APPLICATION OF STAINLESS STEELS IN

WET PROCESS PHOSPHORIC ACID

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ABSTRACT

Presently, more than 95 % of the phosphoric acid is produced by wet processes which consist in attacking natural phosphate rocks by sulfuric acid.

These processes generate a lot of corrosion problems which are described in relation with the different steps of the phosphoric acid production.

In particular, the influence of fluoride and chloride species, so that the effects of abrasion and of heat exchange on the aggressiveness of the process acid solutions are studied by means of laboratory tests previously described.

On the basis of these results a selection of various stainless steels grades and cast-iron is proposed, for apparatus utilized for acid production and for acid storage or transportation.

GENERALS

Due to the demographic growth on our planet, agriculture and consequently the fertilizer industry is insured of a steady an important development. This development makes necessary an increase of production capabilities of intermediate compounds for fertilizers such as ammonium nitrate, potassium chloride and phosphoric acid.

At this time, 95 % of the phosphoric acid is obtained by a wet process which consists in attacking natural phosphate rocks by sulfuric acid. This process generates numerous corrosion problems which are described in this paper in relation with the different steps of the phosphoric acid production.

In particular, the effect of corrosion by fluorides and chlorides, the effect of abrasion during the first stage of attack of phosphate rocks for production of the slurry, and the effect of heat transfer during the concentration of this slurry are analysed by means of specific laboratory corrosion tests.

Then, the results are discussed and a selection of special stainless steels is proposed for agitators, pumps, filtres, heat exchangers, and so on ...

PHOSPHORIC ACID PRODUCTION

Mains stages

Whatever the particular process may be, the main steps in phosphoric acid production by wet processes will generally include :
- an attack
- a filtration
- a concentration

- attack of natural phosphates : the phosphoric acid required to produce fertilizers is obtained by sulfuric acid reacting on natural phosphate rocks, whose main compound is the $Ca_3 (PO_4)_2$ Tribasic Calcium Phosphate.

The following reaction (simplified form) :

$$Ca_3 (PO_4)_2 + 3H_2 SO_4 ------> 2H_3PO_4 + CaSO_4$$

results in the generation of a mixture made up of more or less hydrated Calcium Sulphate crystals in suspension in liquid phosphoric acid which titrates about 30 % P_2O_5 (or 40 % H_3PO_4). Secondary reactions, particularly with Calcium fluoride and Silica contained in phosphate rocks, accompany the main reaction and increase the phosphoric acid corrosiveness due to the generation of compounds containing fluorine such as hydrofluoric acid or hydrofluosilicic acid :

$$CaF_2 + H_2SO_4 ------> 2 HF + CaSO_4$$
$$6 HF + SiO_2 ------> H_2SiF_6 + 2 H_2O$$

- filtration of the slurry : the slurry (calcium sulphate crystals) is separated by filtration under partial vacuum condition.

- acid concentration : the 30 % P_2O_5 acid slurry is concentrated by vacuum evaporation up to about 54 % of P_2O_5 thus cutting down transportation cost.

Main industrial processes (Table 1)

They roughly belong to two main groups according to the type of calcium sulphate which is generated.

- dihydrate process ($CaSO_4. 2 H_2O$) : this is presently the most common process (90 % of the units). Simple, reliable, needing only low investments. It perfectly suits the needs of developing countries. The rather low temperature required for attacking phosphates (80°C) notably limits corrosion problems during this phase of the process.

The most used dihydrate processes are : Dorr-Oliver, Singmaster and Brayer, Prayon and Rhone Poulenc (Figure 1).

- hemi-hydrate process ($CaSO_4, 1/2 H_2O$) : the thirst process was developed by Fisons to produce directly high concentrated phosphoric acid (45/50 % P_2O_5) without concentration stage. The hemi-hydrate precipitation occurs at 110°C. But this process exhibited a rather bad yield.

- hemihydrate/dihydrate processes : they have been among the first ever developed because they theoretically had three advantags if compared with dihydrate :
. improved yield rate

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. higher P_2O_5 concentration enabling to suppress the concentration stage
. better calcium sulphate enabling the transformation into plaster.

In fact, such processes did not reach a significant industrial development because on the one hand their various features did not prove really efficient, and on the other hand, they were much more complex to handle (double crystallization). Moreover, they required a higher reaction temperature (100°/110°C) thus generating much more difficult corrosion problems during the attack step.

Among hemihydrate/dihydrate processes are : Fisons, Nissan and Central Prayon (Figure 2).

Aggressiveness of natural phosphates and phosphoric acid

The phosphoric acid is not very corrosive. However, the impurities it contains (i.e. hydrofluoric and fluosilisic acids, sulfuric acid in excess, and also chlorides generated either from the phosphates themselves or by their washing process) make the medium highly corrosive.

The chemical composition of the main natural commercial phosphates are listed in the Table 2. Some of them are very corrosive.

The chemical composition of the main phosphoric commercial acids (54 % P_2O_5) are listed in the Table 3.

The main impurities which determine the corrosive power of the different industrial phosphoric media are listed in the Table 4.

CORROSION PROBLEMS

Both the phosphate aggressiveness and the type of process selected lead to a more or less rapid deterioration of the apparatus (tanks, agitators, pumps, piping, etc ....).

First step : attack of phosphate rocks

The two following features can be underlined :
- a high chemical aggressiveness of the phosphoric mixture due to the above mentioned impurities
  This aggressiveness would be even higher if it were not, to some extent, tempered by oxidizing metal ion (Fe^{3+}, Al^{3+}) which favour the passivation process of steels and stainless alloys used in such a medium
- a very high abrasive capacity of the mixture which generally contains 30 or 40 % of solid matters, in suspension (mainly Gypsum). Those matters are churned and carried on to the filtration stage and they partly or even totally deteriorate the passivity of the different stainless steels used for pumps and agitators. The higher the rotation speed the faster this deterioration process develops.

Second step : filtration of the 30 % P_2O_5 slurry

This stage of the industrial phosphoric acid production involves a medium much less corrosive because the temperature is much lower, i.e. about 50°C.

The high chloride rate however sometimes favours the generation of :
- crevice corrosion in some stagnant areas of the filter where the solution is not renewed under satisfactory conditions
- corrosion-fatigue due to cyclical strains suffered by the filter on account of its shape and rotation. Such mechanical factors added to local depassivation by chlorides may generate cracking in the filter plates.

Third step : concentration of the filtered solution

Concentration of the 30 % P_2O_5 acid which enables to obtain a 54 % acid is generally performed under partial vacuum within a circuit including a tubular exchanger inside which the temperature of the flowing acid reaches about 80°C ; the heat is supplied by steam at about 140°C. In such operating conditions, the steel skin temperature reaches about 110°/120°C.

Circulation is performed by means of a very large pump with a high rotating speed. In this circuit, the pump is attacked by gypsum particles which are not retained by the filter. Corrosivity of 54 % P_2O_5 acid is lower on account of its low fluoride and chloride concentration during this phase, and also on account of the acid high oxydizing power which favours stainless steels passivation (refer to pictures).

On the other hand, metallic tubular exchangers are subjected to a high corrosion rate due to heat transfer. Indeed, heat transfer notably increases the rate of the metal-solution exchange reaction kinetics which mean a dramatic increase in the corrosion rate. Then, in most of the phosphoric acid plants, concentration is performed through graphite exchangers in spite of their brittleness because of the very high corrosion resistance of this material.

This brief survey of the different destructive actions on materials which can be met during the phosphoric acid production processes brings to light the high corrosivity of the 30 % P_2O_5 slurry as well as its higly abrasive action which entails a very fast wear of pumps and agitators.

MATERIAL SELECTION FOR PHOSPHORIC ACID PRODUCTION

The selection of materials must be performed only after a careful and detailed study of the operating conditions of each device and by analysing the ratio of investment costs to maintenance costs.

Table 5 lists the nominal compositions of the different stainless materials likely to be used for phosphoric acid production.

Attack of phosphate rocks

- Reacting vessel : the traditionnal construction i.e. concrete + bricks give satisfaction. So, except in some very specific cases of for minimizing maintenance strip, there are a few reasons to use stainless steels (but for these reasons, some Italian companies, for example, chose theUR B6 grade which gives full satisfaction). The superaustenitic grade UR SB8 appears to be the best material in the most aggressive conditions (abrasion and corrosion), specially for hemi-hydrate processes.

The main central agitator and surfaces agitators used for mixing reaction products must resist to a severe abrasion phenomenum (due to gypsum) and a general corrosion due to temperature (110°C) and sulfuric acid addition. They are currently made from UR B6 or for most severe cases from UR SB8.

- Pumps : they must be made of a corrosion and abrasion resisting grade : the material must repassivate easily when depassivated by abrasion, and must have good hardness characteristics.

When selected phosphates and process lead to low aggressiveness, it is possible to use a 30 % Cr and 2 % Mo casting which is highly resistant to abrasion effects. Under more corrosive conditions UR B6 is selected, or even better UR B6P which is harder and offers an excellent resistance to a phosphoric solution highly polluted with chlorides. The more alloyed grade UR SB8 is used under the most corrosive conditions.

Figures 3, 4, 5 and 6 show laboratory test results which accurately underline the influence of temperature and of chloride contents as well as the consequences of the abrasion process [1] [2] [3].

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Filtration of the slurry

- filters : in the most common cases, AISI 316 L and 317 L grades are experiencing quite a good resistance. When temperature is high (for some hemihydrate processes) or when phosphates are aggressive (F^- and Cl^- ions) it becomes necessary to select the ICL 170 HE steel. But, it is also possible to use the duplex grades UR 47 N and 52 N which offer a very good compromise between an excellent general corrosion resistance and a local corrosion resistance (pitting, crevice and stress corrosion cracking), a very good resistance to abrasion problems, very good mechanical properties (double than the one of the austenitic grades) and are in a rather cheap range of material.

The best possible relation between mechanical properties/corrosion resistance/price is obtained with the UR 47 N or UR 52 N duplex grades. In most difficult cases (high chloride content) the grade UR B6 (UNS 08904) must be used.

To make a very accurate selection according to chloride concentration refer to figure 5 results : though they are obtained at a temperature much higher than the temperature of a normal filtration process they still give an accurate classification as concerns corrosion resistance of the different stainless steels likely to be used for making filters or manufacturing various piping systems types.

- cast pieces such as circulation pumps : 30 % Cr, 2 % Mo casting may be used, although its abrasion strength is not required for this application.

Then, UR 55 M austenitic-ferritic grade will be prefered because it is much less brittle and displays a higher corrosion resistance.

Concentration stage

- exchangers : graphite tube or block exchangers are commonly used for their high corrosion resistance (UR B6 is not suitable : its corrosion rate is about 0.5 to 1 mm/year). The super-austenitic grade UR SB8 proves very efficient for this application [3] and then can replace graphite which is brittle material (refer to test results of figure 7).

- circulation pumps : in the media which have the lowest contents in F^- and Cl^- ions, 30 % Cr, 2 % Mo casting can be selected for its high abrasion resistance. Very often UR B6 is selected, chiefly when the phosphates prove to be aggressive.

In the most difficult cases UR B6P and UR SB8 are selected.

MATERIALS SELECTION FOR TRANSPORTATION OR STORAGE OF PHOSPHORIC ACID

54 % P_2O_5 acid

54 % P_2O_5 acid 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 transportation conditions as they are planned and more particularly the temperature and the effective ion Cl^- concentration either generated by the acid itself or by casual pollutions as it often happens during sea shipment.

Test results (Figure 8) enable to select with a high accuracy the best suited stainless steel according to transportation and storage conditions.

In most cases, the grade UR 45 N offers the best ratio corrosion resistance/mechanical properties/price.

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70 % P₂O₅ concentrated acid

As it can be noted on Table 6 the transportation of non-chloride-polluted concentrated phosphoric acid does not entail any corrosion problem.

When some chlorides are present, a torough study of the various transportation conditions must be carried out because this highly oxydizing and thick acid may cause important localized corrosions thus requiring the use of a highly alloyed stainless steel (for example UR B6 grade).

Among these other possibilities, a grade like the UR 52 N could aso be considered as a good possible choice.

REFERENCES

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3 - J.P. Audouard, A. Desestret, G. Vallier, "Nouveaux résultats relatifs au comportement des aciers inoxydables spéciaux dans les milieux phosphoriques industriels", IVe Colloque International de l'abrasion, Grenoble, 9-11 Mai 1979.

| Process | Reacting conditions of the phosphate | | P₂O₅ after filtration | | Interest of the process Notes |
	Ca sulphate	Temperature °C	Concentration %	Yield	
Dorr Oliver	di-hydrate	80 / 85	28	96,5	- simple
Singmaster & Breyer	di-hydrate	85 then 65 (*)	28		- tried and tested
Fisons - Lurgi	di-hydrate	80 / 85	28	96,5	- low investments
Prayon	di-hydrate	80 / 85	26	> 95	
Rhône Poulenc	di-hydrate	80 / 85	28	97	
Fisons	hémi-hydrate	85 / 110	45	94	- concentr. acid lower energy required
Nissan	hémi-hydrate -→ di-hydrate	90/110 then 65(*)	30	> 98	- P₂O₅ good purity - high yield rate - good plaster quality
Prayon-Central Glass	di-hydrate -→ hémi-hydrate	80 then 65	30	98	- good plaster quality - high yield rate
Fisons	hémi-hydrate -→ di-hydrate	90/110 then 65(*)	45		- more concentr. acid lower energy required
Nissan	hémi-hydrate -→ di-hydrate	90/110 then 65(*)	45	> 98	- medium plaster quality

(*) 2 steps (1st : attack - 2nd : crystallisation)

Table 1 - Main wet phosphoric acid processes

| Country | Area | Main constituents | | | | | | | | | |
		P₂O₅ %	Ca O %	Si O₂ %	SO₃ %	F⁻ %	Cl⁻ ppm	Al₂O₃ %	Fe₂O₃ %	Mg O %	S⁻⁻ ppm
U.S.A.	Floride	35	50	2		3,8	300				< 100
	Floride	30,5	46,5	8,4 *	1,65	3,95	200	0,9	1,65	0,44	< 100
	Caroline Nord	32,1	50,6	4,4	2,3	3,87	90	0,8	0,8	0,56	1300
Maroc	Yousoufia	35	50	2		3,8	< 500				?
	Ben Guérir	31,3	49,9	1,9	1,8	3,74	320	0,4	0,2	0,8	< 100
Tunisie		30	49	2,5		2,8	900				
U.R.S.S.	Kola	34					< 500				
Sénégal	Taïba	37,7	51,7	1,75	< 0,1	3,87	20	0,7	0,5	0,05	< 100
Togo		37	49	3,5		3,80	< 500				
Jordanie		34,5	51,1	4,05	1,3	4,04	1500	0,2	0,2	0,3	< 100
Océanie		39					< 500				
Israël		32,3	51,9	1	2,55	3,50	1500	0,3	0,1		

* Si O₂ is partly under the form of a highly abrasive quartz

Table 2 - Mean composition of the main commercial phosphates

Source of acid	Morocco 1	Morocco 2	Kola	Florida	*	*	Tunisia	*	Texas 1	Texas 2	*	*	Asturia	Windmill Holland 1	Windmill Holland 2	Windmill Holland 3	Huelva	*	*	
P_2O_5	50	55	49.09	46.7	50.4	55.8	54	52/55	51.5	55.08	53.45	55.40	50/55	50.7	49.5	49.6	53.5	52.8	-	46.7/55.8
F	0.50	0.7	0.37	1.12	0.49	1.23	0.6	0.6/1.2	0.13	0.67	0.85	0.65	0.4	0.7	0.65	0.54	0.30	0.52	0.3	0.13/3.23
Cl	-	0.02	-	•	-	-	0.14/0.15		/0.005		0.0017	0.001	0.04	0.02	0.06	0.058	absent	0.02	0.04	0.001/0.15
SO_4^{3-}	3.00	3	0.84	2.88	4.3	4.9	2.5	3/5	3.40	3.08	3.20	4.70	3.24	4.2	2.0		3		3	0.84/5
Fe_2O_5	0.53	0.9	0.8	1.40			0.30/0.50	1.3/1.6			1.70	1.27	0.8	1.5	1.60	1.6	0.34	0.23	0.3	0.23/1.70
Al_2O_3	0.40	0.6	0.5	0.70			1.15	0.8/1.0			0.85	0.70		0.9	0.34	0.32	0.33	0.74	0.8	0.32/1.15
SiO_2	0.50	0.2	0.22	0.80													0.01	0.02		0.01/0.80
MgO	0.42	0.1	0.25	0.40			1.20/1.70							0.27	0.24	0.34	0.50	0.45		0.10/1.70
CaO	0.03		0.02	traces				0.2/0.4			0.11	0.07	0.08	0.36	0.47	0.47	0.1		0.1	0.02/0.47
Na_2O	0.07																absent			
K_2O	0.03																0.04			
H_2O								15/19						23.3	23.7					15/23.7
Solids							0.50/1,0	0.7/1.2	0.16		2.30	0.35		0.8	0.5		1 max			0.16/2.30

* Not known

Table 3 — Chemical composition of the main phosphoric commercial acids of the wet process (% by weight)

		Phosphate	Filtered slurry	Concentrated acid	Corrosive effect	Abrasive effect
P_2O_5		30 / 38	28 / 32	48 / 54		
Impurities	SO_3 %	1,5 / 3	1,5 / 4,5	2,5 / 6,5	+	
	F^- %	2,5 / 4	1,5 / 4	0,5/1,5 {80% H_2SiF_6 / 20 % HF}	++	
	Cl^- ppm	20 / 2500	20 / 2500	5 / 300	++	
	SiO_2 % active	1 / 3	< 1 / < 3	0,01 / 0,05	—	
	SiO_2 % quartz	0,5 / 3	0,5 / 3		néant	++
	S^{--} ppm	50 / 1500	$[H_2S] = ?$	$[H_2S] = ?$	++	
	Al_2O_3 %	0,2 / 1	~ 0,5	~ 1,5	-	
	Fe_2O_3 %	0,2 / 1	~ 0,5	~ 1,5	-	

Table 4 — Main impurities which determine the corrosivity of industrial phosphoric acid (average values mini/maxi)

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AISI UNS or ACI	Grade Trademark	C : cast F : forged R : rolled	C	Cr	Ni	Mo	Cu	N2	W	Others	Fe
316 L	ICL 164 BC (1)	R	0.02	17	12	2.2					bal
316 LN	ICL 166 HE (1)	R	0.02	18	11	2.7		0.15			•
317 L	ICL 168 BC (1)	R	0.02	19	15	3.2					•
317 LN	ICL 168 HE (1)	R	0.02	19	15	3.5		0.15			•
317 LN (4 % Mo)	ICL 170 HE (1)	R	0.02	18	15	4.5		0.15			•
08 904	UR B6 (1)	R	0.02	20	25	4.3	1.5				•
	UR B6P (1)	F/C	0.02	20	25	4.3	2.5		2.0		•
	UR SB8 (1)	R	0.01	25	25	4.8	1.5	0.20			•
31 803	UR 45 N (1)	R	0.02	22	5.7	2.8		0.12			•
32 550	UR 52 N (1)	R	0.02	25	6.5	3.0	1.5	0.17			•
	UR 47 N (1)	R	0.02	25	6.5	3.0		0.17			•
CD4 MCu		C	0.03	26	5.7	2.0	3.0				•
	Cast 30 Cr-2 Mo	C	1	30		2.0					•
	Hastelloy C (2)	R	0.01	15.5	54	16.0					•
	Hastelloy G (2)	R	0.03	22.5	45	6.5	2.0			0.5 Nb+Ta=2	•

(1) Creusot-Marrel
(2) Cabot Corporation

Average composition (% weight)

Table 5 – Nominal composition of tested stainless materials

GRADE	TEMPERATURE	
	85° C	100° C
AISI 316 L	/10	/10
ICL 170 HE	"	"
URANUS 45	"	"
URANUS 47	"	"
URANUS 50	"	"
URANUS B6	"	"
URANUS SB8	"	"

Table 6 – Corrosion rate (mdd) of various SS samples immersed in 75 % P_2O_5. Effect of tempe-rature (25 mdd = 0.1 mm/yr)
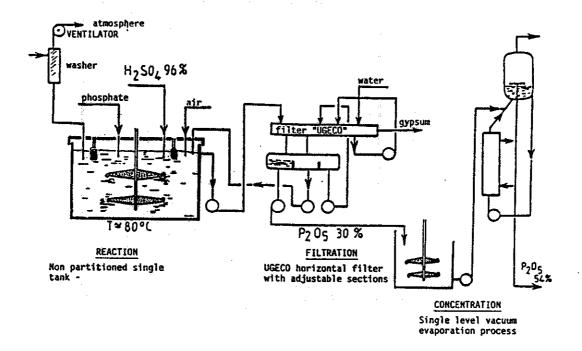
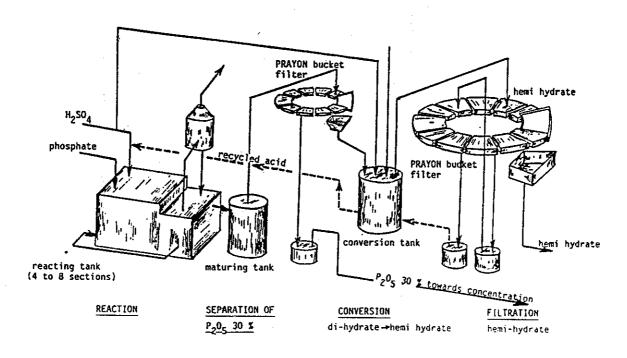Fig. 1 – Sketch of the di-hydrate Rhone-Poulenc process

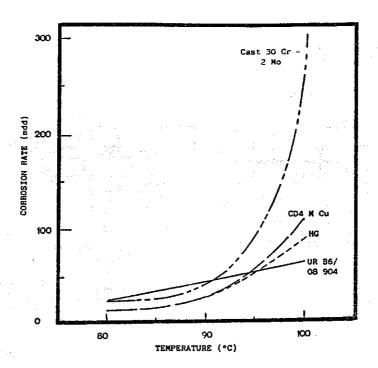Fig. 2 – Sketch of the hemi-hydrate/dihydrate Central Prayon process

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Fig. 3 - Influence of temperature on the corrosivity of the 30 % P_2O_5 slurry (1)
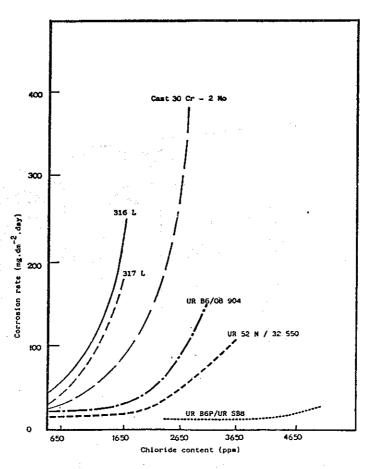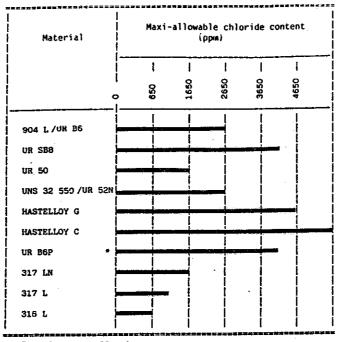

Fig. 4 - Influence of the chloride content on the corrosivity of a 30 % P_2O_5 slurry at 80°C (1)

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Fig. 5 - Selection of stainless materials depending on the phosphoric acid chloride content. Tests performed in a 30 % P_2O_5 industrial solution at 83°C (1)
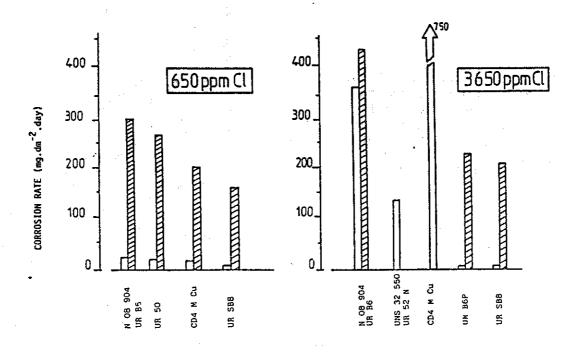

Fig. 6 - Influence of the abrasion process in relation with the chloride content of the 30 % P_2O_5 phosphoric acid at 80°C (1)

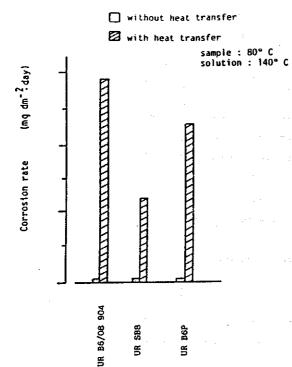(1) Industrial phosphoric acid from SATEC plant, Bayonne, France

□ without heat transfer

▨ with heat transfer

sample : 80° C
solution : 140° C

Corrosion rate (mg dm^{-2}.day)

UR B6/08 904

UR SB8

UR B6P

Fig. 7 - Influence of heat transfer on the corrosion rate of various stainless steels (54 % P$_2$O$_5$ solution from SATEC plant, Bayonne, France)

Fig. 8 - Chloride content limit allowable during transportation of 54 % P$_2$O$_5$ acid, depending on temperature (values garanteed for an industrial phosphoric acid with H$_2$SO$_4$ ⩽ 4 %, F ⩽ 1 % where HF < 0,2 %

2000

UR SB8

UR B6/08 904

UR 52 N/32 550

UR 45 N/31 803

317 LN (Mo 4 %)

317 LN

316 LN

316 L

Chloride concentration (ppm)

1000

0

0   20   40   60   80   100   120

Temperature (°C)