SELECTION OF STAINLESS STEEL FOR USE IN PHOSPHORIC ACID PLANTS, NEW TRENDS AND EXPERIENCE

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Summary - Laboratory tests as well as field tests have shown that the super-duplex grade UNS 32520/UR52N^{+} is more resistant to corrosion and erosion-corrosion in industrial phosphoric acids than the conventional N 08904 alloy. This is explained by the combination of high chromium content and Mo-Cu and N additions together with high mechanical properties .

These properties, which in some circumstances permit thickness reductions, when combined with the low Ni content and the good ability of this material to be cut, formed and welded led to a relative low cost which explain why UNS 32520/UR52N^{+} has been considered as a candidate material for manufacturing several major equipment in two phosphoric acid plants in US.

In addition to lower initial capital costs, the savings due to lack of down time and expense due to rubber and refractory repairs is immense. Such items as adding a pump suction to an attack tank can be accomplished without a major capital outlay. We feel this practical material has perhaps many other applications yet to be realized for this industry

CORROSION PERFORMANCE EVALUATION

Industrial phosphoric acid solutions are chemically complex and their analysis change from one plant to another, depending on the quality of phosphate rocks and on the process utilised. So, in order to elaborate an accurate basis for material selection, a reference synthetic solution representative of the average aggressivity of industrial acids was designed [1].
Then, the effects of the main corrosion determining parameters like free fluoride, hydrofluorsilisic acid, sulfuric acid in excess and chlorides were investigated by adding these elements to the reference solution. The effect of process temperature was also studied. Finally, erosion-corrosion tests were carried out using a laboratory equipment especially designed to simulate the effect of actual industrial parameters which are considered as to be rate determining for this form of corrosion [2].
The corrosion tests were carried out in the Research Centre for Materials of CREUSOT-LOIRE INDUSTRIE (CLI) in Le Creusot, France ; various stainless steels were tested (Table 1).

Table 1 - Average composition of the candidate stainless steels and alloys

AISI UNS	CLI Trademark	C	Cr	Ni	Mo	Cu	N2
		Average composition (% weight)					
Austenitics							
316 L	ICL 164 BC	0.02	17	12	2.2		
316 LN	ICL 166 HE	0.02	18	11	2.7		0.15
317 L	ICL 168 BC	0.02	19	15	3.2		
317 LN	ICL 168 HE	0.02	19	15	3.5		0.15
317 LNM	ICL 170 HE	0.02	18	15	4.5		0.15
N 08 904	UR B6	0.02	20	25	4.3	1.5	
Super Austenitics							
N 08 028	UR B28	0.01	27	31	3.5	1	
N 08 926	UR B26	0.01	20	25	6.2	1	0.20
Duplexes							
31 803	UR 45N	0.02	22	5.3	2.8		0.16
32 520	UR 52N^{+}	0.02	25	6.5	3.5	1.5	0.25

1- EFFECT OF IMPURITIES (Attack Stage)

The very detrimental effect of free **hydrofluoric acid** is shown in Fig.1. In particular, the corrosion rate of the UNS 08904 grade increases from 0.08 mm/y to 0.15 mm/y when the HF content increases from 0 to only 0.2 %. The duplex grade UNS 32520 (UR 52N+) and the super austenitic grade UNS 08926 (UR B26) are less affected when the HF content increases, but this acid remains very detrimental. It appears quite clearly that high chromium countaining grades exhibit the best corrosion resistance.

Hydrofluorsilisic acid is less agressive than hydrofluoric acid, as shown by electrochemical tests which consisted in measuring the passive domain taken from polarisation curves (Fig.2). Thus, adding 1.5 % H_2SiF_6 to the synthetic solution has very little effect when compared to HF.

The effect of **sulfuric acid** concentration is shown in Fig.3. An increase of 2 % (from 2 to 4 %) has about the same influence as the one observed with HF additions in the range 0 to 0.2 %. High chromium containing austenitic grades either austenitics or duplexes are the best resistant materials.

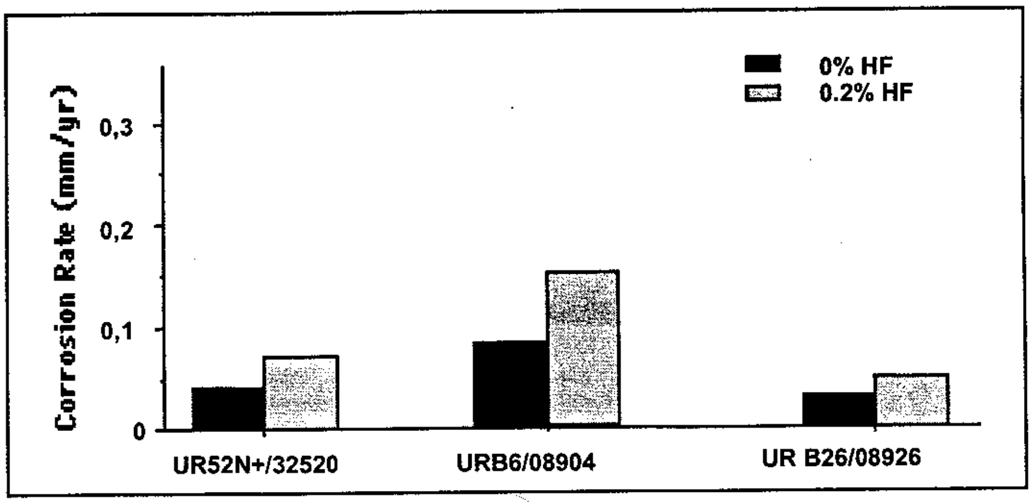

Fig. 1 - Effect of Hydrofluoric Acid on the corrosion rate of stainless steels. Temperature 80°C/176°F.

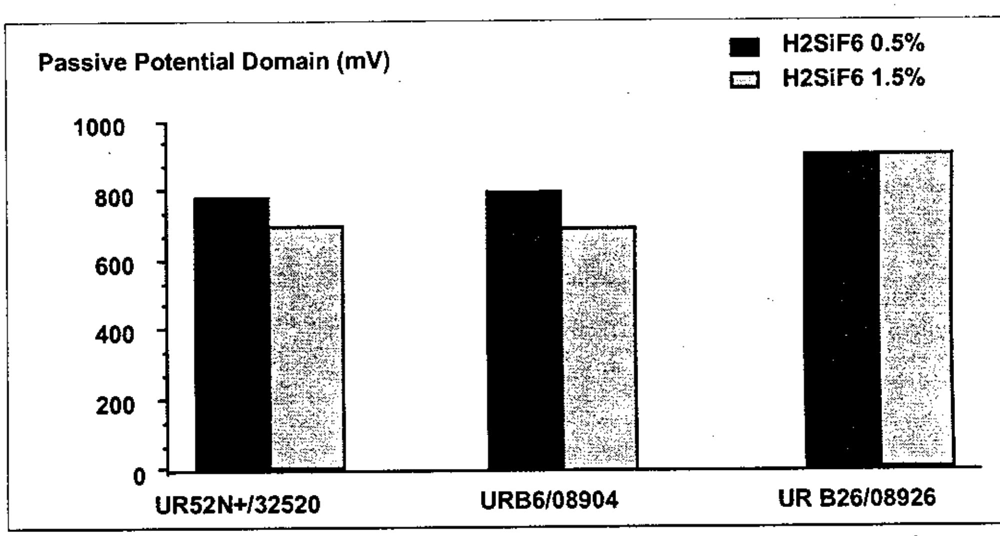

Fig. 2 - Effect of hydrofluosilicic acid on the corrosion rate of stainless steels. Temperature 80°C/176°F.

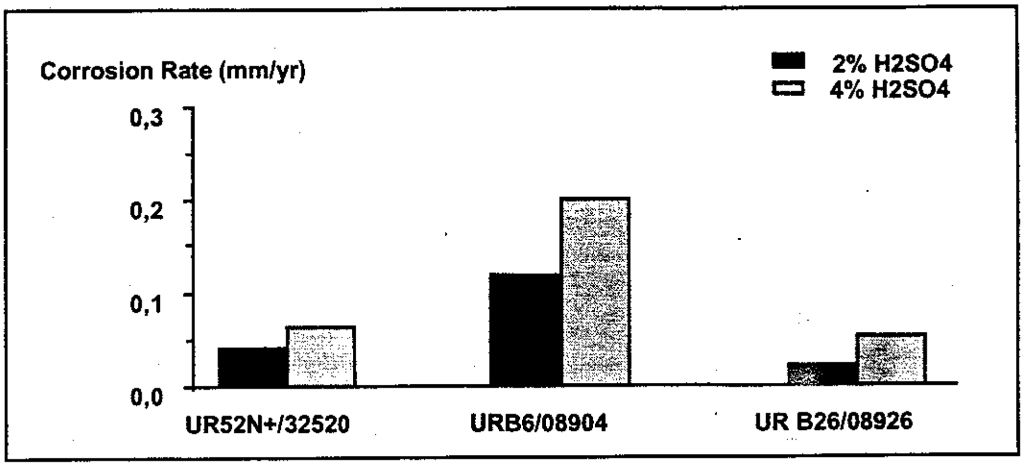

Fig.3 - Effect of excess of Sulfuric Acid on the corrosion rate of stainless Steels.
Temperature 80°C/176°F.

The effect of **chloride** concentration on uniform corrosion was also investigated. Fig.4 summarizes the results of tests with several chloride concentrations from 600 to 4600 ppm at 80°C. It clearly appears that chromium, molybdenum and nitrogen additions increase the resistance to corrosion; thus, the threshold chloride concentration is directly dependant on the concentration of these alloying elements. In this respect, the PREN value = Cr% + 3.3 Mo% + 16 N% which is generally utilized to rank the resistance of stainless steels to localised corrosion in chloride containing media seems to be rate determining for corrosion in the tested conditions.

In regular industrial conditions, i.e. when the chloride concentration does not exceed 1000 ppm, the UNS 08 904 grade can be utilized in erosion free conditions; in solutions containing higher chloride levels, one must select either the super-duplex grade UR $52N^+$ or the super-austenitic grade UR B26 up to about 2000 ppm and the super austenitic-grade UNS 08 028 up to about 3000 ppm.

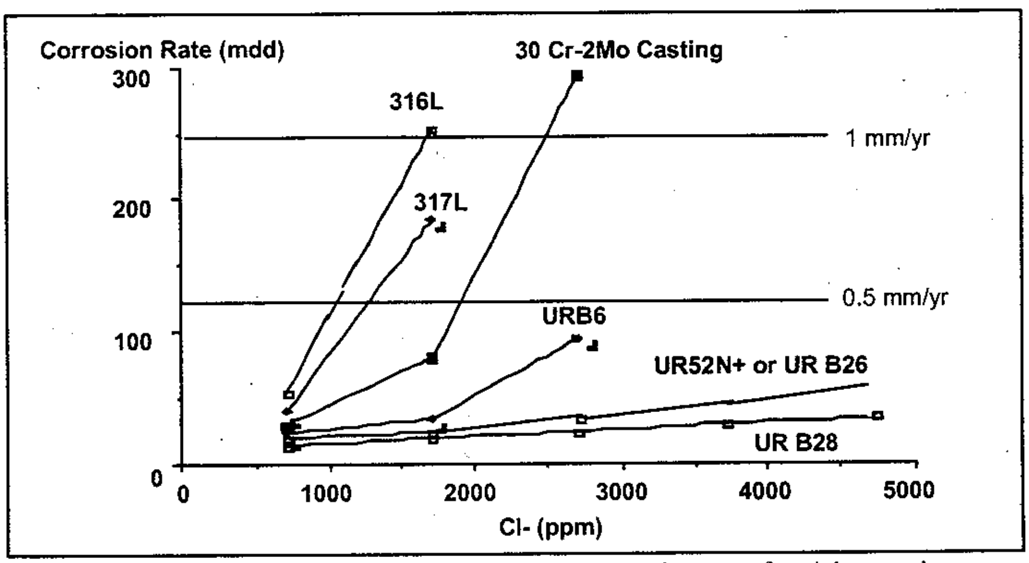

Fig. 4 - Effect of Chloride concentration on the corrosion rate of stainless steels.
Temperature 80°C/176°F.

2- EFFECT OF ATTACK TEMPERATURE

Corrosion tests were carried out at 110°C (230°F) in order to simulate the conditions of hemi-hydrate processes. Figure 5 shows the corrosion rate of all the tested grades to be multiplied by three when the temperature increases from to 80°C/176°F to 110°C/230°F.

At the highest temperature, the UNS 08904 grade is no longer recommended while the grades with high chromium content (25 %) exhibit a corrosion rate of about 0.15 mm/y.This means that either UNS 32520 (UR52N+) or UNS 08926 (URB26) grades can be considered as candidate materials to build phosphoric reacting vessels but the higher mechanical properties of the super-duplex grade provide a decisive advantage compared to the super austenitic grade.

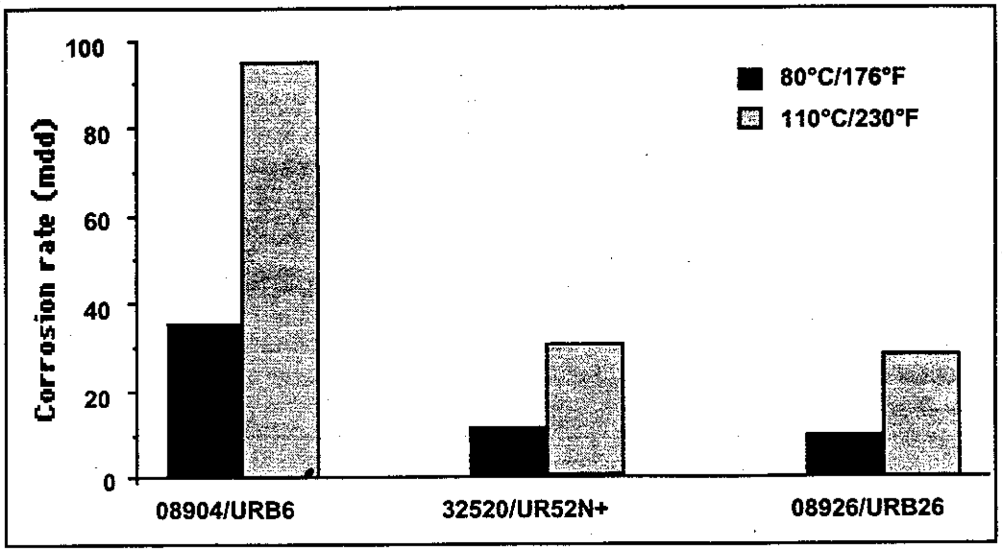

Fig. 5 - Effect of Temperature of Attack on the corrosion rate of stainless steels.

3- EROSION-CORROSION

The main central agitator and more particularly surface agitators used in some processes for mixing reacting products must resist to a severe abrasion phenomenon (due to gypsum and non reactive silica) and to general corrosion due to temperature and sulfuric acid addition. They are currently made from UNS 08904 grade with some rubber lined parts (sometimes from 29Cr-4Mo casting, especially for small surface agitators) but the operating conditions are generally so agressive that agitators must be replaced annually or every two years, depending on the process.

Pumps utilized to transfer the phosphoric mixture from the reacting vessel to the filter are also submitted to very severe abrasion so that they have to be replaced every year.

Laboratory tests carried out by means of a specific device using 100 microns silicon carbide as abrasive particles [1] in the synthetic solution at 80°C/176°F shown that abrasion increases drastically the corrosion rate of stainless steels (Fig.6). For example, the UNS 08904 grade exhibits a corrosion rate of about 1.2 mm/yr. In the same conditions, the corrosion rate of the 25% Cr grades is only about 0.6 mm/yr i.e. 50% lower. One must stress that the super-duplex grade UNS 32520 (UR 52N+) is as resistant as the super-austenitic UNS 08926 grade (UR B26).

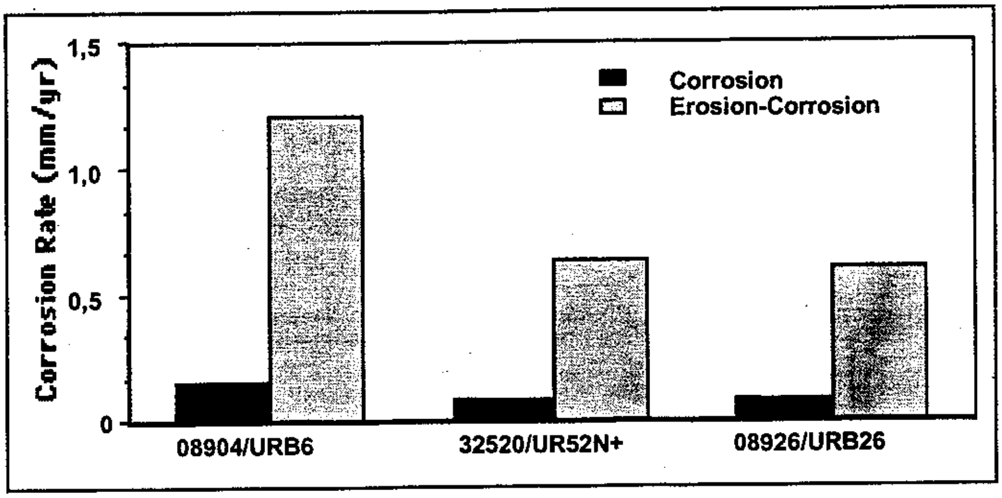

Fig.6 - Effect of Erosion by Solid Particles in suspension in Phosphoric Acid. Temperature 80°C/176°F.

4- STORAGE OF 54% PHOSPHORIC ACID: EFFECT OF CHLORIDES

The 54 % P_2O_5 acid solution is not as aggressive as the 30 % mixture. Normal contents in fluoride and chloride containing compounds are in fact notably lower than in the mixture. However, the most economical material must be selected taking into account the actual storage conditions i.e. the temperature and the Cl^- concentration in the acid

Results of laboratory tests conducted in an actual concentrated industrial phosphoric acid at several temperatures and several Cl- contents (Fig.7) indicate the threshold chloride vs temperature values for which localized corrosion does not appear on industrial hot rolled stainless steel samples.

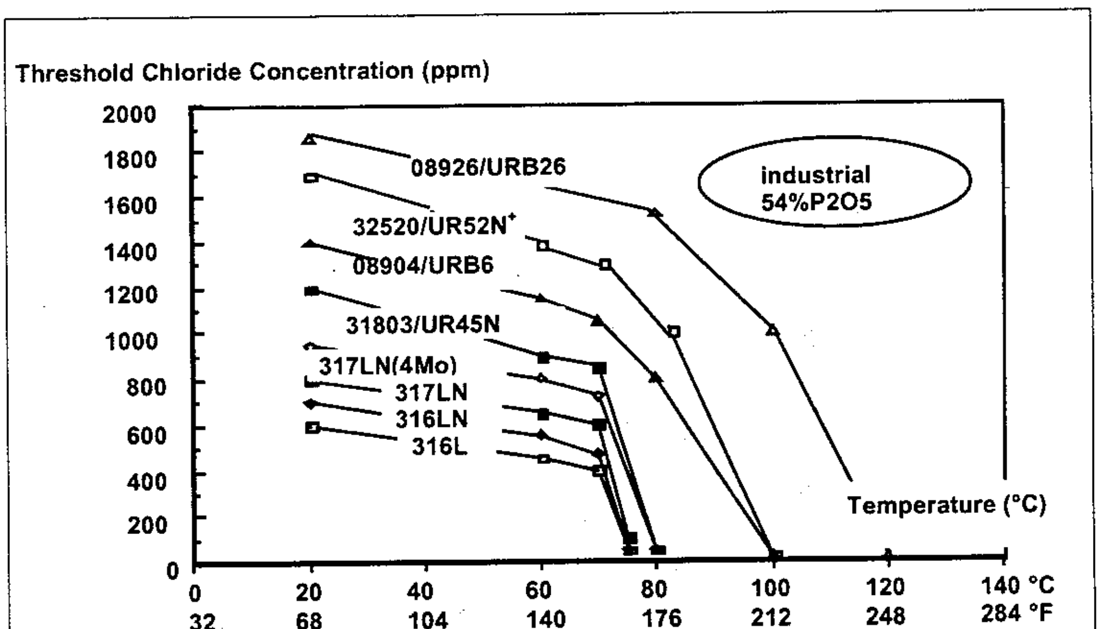

Fig. 7 - Selection of stainless steels for transportation of 54 % P205 as a function of Chloride content.

If one consider 900-1000 ppm chlorides which is probably representative of the upper content in actual 54% P2O5 industrial acids, the duplex grade UNS 31803 withstand localized corrosion up to 60°C/140°F while the super-duplex grade UNS 32 520/UR 52N+ has to be selected at 80°C/176°F. Types 316L, 316LN and even 317LNM are much less resistant.

Such results, together with the good resistance to erosion-corrosion as previously shown, suggest that UNS 32 520/UR 52N+ is a very good candidate for construction of phosphoric acid storage tanks.

5- FIELD TESTING

Field tests were carried out in two plants using di-hydrate Rhône-Poulenc processes in Belgium and in Greece. Samples taken from industrial hot-rolled plates (N 08 904, N 08 028, N 08 932, 32 550 and Nickel Base N 06 625 grades) were attached on surface agitator blades during several months.

The results in Fig. 8 and 9 show that super-austenitics and super-duplexes are about twice as resistant to erosion-corrosion than 08 904 grade in these very agressive conditions. The super-duplex grade UR 52N+ exhibits the best performance among all the materials tested including N06 625 Nickel Base alloy.

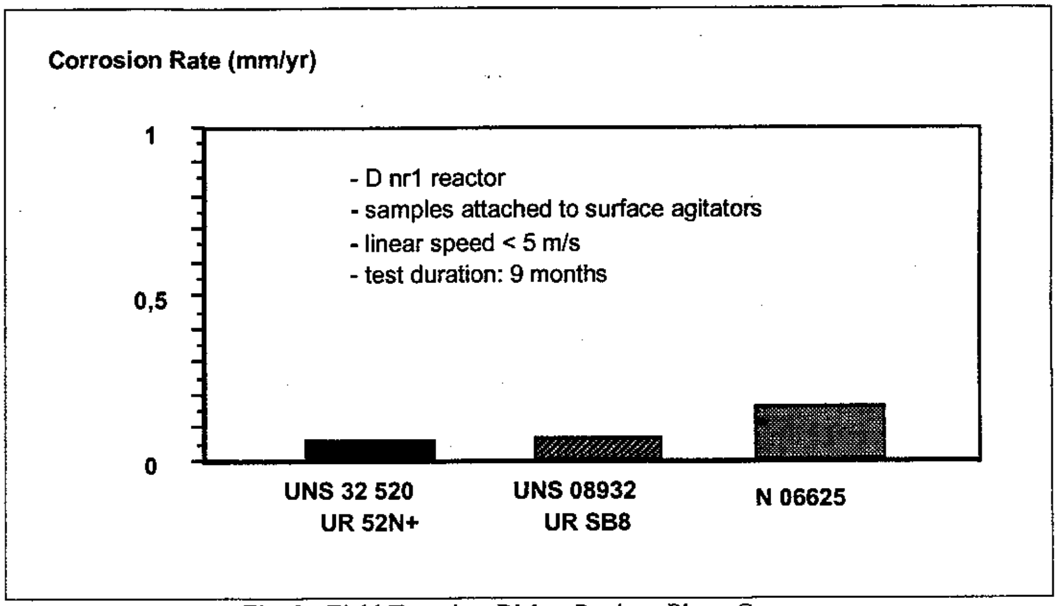

Fig. 8 - Field Tests in a Rhône-Poulenc Plant, Greece.

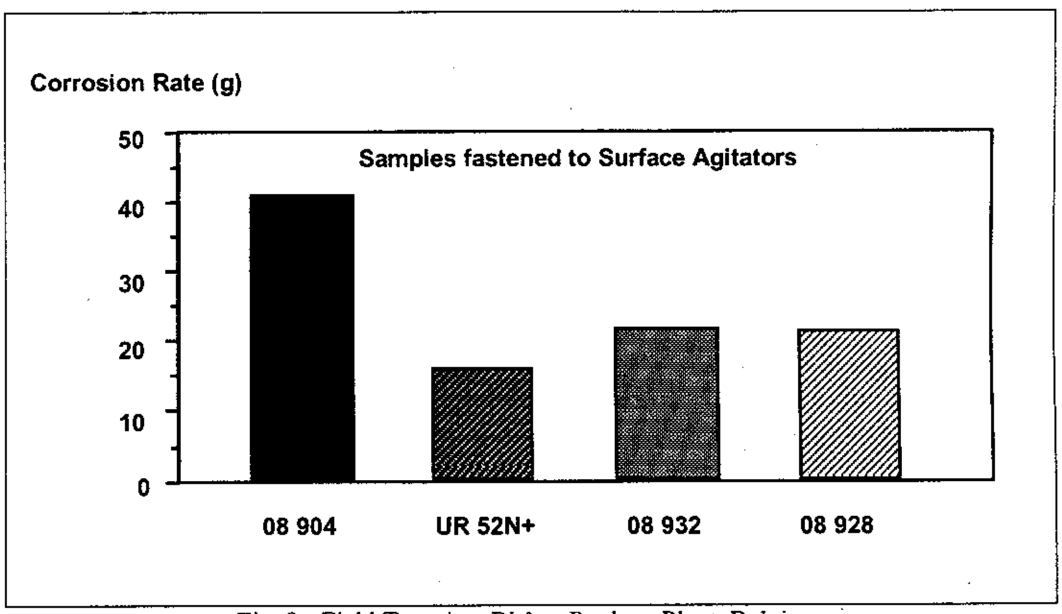

Fig. 9 - Field Tests in a Rhône-Poulenc Plant, Belgium.

MECHANICAL PROPERTIES

The minimum guarantied values for mechanical properties of various stainless steels are mentionned in Table 2. One can observe that whatever the microstructure, higher alloyed grades exhibit higher yield and ultimate tensile values. Particularly, nitrogen is the most beneficial element.

Nevertheless, the combination of austenite and ferrite in the duplex microstructure provides very high mechanical properties which are at least twice those observed on austenitic grades like the N 08904 commonly used in phosphoric acid industry.

The high corrosion resistance of the duplex grade UR 52N+/UNS 32520 combined with its high mechanical characteristics generally permit to reduce the thickness of the plates and consequently to save money.

Table 2 - Mechanical characteristics of stainless steels.

AISI or UNS	TRADENAME	Y.S. 0.002		U.T.S.		E
AUSTENITICS		Mpa	KSI	Mpa	KSI	%
316L		225	33	520	75	45
316LN		250	36	590	86	40
317LNM		290	42	580	85	40
N08904	UR B6	245	36	550	80	40
N08926	UR B26	320	46	650	94	40
N08028	UR B28	220	32	500	73	40
DUPLEX						
S31803	UR 45N	480	69	680	98	25
S32520	UR 52N+	550	80	760	115	25

FABRICATION WITH UR 52N+ IN THE US PHOSPHATE INDUSTRY

Uranus 52N+(S 32 520) has proven to be a durable, cost effective, and relatively easy metal with which to fabricate corrosion resistant vessels and devices for the phosphate industry.

To date this material has been used to fabricate preneutralizers, attack tanks, piping, fittings, and other proprietary devices. Vessels have ranged in size from small five feet diameter vessels to thirty feet diameter attack tanks. After designing, fabricating, and using this material in the phosphate industry, the following observations and suggestions are made concerning it's use:

1- FORMABILITY –This material has been rolled, formed, and broken to the various required shapes. While these processes can be accomplished, in some cases, for example, the fabricator chose to cut out the top leg of a rolled angle as this proved easier. In any case, the material can be formed within advised limits.

2- WELDING – We recommend researching the material, developing a welding procedure, and then working closely with Creusot-Marrel Inc./CLI to check the procedure. CLI's policy is to develop a very close cooperation between its corporate metallurgists and welding experts and their client conterparts (fabricators and end users) in order to insure the best performance of the equipment in service.

Vessels to data have been constructed using FCAW in the flat position and stick electrodes for all other positions. A tabulation of approved filler materials for these and other methods was supplied by Creusot-Marrel Inc./CLI. The fabricators reported no particular problems with welding.

3- ISOLATION FROM CARBON STEEL EXTERNAL SUPPORTS – Digesters designed from Uranus 52N+ typically will be low overhead, externally supported API 650 type vessels. In construction to date, care was taken with welded external connections to carbon steel supports to avoid dilution contamination of wetted plates. External welded connections on vessels in service to date were designed with isolation pads to prevent such contamination. Bolted connections are another options for external supports such as that necessary for digester construction. Nevertheless, duplex stainless steels can be welded directly onto carbon steel using duplex filler material without any microstructural problem. This is an advantage when compared to 316L for which a first pass with 20Cr-25Ni type filler material has to be used in order to avoid cracking due to martensite.

REFERENCE OF URANUS 52 N + IN THE US FERTILIZER INDUSTRY

1- MISSISSIPPI PHOSPHATES - Pascagoula - MS

The main equipment built in Uranus 52 N^+ are :

- An additional **attack tank** in the phosphoric acid unit of about 100,000 gallons working volume. The metal thickness is ¼" at the bottom, 3/8" on the shell and ¼" for the cover, and includes 0.125" corrosion allowance. The total weight of stainless steel is 44,244 pounds.

  Except for protection of the bottom against abrasion with an acid resistant material, there is no other lining on the stainless steel. This solution was less expensive than any other material requiring a rubber and brick lining.

- A new **preneutralizer** in the DAP granulation unit of about 30,000 gallons working volume. As with the attack tank, there is no lining except the bottom protection with an acid resistant material. Total weight about 19,500 pounds.

- A new **central valve**. A first valve in 904 L of similar design was commissioned in January 1989 as part of the additional 24 C filter. As soon as the company was granted a permit for a long term operation, the decision was made to modify the filtration section of the other 24 C filter with the design of the first one. The main difference is the material of construction of the last valve which is Uranus 52 N +.

All this equipment was designed by Metro Technical Services and commissioned in March 1998. They have since behaved well.

2- AGRIFOS - Pasadena - TX

The plant is located in the port of Houston and was purchased by Agrifos from Mobil in September 1998. Agrifos decided to uprate the capacity of the phosphoric acid unit by 50 %, using Bartec technology for the process design and Metro Technical Services for the detailed engineering and project management. The first phase of the uprate is planned to be commissioned in July 1999, and the second phase in 2000. Many large and small equipment are or will be made in Uranus 52 N + for a total weight of 800,000 pounds. The main equipment in this material are:

- The **vapor head** of the new evaporators, 18' 4" diameter, 28' high, about 1" thick, are special Bartec design with dished heads on top and bottom. First they were considered in rubberlined carbon steel with the rubber protected against temperature and water blasting by a carbon tiles lining on the bottom and on the shell. Then it was found not much more expensive to make the whole vessels in stainless steel.

- The **condensers** of the new evaporators are also in Uranus 52 N +. Although condensers in rubberlined carbon steel would not have included carbon tiles, the smaller diameter of these vessels allowing a thinner wall made the material attractive as regards all advantages.

- The **circulation loop** including the pipes and the strainer are made in Uranus 52 N +. The pipes are quite large in diameter due to the large flow needed to get an acid velocity of 10.6 ft/sec in the tubes of the heat exchanger.

- The **acid desupersaturation unit** is totally made in Uranus 52 N^+, including the circulation tank, the vacuum cooler and the condenser. The purpose of this section is to release part of the supersaturation of the acid from the filter by forced circulation in a small vacuum cooler. That decreases the further precipitation of impurities in the downstream equipment and particularly in the heat exchangers of the evaporators while increasing the acid strength by 0.5 % and removing more impurities from the 29 % settling tank.

- Studies will be made to decide whether or not **large storage tanks of phosphoric acid** could be economically made in stainless steel clad plates. The answer will probably depend on the acid quality and corrosiveness and on the size of the tanks.

- The new **filter pans** of Bartec design are not made in Uranus 52 N^+ because there is no requirement for a grade highly resistant to corrosion. For corrosive slurries, for example when the rock has a high chlorine content and with hemihydrate route, Uranus 52 N^+ is preferentially selected since it is more corrosion resistant, has better mechanical properties and is less expensive than 904 L.

3- WHY BARTEC IS MAKING A LARGE USE OF STAINLESS STEEL

Bartec is owned by the fertilizer producer Agrifos, and thereby is designing the process equipment in close collaboration with the people in operation to meet their requirement for an easy and maintenance free operation, while still taking care of low capital cost. Bartec is also innovative in the design of its process and proprietary equipment and has the opportunity to test new unconventional and efficient solutions in Agrifos facilities. In this respect, the use of new grades of stainless steel at relatively low cost has the following advantages :

- Rubberlining is troublesome, particularly in evaporators running at high temperature where damage in rubberlining results in clogging the heat exchangers, air leaks, maintenance and down time. Water blasting rubber and carbon brick erodes the surface which is afterward scaling faster and harder. An equipment in stainless steel resistant to corrosion is trouble free for a life time.

- Some Bartec equipment may have to be optimized after commissioning or to be adapted later on to some changes in the design or operating conditions such as rock quality, capacity or others. A rubber or brick lined equipment cannot be easily modified, and doing it is expensive and requires a down time for curing. A stainless steel equipment can easily be modified by adding, removing or modifying nozzles, overflows, internals etc ...

The detailed engineering, the selection of the fabrication shops and the supervision of fabrication is made by Metro which has a good expertise of Uranus 52 N + after designing the equipment for Mississippi Phosphates. That made the selection of the equipment in this material easier and speeded the detailed design.

CONCLUSION

Industrial phosphoric acid solutions are very agressive due to impurities coming from natural phosphate rocks. Solid particles of silica and gypsum lead to erosion-corrosion processes which depassivate stainless steel equipment, particularly agitators and pumps during the attack stage.

Laboratory tests showed the 25Cr super-duplex grade UNS 32520/UR 52N^+ to be much more resistant to corrosion and erosion-corrosion than the conventional austenitic alloy N 08 904 grade which has been widely utilized for more than 30 years now . Among 25% chromium containing grades, the super-duplex grade appeared to be at least as resistant as the super-austenitics which are more expensive. These results are confirmed by long term exposure field tests.

By the use of the super-duplex grade UNS 32 520/UR 52N+ and other innovative design methods, a low cost, durable vessel such as a preneutralizer and an attack tank were constructed completely free from expensive rubber and acid brick. Additionnal equipment are planned to be built using this material. In addition to lower initial capital costs, the savings due to lack of down time and expense due to rubber and refractory repairs is immense. Such items as adding a pump suction to an attack tank can be accomplished without a major capital outlay. We feel this practical material has perhaps many other applications yet to be realized for this industry.

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