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EXPERIENCE WITH NICROFER 3127 HMO – ALLOY 31: A COST-EFFECTIVE ALLOY IN EXTENSIVE USE IN THE PHOSPHORIC ACID INDUSTRY

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ABSTRACT

Nicrofer 3127 hMo – alloy 31 (UNS N08031) is a high-alloy stainless steel with exceptional resistance to localized corrosion in acid solutions of chlorides, fluorides and sulfides (1,2). It has also been shown to have excellent resistance to attack in oxidizing sulfuric acid over a wide range of concentrations (3). These properties, and its high chromium content, suggested that it should be a candidate material for severe service in wet-process phosphoric acid manufacture.

The paper provides the results of a wide series of tests, both in plant and in the laboratory, which have resulted in alloy 31 being specified for a number of applications in several countries, under service conditions which could previously only be handled by the use of more expensive nickel-base alloys.

Keywords: Nicrofer® 3127 hMo, Alloy 31, NO8031, phosphoric acid, sulfuric acid, erosion-corrosion, localized corrosion, seawater corrosion, chlorides, fluorides, sulfides.

INTRODUCTION

Corrosion of metals in the wet process of phosphoric acid production is strongly influenced by impurities in the acid: chlorides, fluorides and sulfides, individually or synergistically, produce localized corrosion, whilst sulfuric acid and fluorides are the cause of general corrosion. The impurities depend on the origin of the phosphates and their processing - washing with seawater increases the level of chlorides in the ores. The degree of corrosive attack is aggravated by erosion resulting from the presence of abrasive solids such as phosphate rock particles and gypsum crystals, by turbulence, by deposit formation, and by increases in temperature. Thus as impurity levels in phosphate rocks rise, and process temperatures increase, the corrosion of metals used in phosphoric acid manufacture becomes more severe.

It is well established that resistance of stainless steels and nickel-base alloys to localized corrosion is improved by increases in their chromium, molybdenum and nitrogen contents (4). Likewise it is known that high chromium levels are desirable for resistance to corrosion by phosphoric acid and by sulfuric acid. Such considerations led to the development and wide use of materials such as alloy 28 (UNS N08028) in wet process phosphoric acid manufacture. However, it became clear that even this alloy would not resist the increasingly severe conditions which result from the use of contaminated ores and higher process temperatures. Krupp VDM therefore set out to develop an alloy with increased resistance to the various types of corrosion encountered in phosphoric acid production, using the considerations outlined above. The result of this development was the alloy Nicrofer 3127 hMo - alloy 31 (UNS N08031).

ALLOY 31: PROPERTIES AND CORROSION RESISTANCE

The chemical analysis of Alloy 31, and of some other alloys used in phosphoric acid production, is given in Table 1. Also given is the 'Pitting Resistance Equivalent', or PRE, represented by %Cr+3.3x%Mo+30x%N, which is a measure of the resistance of an alloy to localized corrosion. Nickel has been kept as low as possible for reasons of cost, whilst retaining a fully austenitic structure. At the same time, nitrogen has been added to improve the stability of this austenitic structure, and also to increase the resistance of the alloy to localized corrosion. The chromium and molybdenum levels are the highest possible consistent with a fully austenitic alloy.

The properties and corrosion resistance of Alloy 31 have been described in detail elsewhere (5). They can be summarized as follows:

- high mechanical strength, combined with good ductility (Table 2);
- readily weldable either with matching fillers (for special applications) or with high-alloy fillers such as Alloy 59 (UNS N06059);
- resistance to pitting corrosion and to crevice corrosion in chloride solutions superior to those of comparable alloys, and at least equivalent to those of Alloy 625 (UNS N06625) (Table 3);
- very high resistance to many acid solutions of sulfides and fluorides;
- outstanding resistance to oxidizing sulfuric acid over a wide range of concentrations and temperatures (Figure 1);
- excellent resistance to corrosion in seawater or brackish waters (6)
- cost significantly lower than that of nickel-base alloys of similar properties.

Alloy 31 is covered by ASME Section VIII, Div. 1, for service at temperatures up to 800°F. and by the German pressure vessel regulations to 550°C.

This combination of properties and behaviours appeared to make Alloy 31 an obviou potential candidate for application in wet-process phosphoric acid plants. A wide series of laborato and industrial tests was therefore made to verify this assumption.

PHOSPHORIC ACID TESTING OF ALLOY 31

Laboratory Tests

a) Initial evaluation. Laboratory tests by Krupp VDM in synthetic phosphoric acid media, with no solids present (Table 4), did indeed confirm that the corrosion resistance of Alloy 31 was superior to those of alternative alloys 926 (UNS N08926) and 28 (UNS N08028), and comparable to, or even better than Alloy G-30 (UNS N06030). These tests also confirmed the rôle of chlorides in the corrosion of metals in phosphoric acid, and suggested that corrosion rates could increase rapidly above a certain threshold temperature. These two aspects have important practical implications, as will be seen later.

b) Effect of hardness. One question which needed to be answered before pre-selecting a material for service in such applications as mixers or pumps concerned the respective influences of the corrosion resistance and of the hardness of a metal on its behaviour under erosion-corrosion conditions. This was the subject of studies in the laboratories of the Ecole Nationale de l'Industrie Minérale (E.N.I.M.), in Rabat, Morocco. Three nickel-base alloy were investigated, with broadly-similar chromium contents but with respectively 3, 6 and 9% Mo, and which could all be age-hardened. Their rates of degradati under erosion-corrosion in a synthetic phosphoric acid slurry were determined in both the annea and the age-hardened conditions (7). The main conclusions of this study were:

- the highest resistance to degradation was given by the alloy with the highest molybdenum content (alloy 625)
- for any one alloy, the resistance in the age-hardened condition was greater than that of the annealed condition, but
- annealed alloy 625, with 9% Mo, showed higher resistance than the much harder aged alloy 718, of 3% Mo.

Conclusion: corrosion resistance is a more important criterion than hardness in selecting materials for service in abrasion-corrosion conditions.

c) Influence of sulfides. Practical experience had shown that the rates of erosion-corrosion of metals in wet-process phosphoric acid could increase significantly if sulfides were present. A detailed study was therefore made in the E.N.I.M laboratories of the influence of chlorides and of sulfides, individually and together, on corrosion of Alloys 31, 59, 2418 MoN and 30% Cr cast iron in synthetic phosphoric acid at various temperatures (8). Conclusions included:

- chlorides destroy the passive layer on metals, provoking localized corrosion such as pitting and crevice corrosion;
- sulfides, in the presence of chlorides, significantly increase the general corrosion rates, b producing a marked increase in the passive current densities (Figure 2);

- only very low levels of sulfides (below 20ppm) are needed to produce such increases in corrosion rates (Figure 2);
- best behaviour was shown by the alloys with the highest molybdenum contents, i.e. Alloy 59, followed by Alloy 31.

d) Rotating electrode tests. A very extensive series of laboratory tests has been made in which a wide range of stainless steels and nickel alloys was evaluated in industrial phosphoric acid slurries of varying compositions and at ca. 80°C (9). These were electrochemical tests, using a rotating electrode so as to simulate the dynamic conditions encountered in pumps or mixers. Table 5 summarizes the most significant results of tests in a 28% P_2O_5 slurry, and at a particularly high level of chloride contamination, i.e. under very aggressive conditions.

It is clear that for all alloys, corrosion rates increase under dynamic conditions. This observation demonstrates the validity of Aakka's observations (7), to the effect that at a given resistance to corrosion, erosion-corrosion resistance increases with hardness. The results also illustrate the necessity for laboratory testing to simulate all of the conditions encountered in service.

A comparison of the relative behaviours of the various alloys tested shows clearly the excellent performance of the special stainless steel Alloy 31 under these aggressive conditions, even when compared to the much more expensive nickel-base alloys. Of these, Alloy G-30 is already in service in phosphoric acid plants.

One of the general conclusions of the IMI study was that adequate corrosion resistance under their test conditions would only be obtained with an alloy containing at least 31% nickel, and with chromium + molybdenum in the range 33.5 - 39%. Only the nickel-base alloys, and Alloy 31, meet these criteria.

These laboratory tests confirmed the interest in testing Alloy 31 under plant conditions.

Plant tests

a) Mixers, digestion stages. The OCP Safi site employs the Rhône Poulenc process, the Prayon process and the Nissan hemi-hydrate process. The main process difference of influence on the performance of mixer materials in the digestion stages is temperature: 80°C for the Rhône Poulenc process, but 95°C for the Nissan process. This means that the mixers of the digestors are much more severely solicited in the latter process; neither 904 L nor coatings have given satisfaction. A very extensive series of 6-month plant tests was therefore initiated for both processes with 15 metallic materials, with samples attached to the periphery of the central mixer, where the speed of rotation is 8m/sec. The acid contained 27% P_2O_5, 34% solids and 8% SO_4^{--}.

In the three series of tests run, four materials placed consistently in the top five out of the fifteen tested: Alloy 31, Alloy G-30, Alloy 625, and cast 30% Cr - 2% Mo. Of these, Alloy 625 has the handicap of price, and the cast alloy of being difficult to use in practice. These tests confirmed that Alloy 904 L would be adequate for the Rhône Poulenc process, but not for the digestion stage of the Nissan process.

A second series of 12-month tests was therefore made in the Nissan process with full mixer blades in Alloy 31 and in Alloy G-30. These confirmed that both alloys would be expected to show satisfactory life under the conditions of service of this process.

b) Evaporation plant. In another plant in the Mediterranean Basin, phosphoric acid is concentrated from 28% to 54% P_2O_5 using graphite evaporators and rubber-lined vapour recirculation systems. The latter pose severe practical problems in that their life is difficult to predict, and that when failu occurs, the unit has to be taken down using a 90-tonne crane, allowed to cool, cleaned, recoated. lifted back into place, with the consequent loss of up to 2 weeks production. A metallic solution would allow repairs to be made in situ, with virtually no production loss.

Two full vapour elbows were therefore manufactured in Alloys 31 and G-30. The alloy 31 was welded using Alloy 59 filler, and the Alloy G-30 with matching filler. These were placed in service for a year. The 54% acid contained about 1.45% H_2SO_4, 0.22% fluoride, 300ppm chloride. Vapour temperature was 90°C. Heavy deposits formed in service, and were washed once per week using cold water - inspection showed this washing to be incomplete.

An inspection after this first year's service showed both alloys to have suffered pitting attack, and under-deposit attack. The attack was more general on the Alloy 31, but deeper on the Alloy G-30. The Alloy 59 welds on Alloy 31 were unattacked; those of Alloy G-30 showed extensive fissuring, which were probably welding defects, or corrosion due to micro-segregation in the weldments.

The units were placed back in service for a second year. The second inspection showed some weld repair to be necessary, but the conclusion of the customer was that both alloys could be used as better alternatives to rubber lining for vapour recirculation systems, with Alloy 31 being selected because of its much lower cost.

c) Sulfuric acid coolers. Many phosphoric acid plants are in coastal locations, and seawater is thus a common coolant. It is also a powerful corrodent. In some older plants, produced sulfuric acid is cooled in the so-called cascade coolers, where the acid is inside 150mm dia. pipes, and raw seawater flows over the outside. The pipes are often centrifugal castings. Failure is almost always due to pitting crevice corrosion on the seawater side.

In December 1992, OCP Safi installed a test length of Alloy 31 at the inlet to their sulfuric acid cascade coolers. Acid concentration was 98.5%, and temperature 105° - 110°C. An inspection in November 1994 showed no corrosion, either on the acid side, or on the seawater side. The Alloy 31 was returned to service, and is still functioning more than 6 years after its installation. OCP is now replacing the cascade coolers by new tube-and-shell units.

d) Piping, concentration plant. Alloy 904 L piping has been used by OCP Safi to transport 54% P_2O_5 from the concentration plant to further processing. A length of Alloy 31 piping was tested for a year at 80°C, and was reported to show performance sufficient to make it a preferred choice over Alloy 904 L, despite its higher price.

e) Dilution tubes, flash coolers. The first stage of phosphoric acid production in some OCP plants is the reaction stage, where phosphate ore is attacked by a mixture of 28% P_2O_5 phosphoric and 98.5% sulfuric acid. These are introduced into the reactor through 7-metre long concentric tubes. At the extremity of the tubes, where mixing occurs, very severe conditions arise, both in the liquid phase and in the vapour phase, due to the dilution of the sulfuric acid - which makes it more corrosive - and the increase in temperature from the heat of dilution. Nickel-base alloys such as Alloys C-276 and C-22 have been used for such systems in other plants in the past, but unsuccessfully.

Following a technical evaluation by OCP, Krupp VDM and the French systems manufactu Aoustin, OCP Jorf Lasfar ordered a number of these flash coolers in Alloy 31. Despite some i mechanical problems, these are considered to give satisfaction in one of the most demanding applications encountered in phosphoric acid production.

APPLICATIONS - EXAMPLES

Mixers. Following the successful tests described above, OCP Safi is now using Alloy 31 mixers in the digestion stage of the Nissan process.

Sulfuric acid coolers. Jordan Phosphate Mines, Aqaba, Jordan, has two seawater-cooled sulphuric acid coolers in Alloy 31 in service since June 1993.

Filters. Also at Jordan Phosphate Mines, Alloy 904 L filter drains suffered vapour-phase attack. These were replaced by Alloy 31, which initial inspections suggest will outlive the life of the installation.

Concentration plant. The use of metallic materials for evaporators in high-impurity phosphoric acid plant is usually limited to those where the heating medium - hot water or steam - is at a temperature below 120°C. At higher steam temperatures, deposits form on tube walls which cannot be eliminated by the usual washing techniques. These deposits cause concentration of impurities and temperature increases which can lead to sudden delayed failure.

The Prayon Company has sought to overcome this problem with a design of evaporator where the acid is outside the tubes, and the steam inside. This makes for easier cleaning. Despite this, Alloy 28 evaporator tubes at Prayon have a mean life of only 18 months. In early 1996, Prayon installed a complete set of evaporator tubes in Alloy 31, which are still in service.

Concentration plant, vapour recirculation ducts. See experience described above.

Flash coolers. See OCP experience described above.

DISCUSSION

The severity of corrosion problems in wet-process phosphoric acid plant can be expected to increase as the use of contaminated ores increases. Chlorides, fluorides and sulfides, in particular, are likely to reach levels significantly higher than those seen today, with a consequent increase in the types of corrosion these impurities provoke: pitting corrosion, crevice attack, general corrosion, even stress corrosion. Materials which are giving good service today will fail, sometimes dramatically - Alloy 28 evaporator tubing has been seen to fail suddenly, after 12 months trouble-free service, when the impurity concentrations under deposits reached critical levels.

It is therefore necessary to anticipate this trend, and to have available materials which will resist these more severe conditions, and which are economically viable. Nickel-base alloys would offer the required corrosion resistance, but would be too costly for extensive use. The special stainless steels which have been used to date are acceptable price-wise, but are limited in their corrosion resistance.

Alloy 31 was designed to fill the gap between the existing special stainless steels and the nickel alloys. As Table 3 shows, its resistance to local corrosion in chloride media is at least equivalent to that of Alloy 625, and Alloy 31 is in wide use in industries such as the chemical industry and in pollution control systems as a result. It has been determined to have remarkable resistance to attack by sulfuric acid over a very wide range of temperatures and concentrations, and has thus found major applications in metals processing. It has also been found to have excellent resistance to acid fluoride media, with consequent use in pickling plant. And its composition was designed to give it good resistance to phosphoric acid solutions.

It is therefore not surprising that the many test programmes described above should have confirmed the suitability of this alloy for service in high-severity phosphoric acid plant. Hajji's stu (8) showed it to have good resistance to phosphoric acid contaminated by both chlorides and sulfi. The IMI evaluation (9) suggested that it could be the most cost-effective alloy available for service in severe erosion-corrosion conditions, as encountered in phosphoric acid mixers and pumps. And the very comprehensive plant evaluation made at OCP Safi confirmed that Alloy 31 was the most cost-effective material to replace Alloy 904 L as a mixer material in conditions where this alloy was failing.

These tests also confirmed another advantage of this material - its polyvalency, which enables it to be used in a wide range of applications, thus reducing the number of materials which need to be kept in maintenance stock.

Phosphoric acid plants offer a stimulating challenge to the materials engineer. The types of materials degradation which are encountered in such plants are many and varied: localized corrosion by halides, vapour phase attack, erosion-corrosion, seawater attack, sulfuric acid corrosion over a wide range of concentrations and temperatures, etc., etc. At the same time the scale of these plants is such as to require the use of economic metallic materials; 'ultimate' solutions cannot be envisaged. Thus the availability of a low-cost metallic material with a remarkable degree of resistance to the various types of corrosion met in phosphoric acid production is of obvious interest. Alloy 31 is such a material.

CONCLUSIONS

- Alloy 31 has a composition especially adapted to service in phosphoric acid plants.
- Laboratory and plant tests confirm that Alloy 31 can be used in many high-seve applications.
- Alloy 31 is comparable in performance to higher-alloy nickel-base materials, at much lower cost.
- Standard manufacturing processes can be used with this alloy.
- Typical applications for Alloy 31 in wet-process phosphoric acid plants include:
  - Mixers
  - Filter components
  - Piping systems
  - Sulfuric acid coolers
  - Vapour systems in concentration plant
  - Flash coolers

Alloy 31 is thus a polyvalent and cost-effective alloy for high-severity phosphoric acid service.

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TABLE 1
TYPICAL CHEMISTRIES OF SOME ALLOYS USED IN THE PHOSPHORIC ACID INDUSTRY

Alloy	**Ni**	**Cr**	**Mo**	**Fe**	**Others**	**P.R.E.***
316 L	12	17	2.1	68	-	24
904 L	25	20	4.5	48	Cu	35
28	31	27	3.5	36	Cu	38
625	61	22	9	3	Cb,Ta	52
G-30	45	29	5	15	Cu,W Cb,Ta	46
31	31	27	6.5	33	Cu,N	54

*P.R.E. (Pitting Resistance Equivalent) = %Cr + 3.3 x %Mo + 30 x %N

TABLE 2
TYPICAL ROOM-TEMPERATURE MECHANICAL PROPERTY DATA

ALLOY	**UTS-KSI (N/mm^2)**	**0.2% Y.S.-KSI (N/mm^2)**
625	125 (860)	53 (365)
31	110 (760)	53 (365)
G-30	100 (690)	47 (320)
28	82 (565)	45 (310)
904 L	78 (540)	35 (240)

TABLE 3
LOCALIZED CORROSION RESISTANCE ACCORDING TO ASTM G-48
(10% $FECl_36H_2O$)

Alloy	**Mo**	**Cr**	**P.R.E.**	**CPT (°C)**	**CCT (°C)**
904 L	4.5	21	35	45	25
28	3.5	27	38	60	35
G-30	5	29	46	75	50
625	9	22	52	77.5	57.5
31	6.5	27	54	>85	65

P.R.E. = %Cr + 3.3 x %Mo + 30 x %N
CPT = Critical Pitting Temperature
CCT = Critical Crevice Corrosion Temperature

TABLE 4
LINEAR CORROSION RATES OF NICROFER 3127 HMO – ALLOY 31 AND OTHER ALLOYS IN PHOSPHORIC ACID SOLUTIONS, mm/y

Testmedium	**Temperature °C**	**Corrosion Rates, mm/y**					
		Alloy 31	**Alloy 926**	**Alloy 28**	**Alloy C-22[2]**	**Alloy G-3**	**Alloy G-30[2]**
72% H_3PO_4 (~52% P_2O_5) + 4.5% H_2SO_4 + 0.9% H_2SiF_6 + 1.5% Fe_2O_3 + 400 ppm Cl^-	80 120 ± 2.5	0.02 0.78	0.06	0.075			
52% P_2O_5	116	0.08[1]		1.2	0.28	0.28	0.10
42% H_3PO_4 (30,4% P_2O_5) + 2.4% H_2SO_4 + 2.3% H_2SiF_6 + 1% Fe_2O_3 + 1000 ppm Cl^-	80	0.015	0,03				
44% P_2O_5	116				0.53	0.55	0.18
54% P_2O_5	116	0.05[1]		1.4		0.40	0.20
54% P_2O_5 + 2000 ppm Cl^-	116	2.35[1]		2.3		0.40	0.18
54% P_2O_5 + 2000 ppm Cl^-	100	1.30					

[1] 120°C

[2] From suppliers' data sheets

TABLE 5
SELECTED RESULTS OF INDEPENDENT LABORATORY TESTS OF ALLOYS IN INDUSTRIAL PHOSPHORIC ACID SLURRIES: ELECTROCHEMICAL TESTS USING A ROTATING ELECTRODE (9)

Alloy	Rotation t/min	Temp.°C	Corrosion Rate mm/y
904 L	Nil 25 100	76	0.049 0.489 1.406
28	Nil 25 100	78	0.009 0.354 0.856
Hastelloy G-30	Nil 25 100	78	0.012 0.251 0.825
Nicrofer 3127 hMo - alloy 31	Nil 25 100	79	0.004 0.122 0.672
Nicrofer 5923 hMo - alloy 59	Nil 25 100	79	0.011 0.147 0.611
Hastelloy C-22	Nil 25 100	77.5	0.007 0.306 0.611

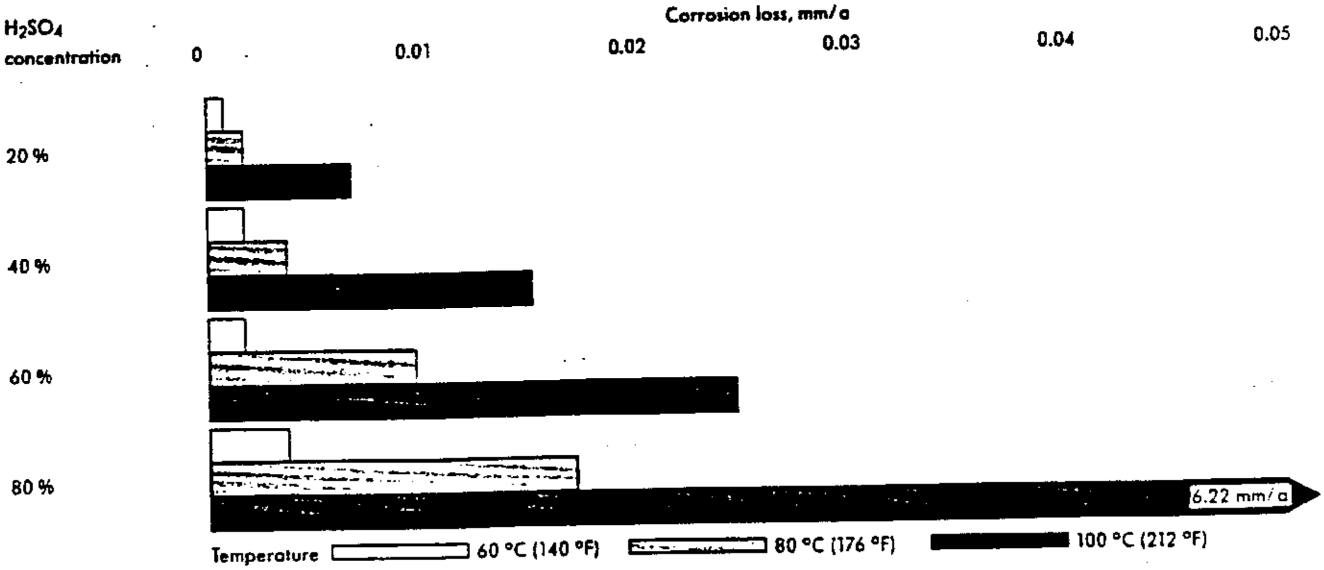

Figure 1: Linear corrosion loss of Nicrofer 3127 hMo - alloy 31 in sulfuric acid of various concentrations and at elevated temperatures.

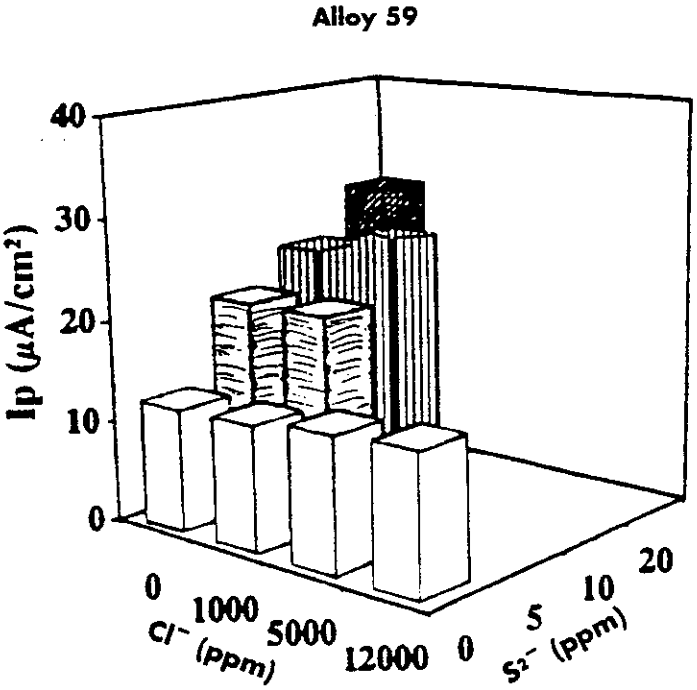

Figure 2: Variation of passive current density of Alloy 59 in synthetic phosphoric acid (40% H_3PO_4), contamined by Cl^- and/or S^{2-}, at T = 90°C (from (8)).