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The use of stainless steels and alloys in
the manufacture of wet process phosphoric acid

By J. Roubinet,

(Société Pechiney-Saint-
Gobain, France)

This paper is not intended to provide a theoretical and complete account of the phenomenon of corrosion of stainless steels by wet process phosphoric acid.

Previous workers have published excellent accounts of the subject and we have found it very valuable to refer to them, in particular to the work of J.J. Porter and G.C. Lowrison, presented to this association in 1953.

We propose, much more simply, to discuss the problems which faced our company concerning the choice and application of metals to be used in our phosphoric acid plants. We shall thus describe the difficulties we have encountered, the research we have carried out and the practical solutions we have arrived at, as well as the results of their industrial application.

We do not pretend that the alloys of varying composition that we have chosen are the most resistant to corrosion, but we believe that they are the ones whose use in France is the most economical. In particular, we know that other alloys exist (especially alloys having a high content of Nickel-Molybdenum) whose resistance is probably better, but their cost price is, at this particular time, too high in France to allow them to be used in place of less noble metals.

The Principle of the Production of Phosphoric Acid

Let us recall briefly that phosphoric acid produced by a wet process is obtained by the action of sulphuric acid on phosphate rock. The slurry so obtained is filtered in order to obtain phosphoric acid as clear as possible.

Unfortunately, the natural phosphate rocks are not pure products. They contain a certain number of impurities, among

which we may mention fluorine, silica, chlorine and some metals.

In the first stage of manufacture, a slurry is obtained containing mainly gypsum and phosphoric acid, but also surplus sulphuric acid, and fluorine in the form of hydrofluoric acid and hydrofluorosilicic acid and sometimes hydrochloric acid.

After filtration and elimination of the gypsum, a phosphoric acid is obtained still containing sulphuric, hydrofluoric and hydrofluorosilicic acids.

Moreover, we should recall that the reaction is carried out at a temperature ranging from 75 to 80° C.

An average composition for the acid so made would be:

P_2O_5	-	30 to 32%
H_2SO_4	-	1.5 to 2.5%
F_2	-	1.5 to 2.5%

The materials used in the preparation must therefore be resistant to phosphoric acid, sulphuric acid and acids derived from fluorine, and above all to a mixture of all these acids at 80° C. It is worth mentioning that very often the mixture of several of these acids is more reactive than the constituents used separately.

It can therefore readily be understood that corrosion of a stainless steel by phosphoric acid will be strongly influenced by:

- 1) the nature of the phosphate rock: the amount of acids derived from fluorine will depend on the content of fluorine, silica, alumina, and metallic salts in the phosphate rock. Moreover, the combination of certain of these substances forms products which have a tendency to deposit as a hard crust on the metallic parts and thus to protect them from the corrosive action of the acid.

- 2) the way in which the attack of the phosphate is carried out and, more particularly, the temperature and strength of the sulphuric acid.

Choice of a Stainless Steel

Taking into consideration the preceding facts and information obtained from the literature, one must choose a corrosion-resistant metal according to the conditions under which it will be used.

The first criterion will be chemical analysis of this steel (chiefly its content of chromium, nickel, molybdenum, copper and carbon).

However, we must point out that our experience has led us to temper the judgment that we might make on a steel as a result of mere examination of its analysis. It quite often happens that alloys of very similar composition show very different behaviour in terms of corrosion.

We think that these differences of behaviour can be attributed to several causes, among which we can mention:

- the presence in very small amounts of certain metals, in combination with other constituents of the alloy. Thus, it seems to us that the presence of copper in combination with molybdenum greatly increases the resistance of a steel.
- the thermal and metallurgical treatment that these steels undergo at the factory. These treatments play a great part in relation to intercrystalline corrosion. A number of workers have already been interested in this subject and excellent studies exist on the formation of the sigma phase at temperatures ranging from 500 to 900° C, its effect on intercrystalline corrosion and the methods of alleviating this formation.

Consequently, we believe that one should not only choose a stainless steel belonging to a well established group, but also one provided by a well known supplier. This is absolutely essential if one wishes to be practically certain of the result one will obtain.

Working of the chosen metal

After having chosen with the greatest care the metal to be used, it must then be worked: moulding, welding, etc. In this second stage also one runs up against a certain number of difficulties and it is necessary to proceed with very great care.

During the moulding one must avoid anything that might create internal tensions (folding at sharp angles, too severe compression, etc.). It is generally the simultaneous effect

of internal stresses and of the above mentioned sigma phase which leads to intercrystalline cracks.

Finally, the welding is very often the beginnings of incurable deterioration. A sheet metal which is to be welded must be chosen with great care. In particular, alloys of low carbon content are preferable. The presence of certain additives, such as titanium and niobium (in stabilised steels) proportional in amount to the carbon, can improve the weldability of the sheet.

The welding rod (electrode) should be specially chosen: its composition should be very close to that of the metal to be welded and its content of carbon should be less or at the most equal to that of the sheet metal in order to avoid a concentration of carbon in the metal close to the weld (this concentration is always reflected as a loss of resistance to corrosion). As a result, if the technique of welding in an inert atmosphere is used, one must cut the welding rod from the same sheet as the piece to be welded. If one is satisfied with ordinary electrical welding, one must choose the type of electrode recommended by the constructor.

Moreover, one must avoid overheating the piece to be welded (creation of sigma phase and stresses). For that reason, one must work at the minimum intensity and intermittently, that is to say by very short strokes diametrically opposed to the piece. One should note that a special manual skill is required and the training of a good welder is very difficult to achieve. It should also be noted that certain authors recommend that the part immediately behind the weld should be quenched by a jet of water following the electrode. Personally, we have never used this method, the operation of which seems to us to be a delicate procedure.

Finally, one must avoid oxidation of the metal, either by working in an inert atmosphere (argon, for example) or using specially coated electrodes.

Process used for testing a metal

All these considerations have led us to believe that one should carry out a series of tests to justify the choice of one steel, rather than another, for any particular use. In order to limit the very considerable costs which are involved in trials on an industrial scale, we operate in three stages.

(a) Laboratory trials

We have at our disposal a certain number of metal samples for testing and of some other metals which are well known and which we use as standards.

These various samples are plunged into a phosphoric acid bath of determined concentration and temperature.

They are then regularly weighed and one can thus follow the loss of weight over a period of time, and consequently the loss of thickness. These first trials lead to the elimination of materials which definitely do not measure up to the required qualities.

Moreover, being always comparative, they allow a relative classification to be made between the different materials.

(b) Trials on samples in the factory

Having proved satisfactory in the laboratory tests under well controlled static conditions, the sample is then immersed in a flow of slurry or acid at the factory.

This trial confirms or invalidates the good performance of this material under more difficult conditions: the constant renewal and varying quality of the corrosive products.

(c) Industrial trials

If the two preceding tests give positive results, one then proceeds to carry out industrial tests by constructing an apparatus (of as small a size as possible) with this metal.

It is put into service and its performance is followed very closely. It is only after these last tests that one can feel confident of a reasonable chance of success in choosing a particular alloy (and a particular supplier). One can then proceed to put new equipment into service.

Results of Laboratory Tests

It would be tedious to give here the results of all the trials which have been undertaken by our research laboratory.

We shall only present the interesting results of materials in current production: the production of acid, of 32 and 50% P_2O_5 , with a series of alloys chosen in the standard ranges available in France.

Finally, in order to make the results as comparable as

possible with one another, we shall give only the results of trials in which Morocco acid at 75 to 80° C was used.

The materials tested can be classified into 5 broad categories:

(a) The "20: 25: 4" series (also called alloy "20"), comprising the following samples:

	<u>A1</u>	<u>A2</u>	<u>A3</u>	<u>A4</u>	<u>A5</u>
Cr	20	20	20	20	20
Ni	25	25	28	24	26
Mo	4.5	4.5	4.5	3	3
C	0.02	0.04	0.03	0.05	0.08
Cu	1.5 to 1.8	1.5	traces	2	2
Si	-	-	1	-	2
Mn	1.2	-	1	-	2

Note: A2, A3 and A5 and only used for castings.

(b) The 18. 13. Mo. low carbon series comprising:

	<u>B1</u>	<u>B2</u>	<u>B3</u>	<u>B4</u>
Cr	17.5	17.5	17/18	18
Ni	16	13	13/14	10
Mo	6	2.5/3	2.5/3	2.2
C	0.03	0.03	0.03	0.02
Cu	3	-	-	-

(c) The 18.13. Mo. series

	<u>C1</u>	<u>C2</u>
Cr	17	15
Ni	12	20
Mo	2.3	4.5
C	0.08	0.08

(d) Alloys of high chromium content (for castings only)

	<u>D1</u>	<u>D2</u>	<u>D3</u>	<u>D4</u>	<u>D5</u>
Cr	30	28	24.5	24	22
C	1	0.8	0.43	0.10	0.7
Si	0.8	1	1.12		
Mn	0.17	0.2	0.66		
Cu	0.1	0	0.13	0	1
Ni	2.2	1.5/2	3.53	5	5
Mo	2.3	1.5/2	0.50	1	0

(e) Alloys of high nickel content

comprising:

	<u>E1</u>	<u>E2</u>	<u>E3</u>	<u>E4</u>
Ni	53	52	40	30
Cr	15	23	21	15
Mo	18	4	3	7
C	0.15	0.15	0.05	0.08
Cu	0	4	1.75	-

In order to make our procedure quite clear we quote below in detail a trial that has been carried out on samples A1, B1, and B2. We shall then give a rough classification of these different alloys.

A sample of each alloy was placed in a receptacle containing acid of 32% and another in acid of 50%. They were then all placed in a drying oven at 80° C.

At the end of each week the samples were washed, dried, weighed and replaced; the loss of weight was indicated on the appended graphs.

In this way a classification becomes distinctly apparent. The weight losses on a yearly scale (mm per year) were as follows:

<u>Sample</u>	<u>In 32% acid</u>	<u>In 50% acid</u>
A1	0.0250	0.0135
B1	0.0615	0.0215
B2	0.0750	0.0350

When considering the results obtained from several trials, it can be seen:

- that this classification is valid in all cases;
- that the amount of loss of thickness varies with the trials ;
(for example, for sample A1 values are obtained between 0.0100 and 0.0475 mm per year, the average being 0.0270 mm per year).

These differences can be attributed to slight differences of composition in the acids used and, perhaps, also to slight differences of temperature.

We are therefore, presenting below the average of several trials. One must remember when reading the table:

- that the classification in relative values is valid (comparative trials);
- that the attributed values are only the averages of trials and can vary according to the reaction conditions;
- that, moreover, we are not operating under industrial conditions.

Classification in 32% acid:

	<u>Sample</u>	<u>Loss of thickness in mm/year</u>
<u>Excellent</u>	A3	0.0145
	D2	0.0240
	A2	0.0245
	A1	0.0270
	D3	0.0350
	B3	0.0380
<u>Very good</u>	D1	0.0390
	E3	0.045
	B1	0.051
<u>Good</u>	B4	0.060
	B2	0.060
	C1	0.065
	D4	0.069

	<u>Sample</u>	<u>Loss of thickness in mm/year</u>
	A4	0.109
	C2	0.150
<u>P o o r</u>	A5	0.290
	E1	0.350
	E2	0.525
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<u>V e r y g o o d</u>	E4	0.970
<u>I n a d e q u a t e</u>	D5	1.330
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One can note that the metals of the first category (20:25:4) are in general excellent, except for A4 and A5 (This illustrates what we said earlier, i.e. that metals of very similar formulas can have very different behaviour).

It would be from the first category that we should prefer to choose materials to be placed in direct contact with the slurry in the reaction medium, particularly for moving parts.

Materials of the second category (18.8 Mo. - low carbon) are classified as very good. They can be used for equipment in contact with the slurry outside the reaction medium.

Metal C1 in the third category can be used for equipment in contact with acid (filter pans, tanks etc....).

Metals of the fifth category (apart from E3, the price of which is very high anyway) are to be avoided.

Among those of high chromium content, certain ones are well placed, such as D1, D2, D3 and, taking into consideration their resistance to abrasion, can be used in difficult conditions (for the hydraulic parts of slurry pumps for example). Nevertheless, their main shortcoming is that they are brittle and difficult to machine.

Other metals of this category, however, should be avoided, such as D4, and even rejected, such as D5.

Classification in 50% acid

	<u>Sample</u>	<u>Loss of thickness in mm/year</u>
<u>Excellent</u>	A1	0.0150
	B4	0.0210
	B1	0.0200
	A2	0.0230
	D3	0.0265
	B2	0.0310
<u>Very good</u>	E3	0.0460
	C2	0.0460
<u>Border line</u>	C1	0.0630

Samples A3, A4, A5, B3, D1, D2, D4, D5, E1, E2, E4 have not as yet been given trials in 50% acid, the problem of their use having not yet been raised.

Nevertheless, one can note:

- that the variation between different trials was very much more limited than with 32% acid (perhaps this is due to the fact that fluorine disappears almost completely during the concentration):
- that the average losses are smaller, in general, than in 32% acid - probably for the same reason.

Of course, these results are not valid for acid in the course of concentration, by reason of the important release of fluorine which occurs during this process.

Influence of various other factors

Another series of laboratory tests has been undertaken in order to measure the influence of other factors on the corrosion of a moving part in the reaction slurry.

Unfortunately, as the operating conditions for these tests were very difficult their number is necessarily limited. It is therefore difficult for us to give them at the moment with certainty. We shall thus restrict ourselves to noting certain trends.

(a) influence of rate of operation in a given reactor:

For a given volume, the greater the rate of operation (measured as the throughput of phosphate rock, for example), the greater the release of fluorine products. We notice similarly during the trials that corrosion is more serious. For example, one finds the loss is 20% greater if the rate of operation is 33% higher.

(b) influence of temperature:

This seems to be very much more important: above 80° C the loss of thickness increases very rapidly with temperature.

(c) influence of the nature of the phosphate

Certain phosphates, such as "Christmas Island" or "Foskorite" are very much less corrosive than Morocco 75, for example (approximately 5 times less).

On the other hand, Togo, Taiba, Pebble 75 and Morocco 75 seem to have rates of corrosion of the same order.

This is only valid for clean, uncrusted metals. It is certain that some of these phosphates (Morocco for example) have a greater tendency to produce scaling than others. In this case, the results can probably be modified for the parts which become easily encrusted and which are therefore naturally protected.

Industrial Results

The first plant, using the UCB-ST-GOBAIN process, which was built at our factory at Grand Quevilly, in 1956, was watched very closely and has served as a basis for our industrial trials. The lessons we have learned from this are as follows:

- the agitators are in alloy Al. They have not been changed since installation, which makes 7 years of use, without apparent corrosion. Only the ends of the paddles have been changed in order to reduce mechanical wear.
- the equipment in contact with the P_2O_5 slurry in the reaction tank (slurry conducting tank - slurry distribution tank) are made of alloy B2, as are certain pieces of stationary equipment inside the reaction tank (float guide and float level indicator). Their minimum life is about 2 to 3 years.

- equipment in contact with the acid (conducting tanks - filter pans) is made of alloy C1. Certain of these have been in place since their original installation. Others have just been changed (life from 6 to 7 years).

The hydraulic parts of certain slurry pumps are composed of alloy D1. Their chemical behaviour is excellent and their resistance to abrasion means that their life is doubled in relation to the same pieces of equipment made of alloy A1.

It should be noted however that this unit has almost always been run on Morocco 75 (except for certain trials with other phosphates) and that the average production concentration was 30% P_2O_5 .

At the end of these encouraging trials with alloy B1, we made an agitator out of this alloy in one of our factories. Unfortunately, it is too early to be able to say that this is a satisfactory solution, although the first indications are favourable.

Conclusions

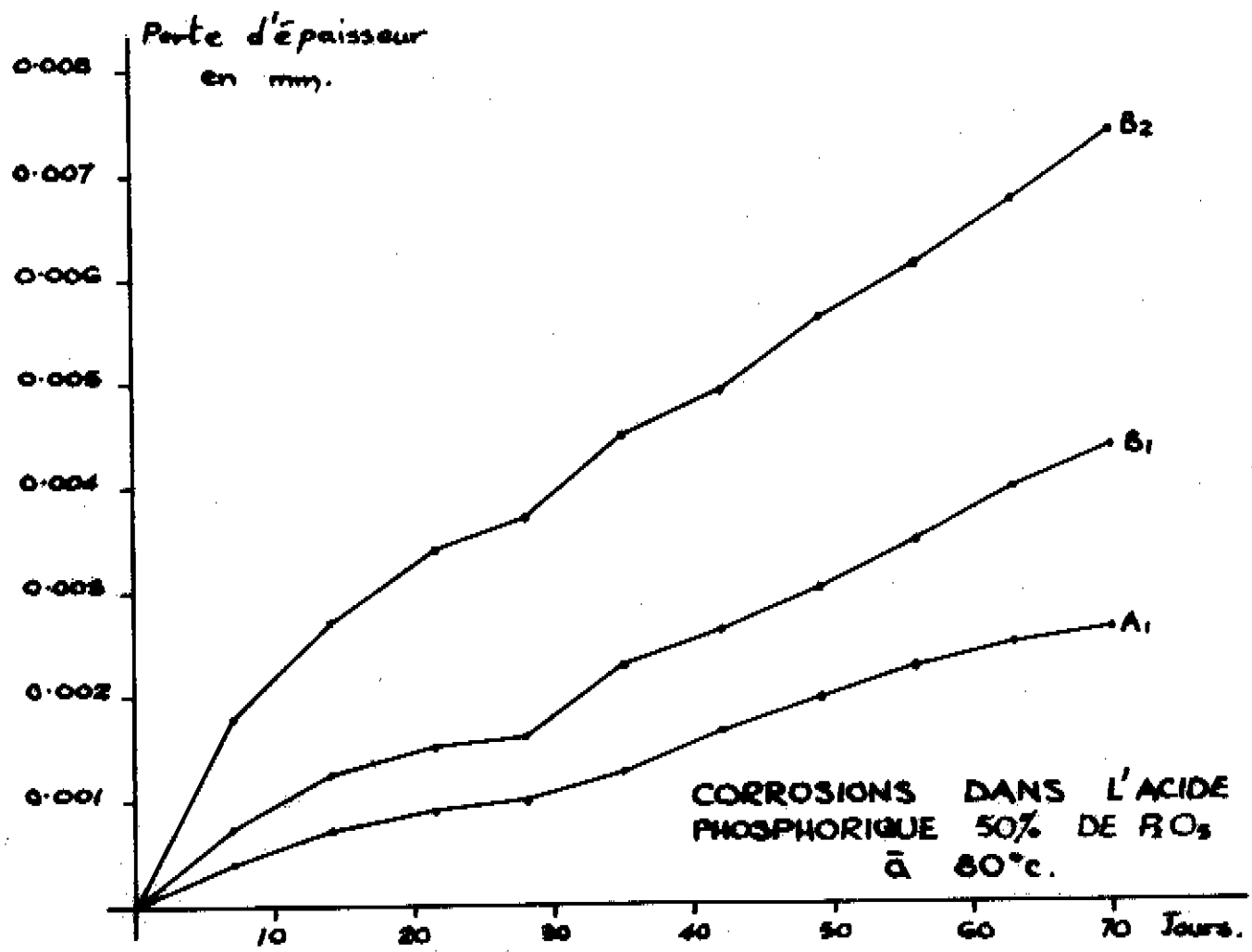
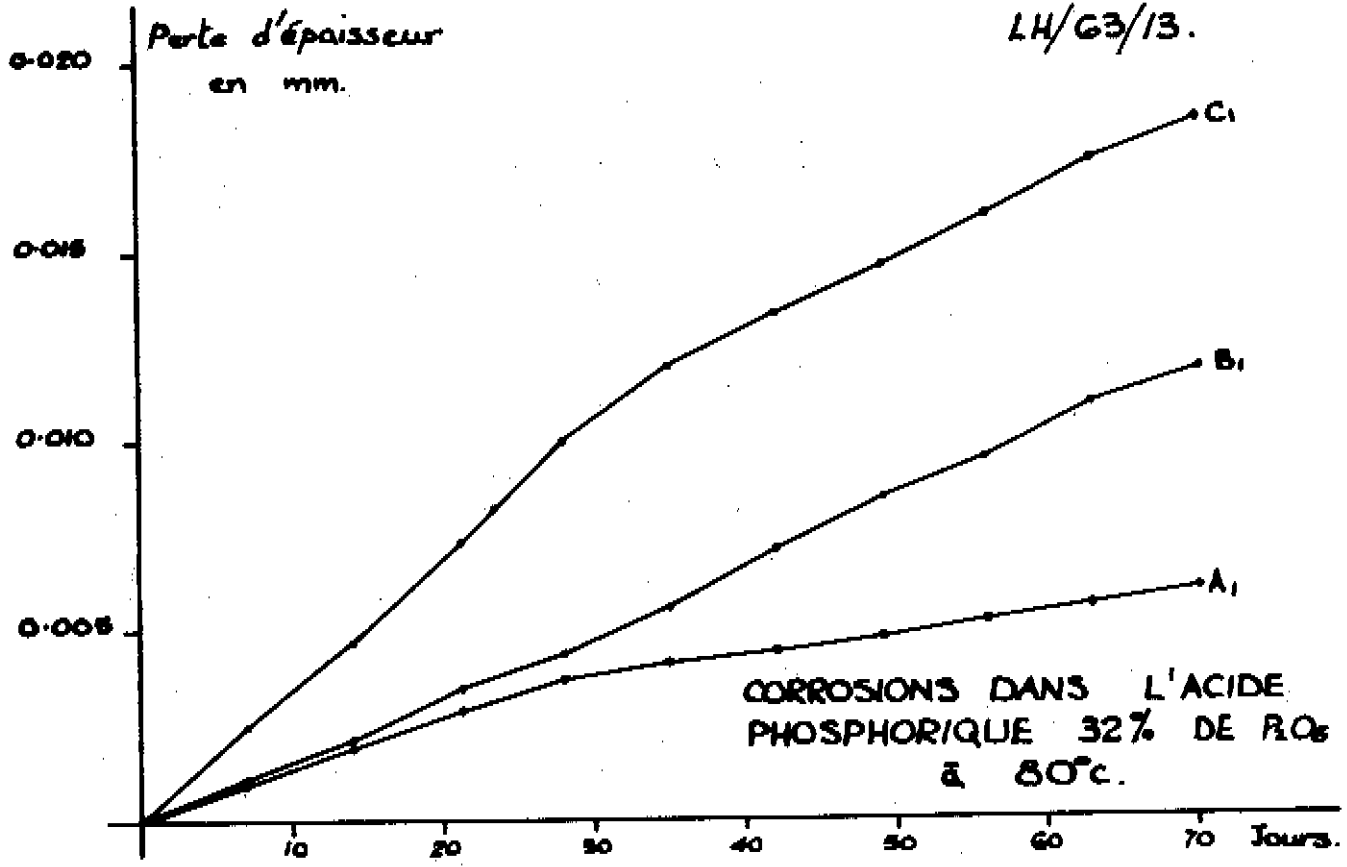
From all our observations we have drawn certain conclusions which we have presented to you in the course of this paper and which can be summarised as follows:-

(a) It is possible to find alloys sufficiently resistant to corrosion, but it is absolutely essential to carry out preliminary trials, because of:

- differences of behaviour between alloys of the same composition, but from different suppliers.
- differences in raw materials
- differences in the conditions of reaction, etc..

(b) The use of these alloys is very tricky and influences their performance. It is therefore necessary to train a specialised staff.

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DISCUSSION

Mr. Ph. MORAILLON (France) : (presenting the paper on behalf of Mr. ROUBINET) : The corrosion of materials, particularly metals, used for the construction of plant for the manufacture of wet process sulphuric acid has already been the subject of several publications. In his paper, Mr. Roubinet has merely wished to inform the members of I.S.M.A. of the experience acquired in this field by the P echiney-Saint-Gobain Company in the course of its long industrial practice. According to the more or less rigorous working conditions to which the apparatus is subjected, one should use either a stainless steel or an alloy with a more or less high content of non-ferrous metals and which is, in consequence, more or less costly. Certain alloys, with a composition comprising 20% chrome, 25% nickel, 4.5% molybdenum and from 1 to 2% of copper, usually have an excellent resistance to corrosion under all conditions normally encountered. We use them, in particular, for the construction of the blungers in a single reaction tank. Certain cast chrome alloys, with a chrome content of about 28 to 30%, have a particularly good resistance to abrasion, and we therefore use them for the construction of our slurry pumps. Stainless steels of the 316 type usually have an adequate resistance outside the reaction tank proper. They are particularly suitable for the construction of filters and acid pumps. Low-carbon varieties are preferable, although we have had an excellent experience with a filter, the pans of which are constructed of ordinary 316 stainless steel with a normal carbon content.

The mere chemical composition of an alloy is, in itself, an insufficient guide to enable one to assert that its behaviour will be satisfactory. Notable differences in the corrosion resistance of materials with very similar compositions have been observed, with variations from one supplier to another. These differences are probably due to different conditions. Before employing a new material

it is therefore prudent to submit it to laboratory tests. These tests immediately eliminate certain materials. But even if a test gives positive results, it can only be pronounced as satisfactory after an industrial experiment of a sufficiently long duration.

When welding stainless steels and alloys, one should take every possible precaution to avoid producing a change in the nature of the metal and thus promoting corrosion. Electric welding under argon is to be recommended. Research in this field should be pursued in order to discover and develop less costly materials. We should perhaps make particular mention of the fact that we have obtained encouraging results with a low-carbon stainless steel with a composition of 17.5% chrome, 16% nickel and 6% molybdenum, which seems satisfactory for the construction of blungers and can thus replace the 20% chrome alloys which I mentioned previously.

Mr. A. H. MØLLER (Denmark) : In the manufacture of wet process phosphoric acid, stainless steels and alloys play the same role as lead does in the manufacture of sulphuric acid. It is therefore evident that to choose the most economical stainless steel or alloy for each step in the production process is most important for all wet process phosphoric acid producers. Mr. Roubinet's paper outlines the procedures adopted by his company, Péchiney-St.-Gobain, to decide upon the possible use of such steels or alloys. I think his method is very logical, but the conclusion is the same as that indicated at the I.S.M.A. Technical Conference in Cambridge, in 1953, by Porter and Lowrison, viz. that the only reliable method of deciding on a material is to try it out.

I should like to put the following questions to Mr. Moraillon. Do you rely entirely on your supplier's analysis of the material, or do you check the analyses of, for instance, sheets of stainless steel before you use them for some apparatus? In our factory, we have had an example of the failure of an agitator in the reaction vessel which seems to be due to the delivery of a material other than that specified.

Referring to p.5. item (c) Industrial Trials, I notice that you put a small apparatus into service. In a case like this, where the material to be tested is in contact with other metals, it

would be interesting if you could say whether any precautions are taken to insulate the new material electrically from other parts. Furthermore, how long do you test the material in this way before passing judgment on it ?

On p.8 you make a classification of various steels in 32% acid based on the calculated average loss of thickness, in mm/yr. Is it not also necessary to mention the tendency to pitting of the different materials ? You mention that the weldability of the stainless steels can be improved by stabilising with titanium. However, titanium is not mentioned in the analyses of the different steels quoted. I take this as a sign that you have a very good welding technique. Do you weld exclusively in an inert atmosphere ? It is obvious that much depends on the technique used and on the welder's ability.

My last question is with reference to p.11, item (c), Influence of the Nature of the Phosphate. Have you made any experiments with Kola apatite ? If so, where would you put it in the rank of phosphates, with respect to corrosiveness ? Have you tried to relate the corrosiveness of a phosphate to the combined content of fluorine and chlorine ?

Mr. MORAILLON : With regard to the question relating to the verification of the materials in the plant supplied by the constructors, we have also observed certain cases of plant corrosion which was due to the fact that the constructor had not used the blend of stainless steel or alloy which he had specified. In a case like this, it is unfortunately impossible, in practice, to verify what material is actually used by the constructor at the moment when the plant is manufactured. One is reduced to taking a sample on receipt of the apparatus - if one has the time to do so - and to checking its composition, but by that time it is already too late, because, if it was defective, the apparatus would have to be completely re-manufactured. The only thing which can be checked is the stainless steel sheeting which is supplied to the factory for maintenance purposes or for the manufacture

of small apparatus which is done by the fertiliser producer himself. Obviously, one cannot intervene at the constructor's factory.

The second question related to the need to insulate a new material electrically, where it constitutes only a small part of an existing apparatus. The problem of contact with a different material can arise, and hence the possibility of corrosion of an electrical nature. This obviously depends on circumstances: from the theoretical point of view, it would be preferable to insulate the two materials electrically, but I do not think that this would be very practical. In any case, if a corrosion is observed near the junction - which may be either welded or riveted - there is no need to take account of it: it is only the corrosion of the external parts which counts. Our experience includes the welding of stainless steels of extremely different compositions, and we have never observed any particular corrosion due to this difference in composition.

The third question related to pitting which might possibly be observed with certain steels or alloys. Obviously, the mere indication of loss of weight is not sufficient. If pitting is observed, one would at least tend to suspect the material, and it is probably caused by defects in the homogeneity of the product. It would be prudent to reject it.

The fourth question concerned the stabilisation of stainless steel by means of titanium. This stabilisation is carried out in the case of stainless steels with a relatively high carbon content, of the order of 0.007 to 0.01%. In general, the titanium content is about 3 times the carbon content. I do not think it is put into low-carbon steels. With regard to welding, we prefer to use an inert atmosphere, for example, under argon, each time it is possible to do so.

The final question concerned the use of Kola phosphate. We constructed a plant for another company to operate our process in Germany, using Kola phosphate exclusively. No corrosion difficulties have been observed. We must therefore consider that this phosphate does not present any corrosion problems.

With regard to the fluorine content in phosphate rock, as all the phosphates in general use have very similar fluorine contents, it is not possible to correlate fluorine content with corrosion. As far as the chlorine content is concerned, I can only say that in one of our factories the water we use for the manufacture of phosphoric acid contains 3 grams per litre of sodium chloride, and this has raised no particular problem : no more corrosion has been observed here than in our other factories which use a chlorine-free water. However, we have no industrial experience of phosphates rich in chlorine.
