphate rock, the produced acid concentration, the degree of impurities in the rock and the temperature. It has been shown⁽¹⁾ that the corrosivity of wet process phosphoric acid is quite complex and presence of impurities such as chlorine, fluorine, silica, aluminum, iron, magnesium, calcium or sodium can dramatically affect the active/passive behavior of metals and alloys. The aforementioned impurities are present as complex salts and compounds and can either be detrimental or beneficial. Due to this, the metallic materials of construction in a plant can range from standard austenitic stainless steels to the more corrosion-resistant, 20 type alloys and duplex super stainless steels or even to high performance alloys of the Ni-Cr-Mo family. Table 1 presents the chemical compositions of the various alloys which are being used in wet phosphoric acid plants.

In the initial manufacturing stage, phosphate rock is digested in attack tanks with sulfuric acid. Agitator mechanisms (shafts and blades) in liquid phase, made of FERRALIUM alloy 255 have given excellent performance at many plants due to its superior resistance to both uniform and localized forms of corrosion such as pitting, crevice and chloride stress corrosion cracking. In addition, the superior erosion and abrasion resistance of this alloy has been put to good use in handling acid slurry via recirculating pumps. Corrosion and erosion data for FERRALIUM alloy 255 is presented later in this paper.

The other major corrosive areas in the wet phosphoric acid process are the concentrators or evaporators and coolers where heat exchangers are used to concentrate the 28% - 32% P_2O_5 to 54% and then to 70% P_2O_5 super phosacid. Traditionally these forced circulation evaporators have been made of impervious graphite due to the severe corrosivity at high temperatures and impurities present in the acid. Even though the graphite has performed well from a corrosion standpoint, scaling necessitates subsequent cleaning which involves severe thermal and mechanical shock often resulting in tube breakage.

HASTELLOY alloy G-30, a new alloy, is "tailor-made" for this service and presents a great improvement over other alloys of the Ni-Cr-Mo family. It can provide a cost effective answer to the graphite heat exchanger problems. This alloy is also being tested for other areas and has shown two to ten times better corrosion resistance than HASTELLOY alloys G/G-3 and alloy 625. It also has better overall corrosion resistance than any of the nickel-base alloys tested to date.

Later sections in this paper present corrosion data and economic comparisons involving this alloy.

FERRALIUM alloy 255

Although standard austenitic grades of stainless steel have been extensively used for many phosacid components such as piping, filters and pumps, they have suffered from pitting/crevice corrosion and chloride stress corrosion cracking.

It has been established by many laboratory experiments and field tests that high chromium content alloys are essential for good general corrosion resistance to the wet phosphoric acid which is oxidizing in nature^(1,2). Furthermore, molybdenum and nitrogen in combination with chromium improve localized corrosion resistance. FERRALIUM alloy 255 (Table 1) is a high chromium containing, ferritic-austenitic duplex stainless steel which has shown superior corrosion resistance over both standard austenitic stainless steels and the 25Ni-20Cr family alloys.

Corrosion and Erosion Resistance

FERRALIUM alloy 255 has excellent uniform corrosion resistance as shown by the isocorrosion diagrams in both reagent grade phosphoric acid and sulfuric acid (Figures 1 and 2). Even though the usefulness of this data is limited due to the presence of many impurities in plant acids, actual field tests in various locations of the wet phosacid plant in attack tanks, holding tanks, etc., confirm the superior performance of this alloy. Table 2 presents the actual field trials conducted in the initial stages of wet phosacid manufacture. The data show very low corrosion rates for the alloy. Table 3 presents some laboratory data in comparison to type 316SS where additions of chloride ions greatly increases the corrosion rate of type 316SS without affecting FERRALIUM alloy 255.

Comparison of localized corrosion resistance and superiority of alloy 255 over other materials is clearly demonstrated in many tests as shown in Tables 4, 5 and 6. Similarly the stress corrosion cracking resistance superiority over type 316SS is shown in Table 7.

The superior abrasion resistance of this alloy was demonstrated in a dry sand and rubber wheel abrasion test conducted per ASTM G65-80. The data are presented in Table 8. Cavitation erosion tests also confirmed the superiority of alloy 255 as shown in Figure 3.

Both the corrosion and erosion resistant properties, along with its high strength, have led to many successful applications as agitator shafts and blade assemblies and recirculating slurry pumps at many plants as shown in Figures 4 and 5.

HASTELLOY alloys G/G-3/G-30

These alloys belong to the Ni-Fe-Cr-Mo-W-Cu family. Even before the development of alloy G-30, which was specifically designed for wet phosacid applications, the older versions of alloys in this family, alloy G/G-3 had given good performance in this industry over the past ten years. This is shown by the excellent performance of an alloy G draft tube installed in 1975 in a Swenson Isothermal Reactor at Farmland Industries in Bartow, Florida. An inspection of this unit in 1983 indicated that this component should last the life of the plant⁽³⁾. At this same location, an evaporator made from alloy G is used to produce super phosphoric acid. The heat exchanger bundle contains nearly 26,000 feet of 1.5" O.D. x .072" wall of tubular products where the original bundle gave over five years of service. A new unit with .095" wall was installed in 1981 and is still in use. Other successful components applications with processing parameters are described elsewhere⁽⁴⁻⁵⁾. Many other plants have successfully used alloy G to solve their corrosion problems.

HASTELLOY alloy G-30

To improve further on the corrosion resistance of alloy G, a major research effort was undertaken at Haynes International, Inc. Since the corrosivity of the wet phosphoric acid produced at different locations varies widely due to the presence of free sulfuric acid, hydrofluoric acid, chloride ions, ferric ions, SiO_2 , Al_2O_3 , H_2SiF_6 , H_3AlF_6 and other impurities, an understanding of the role of various alloying elements was important. The knowledge that wet phosphoric process streams are oxidizing in nature with the presence of free sulfuric acid, an alloy with very high chromium content and some copper was a must. Furthermore, since halide ions impurities in the form of chloride and fluoride are encountered, the presence of molybdenum and tungsten, to combat localized attack, also became critically important. For making the alloy cost effective, an iron addition was needed. This along with extensive testing led to the development of HASTELLOY alloy G-30, an Ni-30Cr-15Fe-5Mo-2.5W-1.5Cu alloy. This alloy shows a better corrosion resistance than SANICRO® 28 which has about the same chromium level but lower molybdenum and no tungsten and much lower nickel. Since the molybdenum and tungsten help reduce corrosion against reducing species such as free H_2SO_4 and HF, the corrosion rate of alloy 690 (same chromium content but no moly or tungsten) is much higher than that of alloy G-30. Tables 9 and 10 clearly demonstrate this.

Corrosion Resistance of HASTELLOY alloy G-30

Hundreds of tests have been conducted in wet phosphoric acids obtained from various companies throughout the world. The tests consisted of both laboratory environments utilizing plant acids and field tests in plants via test coupons and test racks. The results clearly show that alloy G-30 has two to ten times better corrosion resistance than alloy G/G-3 and alloy 625 (depending on the specific phosphoric acid involved) and has better corrosion resistance than any of the other nickel-base or iron-base alloys.

Since wide variations in the corrosion rate are possible in acids of the same concentration, but from different sources, it is important to compare the corrosion rates of alloys tested in the same acid at the same time. Figure 6 clearly shows alloy G-30 to be superior to alloy G-3 which is already an improvement over alloy G. Figure 7 shows the ratio of corrosion rates of alloy G/alloy G-30 for various testing conditions. As is evident, in mild corrosive environments (corrosion rate of alloy G is less than 10 mpy), both alloys show low corrosion rates. Alloy G-30 has less than one-half to one-tenth the corrosion rate of alloy G. In the intermediate to high corrosivity range (corrosion rate of alloy G in the range of 10 to 100 mpy), alloy G-30 exhibits one-half to one-fifth the corrosion rate of alloy G. Similar comparison with alloy 625 is shown in Figure 8. Here again, alloy G-30 is two to ten times better.

Some other laboratory data, comparing the corrosion resistance in 54% P_2O_5 acids from two different manufacturers at 116°C, are shown in Figure 9. Alloy G-30 had the lowest rate when tested against alloy G-3, alloy 625 and SANICRO 28 alloy. Figure 10 shows the similar comparison among the four alloys at 149°C and 116°C in 54% P_2O_5 from one source.

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Again alloy G-30 had the lowest corrosion rate in all cases. While high chromium alloys are expected to perform well in oxidizing wet phosphoric acid, the presence of residual chlorides, fluoride and reducing species, make molybdenum and tungsten contents very important. This has been clearly demonstrated by the superior corrosion resistance of alloy G-30 over SANICRO 28 and alloy 690.

Table 11 shows the corrosion rates of the same four alloys in a variety of commercial phosphoric acids obtained from several plant sites under different conditions. Again alloy G-30 had the lowest corrosion rate of all the alloys tested.

Quite a few wet phosacid manufacturers have conducted tests with alloy G-30 and, as a result, have specified it for tubulars for their concentration units. Others have had some success in certain components of their fluoride plants while some are conducting trials for evaluating its performance as a material of construction for attack tanks.

ECONOMICS

Any economic analysis must not only take into account the original material of construction but must consider the total installed first cost which is the sum of material, fabrication and installation costs. Equally important consideration must be given to the total "life cycle" costs which may consist of maintenance costs over the life of a component, lost revenues from unscheduled shutdowns, time value of money, depreciation, taxes and many other factors. Even though a material cost differential can be four to eight times, when compared to type 316L SS, the total installed cost may only be two to four times depending on the complexity of fabrication⁽⁶⁾.

Annual Cost Calculations

Many techniques exist for economic appraisal of alternate materials of constructions for heat exchangers. These include return on investment, payback period, and the discounted cash flow methods. The last method gives a measure of present worth after taxes and equivalent uniform "annual cost". NACE Standard RP-02-72 describes a method of calculating the latter which is used here for demonstration purposes. Table 12 gives the installed cost of various heat exchanger units utilizing alloy G-30, SANICRO 28 and impervious graphite tubes. Some of the installed cost numbers, life expectancy assumptions, interest rates and depreciation schedules are shown in Table 13. Using the interest rate and depreciation schedule of NACE Standard RP-02-72 and the other financial assumptions, the uniform annual cost is calculated and is shown in Table 13.

It is evident from this table that the lowest uniform annual cost is for graphite. However, if the annual maintenance cost increases or production loss occurs due to graphite tube breakage, then HASTELLOY alloy G-30 becomes the more economical choice. A quick calculation shows a one time production loss occurring in the second year must not exceed \$50K or an annual production loss must not exceed more than \$8K for alloy G-30 to become more economical. One can conduct many sensitivity analyses to suit his own particular situation, but to make any valid comparison, the total life cycle costing must be equated to a common denominator.

At some plants even though the graphite heat exchangers give the lowest uniform annual cost, the attractiveness and benefits of metallic tube heat exchangers make a very strong case. This is particularly more relevant now with the new alloy G-30 which has very low corrosion rates in wet phosacid environments.

CONCLUSIONS

- Alloy G-30 has the lowest corrosion rate over all the nickel- and iron-base alloys tested in various wet commercial grades of phosphoric acid.
- The superior mechanical strength, fabricability and ease of cleaning make alloy G-30 tubular heat exchangers an attractive and cost-effective choice over graphite heat exchangers.
- Economic calculations show alloy G-30 provides a cost-effective solution to corrosion problems as compared to other metals. It also solves breakage problems encountered with graphite heat exchangers.
- FERRALIUM alloy 255 gives good service in the agitator shaft and blade assemblies and recirculating slurry pumps in many wet phosacid plants.

REFERENCES

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Table 1

Typical Chemical Composition of Some Alloys Used in
Wet Phosphoric Acid Industry

<u>Alloy</u>	<u>Cr</u>	<u>Ni</u>	<u>Mo</u>	<u>Fe</u>	<u>Cu</u>	<u>Others</u>
316L	17	12	2.0	Bal	-	-
317LM	19	14	4.3	Bal	-	-
Alloy 904L	20	25	4.5	Bal	1.5	-
JS 700	21	25	4.5	Bal	-	Cb - 0.4 max
SANICRO® 28	27	31	3.5	Bal	1.0	-
CARPENTER® 20CB-3	20	33	2.5	Bal	3.5	Cb - 1
Alloy 825	21.5	Bal	3.0	29	2.5	Ti - 1
FERRALIUM® alloy 255	25	6	3.1	Bal	2.0	N - 0.17
Alloy 625	21.5	Bal	9.0	20	2.0	Cb + Ta - 3.65
HASTELLOY® alloy G	21.5	Bal	6.5	20	2.0	Cb + Ta - 2
HASTELLOY alloy G-3	22	Bal	7.0	20	2.0	Cb + Ta - 0.5
HASTELLOY alloy G-30	29.5	Bal	5.0	15	1.7	Cb + Ta = 0.7
						W - 2.5

Table 2 Phosphoric Acid Field Data for FERRALIUM alloy 255		
<u>Location</u>	<u>Media</u>	<u>Average Corrosion Rate mils per year</u>
Seal Tank	0.2% to 1.0% H_3PO_4 with some fluoride at 85°F (29°C)	2.1
Storage Tank (at top)	30% H_3PO_4 with fluoride ions at 90°F (32°C)	1.0
Holding Tank for aging (at top)	3% H_2SO_4 and 30% H_3PO_4 with some fluoride ions at 150°F (66°C)	1.7
Digester	3% H_2SO_4 and 30% H_3PO_4 with some fluoride ions at 160°F (71°C)	6.1

Table 3 Effect of Chloride Ions on Average Corrosion Rate in 28% P_2O_5 at 185°F (85°C)*		
<u>Alloy</u>	<u>Average Corrosion Rate, mils per year</u>	
	<u>No chloride ions</u>	<u>2000 ppm chloride ions</u>
FERRALIUM alloy 255	0.5-0.8	0.5-0.7
Type 316 stainless steel	3.0-4.4	110-151
*Agitated, 96-hr. test		

Table 4

**CREVICE-CORROSION DATA IN 10% FERRIC
CHLORIDE AT ROOM TEMPERATURE FOR 10 DAYS**

Alloy	Number of Attacked Crevice*	Maximum Depth of Penetration,	
		mils	mm
FERRALUM alloy 255	0	0	0
Type 317LM Stainless Steel	20	12	0.30
Alloy No. 904L	23	19	0.48
Type 317L Stainless Steel	16	77	2.0
20 Cb-3 alloy	24	76	1.9
Type 316 Stainless Steel	24	76	1.9 (Perforated)

*Maximum possible number of crevices was 24.

Table 5

**CREVICE-CORROSION TESTS
IN SIMULATED SO₂ SCRUBBER ENVIRONMENT***

Alloy	Corrosion Rate per year		Number of Attacked Crevice**	Maximum Depth of Crevice Attack,	
	mils	mm		mils	mm
FERRALUM alloy 255	0.4	0.01	0	0	0
Alloy No. 904L	57	1.4	24	6	0.15
Type 317LM Stainless Steel	179	4.5	24	10	0.25
Alloy No. 825	216	5.5	24	10	0.25

*45,000 ppm Cl⁻***, 150°F (66°C), pH 2, SO₂/O₂ (1:1) bubbled through solution.

**Maximum possible number of crevices was 24.

***0.003% FeCl₃, 0.11% KCl, 0.5% MgCl₂, 1.1% CaCl₂, 5.6% NaCl, 0.02% CaF₂ and 200g/l CaSO₄·2H₂O.

Table 6

COMPARATIVE LOCALIZED CORROSION

TEMPERATURE DATA IN OXIDIZING NaCl-HCl SOLUTION*

Alloy	Pitting Temperature,		Crevice-Corrosion Temperature,	
	°C	°F	°C	°F
FERRALIUM alloy 255	50	122	35	95
Alloy No. 904L	45	113	20	68
Type 317LM Stainless Steel	35	95	15	59
Type 317L Stainless Steel	25	77	10	54
CABOT alloy No. 825	25	77	≤ -5	≤ 23
20 Cb-3 alloy	20	68	≤ -5	≤ 23
Type 316 Stainless Steel	20	68	≤ -5	≤ 23

*4% NaCl + 0.01M HCl + 0.1% Fe₂(SO₄)₃. Based on laboratory corrosion tests at 5°C increments until onset of localized attack.

Table 7

COMPARATIVE STRESS-CORROSION CRACKING DATA

Media	Test Temp.,		Type 316 Stainless Steel	FERRALIUM alloy 255
	°F	°C		
ASTM Synthetic Seawater	176	80	No Cracks ^a	No Cracks
0.8% NaCl + 0.5% Oxalic Acid*	286	141	No Cracks	No Cracks
0.8% NaCl + 0.5% Acetic Acid*	286	141	Cracked	No Cracks
0.8% NaCl + 0.5% Citric Acid*	286	141	Cracked	No Cracks
Modified Wick Test ^{ab}	212	100	Cracked	No Cracks
25% NaCl ^{***}	393	200	—	No Cracks
30% NaCl ^{**}	Boiling		—	No Cracks
0.8% NaCl + CO ₂ *	286	141	—	No Cracks
4% NaCl + 1% H ₃ PO ₄ *	Boiling		—	No Cracks
0.8% NaCl + 0.2% H ₃ PO ₄ *	286	141	Cracked	Cracked
25% Magnesium Chloride	Boiling		Cracked	No Cracks (>1000 hrs)
30% Magnesium Chloride	Boiling		Cracked	No Cracks (>1000 hrs)
45% Magnesium Chloride	Boiling		Cracked	Cracked

^aU-bend specimen, 30-day exposure

^{**}U-bend specimen, 100-day exposure

^{***}U-bend specimen, 504-hr. exposure

—Not tested

^aLocalized attack

^b1000 ppm Cl⁻ (as NaCl) and 500 ppm FeCl₃

Table 8**COMPARATIVE RESISTANCE TO ABRASIVE WEAR***

Alloy	Orientation	Volume Loss, mm ^{3**}
FERRALIUM alloy 255	Transverse	97.5
FERRALIUM alloy 255	Longitudinal	101.9
22% Cr-Duplex Stainless Steel	Transverse	110.9
317L Stainless Steel	—	123.3
316L Stainless Steel	—	127.0

*Dry sand rubber wheel abrasion test. Tested in accordance with ASTM G 65-80.

**Average of 2 measurements.

TABLE 9

**Effect of Chromium (And Copper) on Corrosion Resistance
to Phosphoric Acid**

<u>Alloys</u>	Corrosion Rates (Mpy) 46% P ₂ O ₅ (116°C)
C-276 (16Cr)	44
625 (22Cr)	18
G (22Cr, 2Cu)	16
690 (30Cr)	5
G-30 (30Cr)	4

TABLE 10

**Effect of Molybdenum on Corrosion Resistance
to Phosphoric Acid**

<u>Alloys</u>	Corrosion Rates (Mpy) 52% P ₂ O ₅ (149°C)
690 (30Cr, 0Mo)	447
G-30 (30Cr, 4Mo)	61

Table 11

Commercial Phosphoric Acid Corrosion Data

Media	Temp.,		Average Corrosion Rate per year,			
	°F	(°C)	mils			
			G-30	625	G-3	SANICRO 28
28% P ₂ O ₅ + 2000 ppm Cl ⁻	185	(85)	1.0	1.5	0.9	31
42% P ₂ O ₅ + 2000 ppm Cl ⁻	185	(85)	0.9	1.3	11	121
44% P ₂ O ₅	241	(116)	7.0	23	22	-
44% P ₂ O ₅ + 2000 ppm Cl ⁻	241	(116)	7.9	25	22	-
44% P ₂ O ₅ + 0.5% HF	241	(116)	16	60	49	-
52% P ₂ O ₅	241	(116)	3.9	12	11	48
52% P ₂ O ₅	300	(149)	28	79	64	248
54% P ₂ O ₅	241	(116)	8	16	16	55
54% P ₂ O ₅ + 2000 ppm Cl ⁻	241	(116)	7	15	16	92

TABLE 12

Parameters of Heat Exchangers Using Various Materials of Construction

	<u>Alloy G-30</u>	<u>SANICRO 28</u>	<u>Graphite</u>
No. of Tubes	359	359	283
Size	1-1/2" OD x .083" x 18'	1-1/2" OD x .083" x 18'	2" OD x 1/4" x 18'
Shell	Carbon Steel	Carbon Steel	Carbon Steel
Circulation Rate	10,000 gpm	10,000 gpm	10,000 gpm
Fresh Acid Feed Rate	100/125 gpm	100/125 gpm	100/125 gpm
Installed Cost	\$194K	\$181K	\$108K
Expected Life	8 Years	5 Years	8 Years
Annual Maintenance			\$ 11K

Table 13

Uniform Annual Cost for Various Life Expectancies*

	<u>Two Years</u>	<u>Five Years</u>	<u>Eight Years</u>
Alloy G-30	\$62K	\$32K	\$23K
SANICRO 28	\$58K	\$30K	
Graphite**		\$23K	\$19K

* Rate of return after taxes = 10%
Tax rate = 48%
Depreciation = Sum of digest method

** Graphite heat exchangers have a 10% annual maintenance cost.

Resistance to Phosphoric Acid

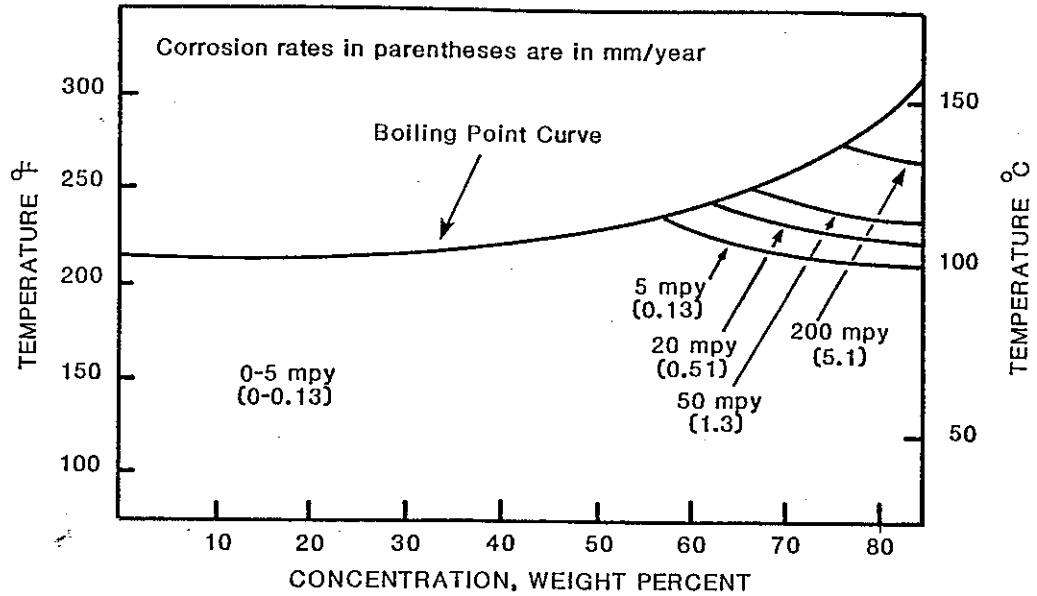


FIGURE 1: ISOCORROSION DATA FOR ALLOY 255 IN REAGENT GRADE PHOSPHORIC ACID

Resistance to Sulfuric Acid

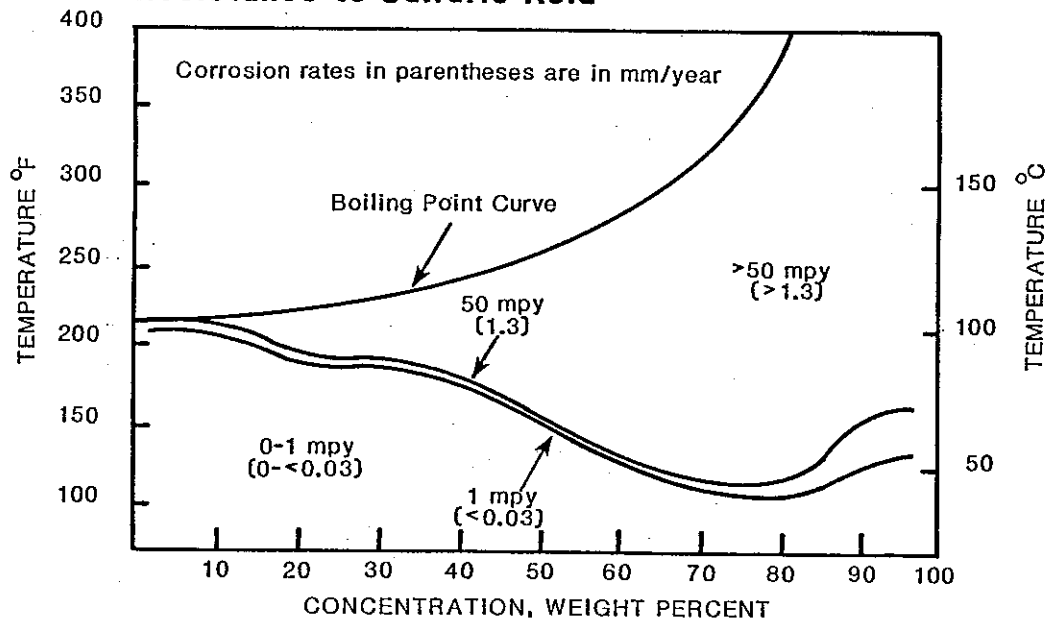


FIGURE 2: ISOCORROSION DATA FOR ALLOY 255 IN REAGENT GRADE SULFURIC ACID

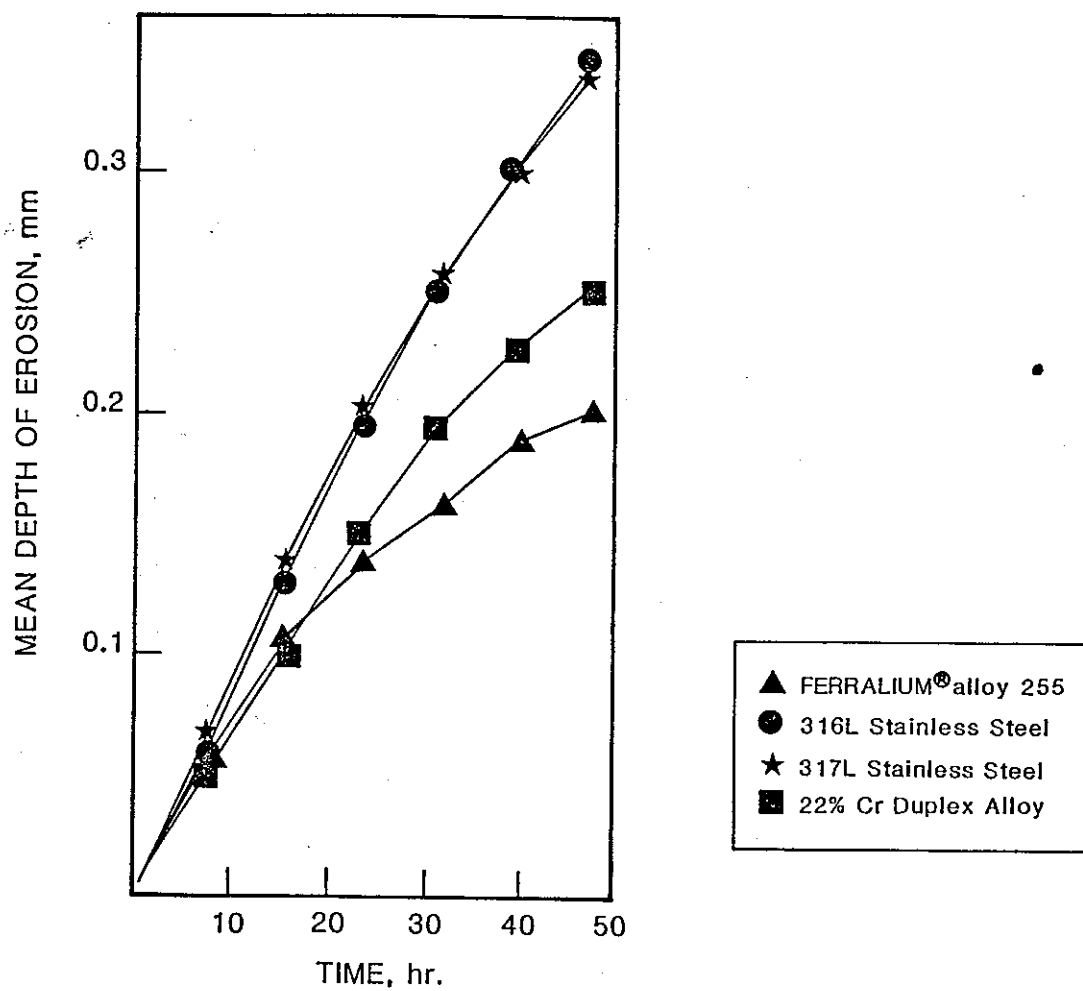


FIGURE 3: COMPARATIVE RESISTANCE TO CAVITATION EROSION

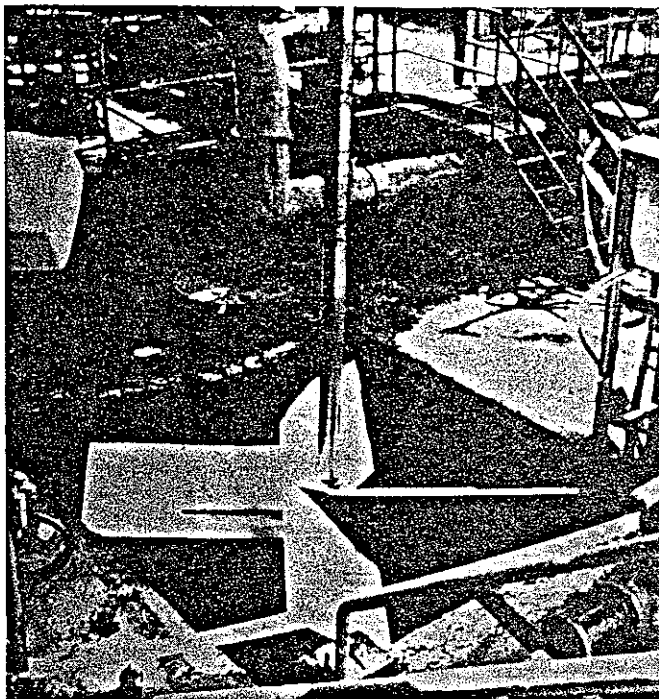


FIGURE 4:

AGITATOR SHAFT AND BLADE ASSEMBLY CONSTRUCTED OUT OF FERRALIUM[®] alloy 255
FOR USE IN REACTOR/ATTACK TANKS OF WET PHOS ACID PRODUCTION.

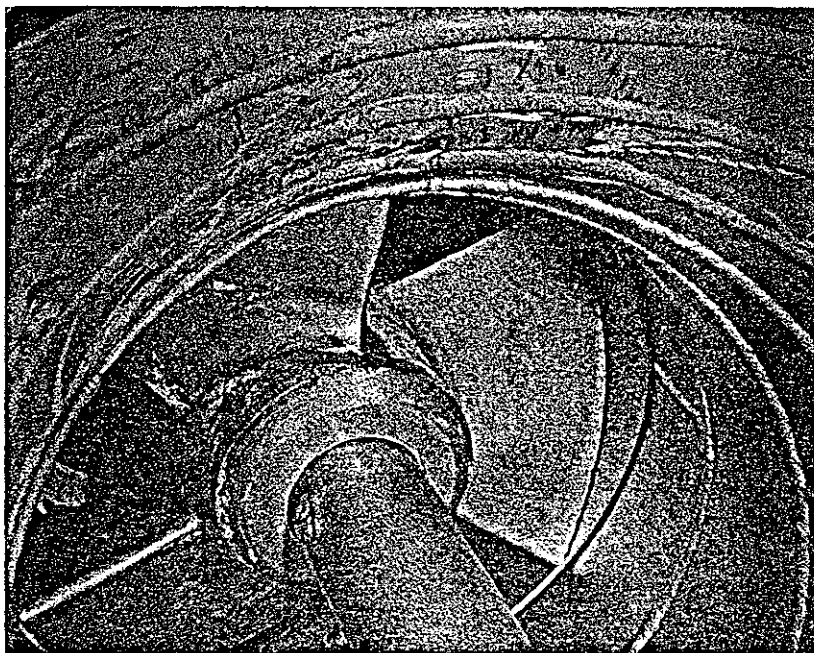


FIGURE 5:

20' DIAMETER FERRALIUM[®] alloy 255 PUMP USED IN WET PHOS ACID PRODUCTION.

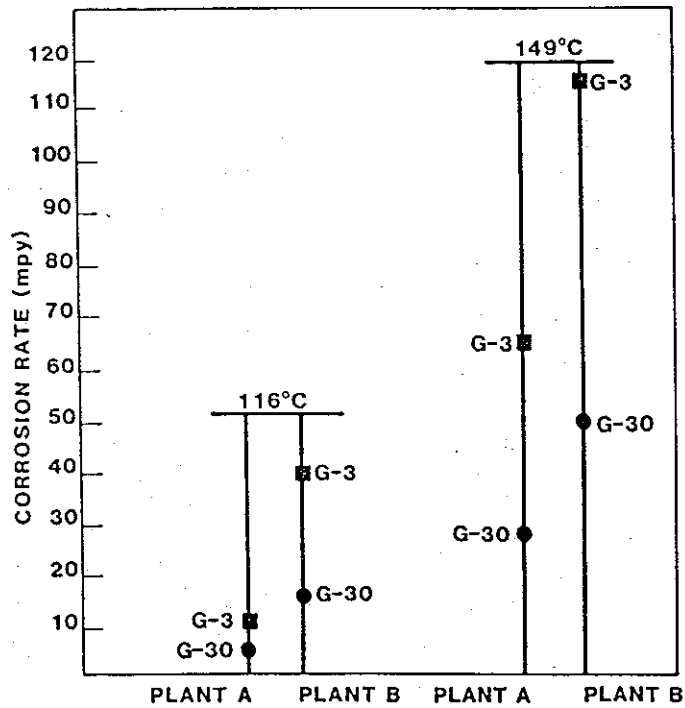
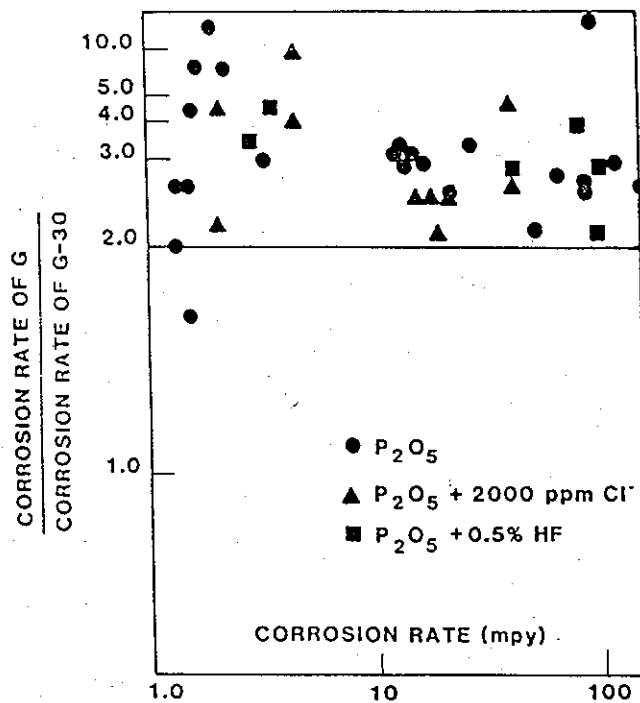


FIGURE 6: CORROSION RATES (MPY) IN PRODUCTION OF PHOSPHORIC ACID (54% P_2O_5) FROM TWO DIFFERENT PLANTS.



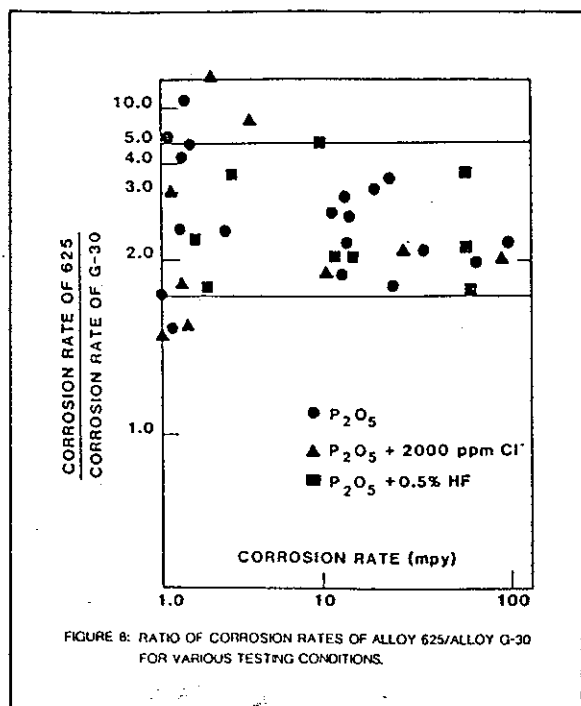


FIGURE 8: RATIO OF CORROSION RATES OF ALLOY 625/ALLOY G-30 FOR VARIOUS TESTING CONDITIONS.

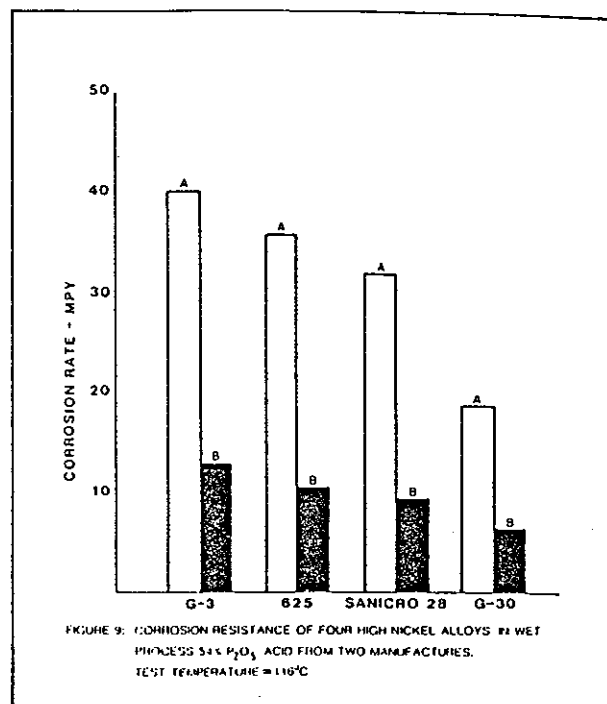


FIGURE 9: CORROSION RESISTANCE OF FOUR HIGH NICKEL ALLOYS IN WET PHOSPHORIC ACID FROM TWO MANUFACTURERS. TEST TEMPERATURE = 116°C

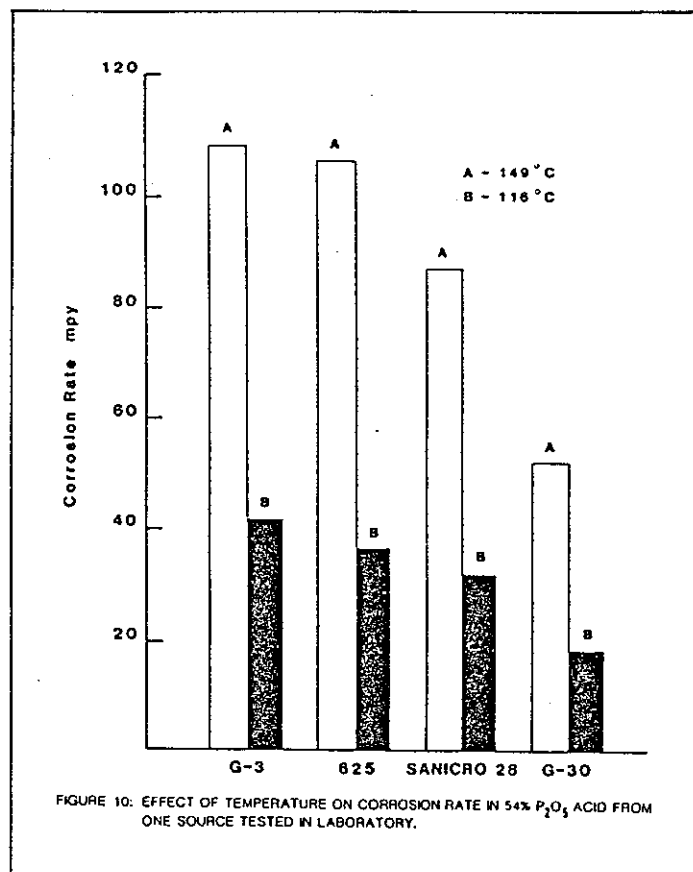


FIGURE 10: EFFECT OF TEMPERATURE ON CORROSION RATE IN 54% P_2O_5 ACID FROM ONE SOURCE TESTED IN LABORATORY.