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**In 1982, the name of the International Superphosphate Manufacturers' Associations (ISMA) was changed to International Fertilizer Industry Association (IFA).*

FACTORS GOVERNING THE RATE OF CORROSION OF STAINLESS STEELS DURING THE
PRODUCTION OF WET PROCESS PHOSPHORIC ACID

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SUMMARY

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A) CURRENT ECONOMIC IMPORTANCE OF CORROSION IN THE PRODUCTION OF WET PROCESS PHOSPHORIC ACID

The steel and chemical industries today offer the phosphoric acid manufacturer a whole range of materials undreamt of a few years ago, and this enormous choice has significantly improved the current options in phosphoric acid plant construction.

However, while the materials have improved, the same cannot be said for the raw materials. Constant increases in consumption, together with a delayed but important readjustment of prices over the last decade have accelerated the appearance of a certain number of new grades, which frequently contain corrosive impurities, or more corrosive combinations of constituents.

Corrosion therefore remains economically important. It is responsible for between 15 and 50% of maintenance costs depending on the plant. This can amount to US\$5-10/t of P_2O_5 in the case of normal production but much more during a bad start-up. Then, the figures could be multiplied by a factor of two or much more.

This study does not claim to offer solutions to the problems of corrosion but:

- 1. to offer a method of studying corrosion in specific cases
- 2. to predict it quantitatively
- 3. to investigate protection either by modifying the medium or by the choice of materials.

B) TYPES OF CORROSION

The term "corrosion" applies in a general way to the disintegration of a material in an aggressive medium. This erosive destruction can occur in various forms.

FONTANA (1) drew up a classification of types of corrosion according to the material's appearance. Today, despite the differences in appearance, corrosion is generally explained electrochemically.

Without going as far as to list the different types of corrosion mentioned in the literature, we will concentrate on those which cause problems in phosphoric acid plants.

We will therefore concentrate on the problem of abrasion corrosion and pitting.

Abrasion corrosion is a fairly uniform disappearance of the metal under the combined effect of chemical and mechanical aggressiveness. Pitting is where the metal is attacked at points, as in the case of corrosion due to chlorine.

C) METHODS OF TESTING AND MEASUREMENT

In their catalogues manufacturers of special steels give tables of the weight loss of their steels in corrosive media with details of concentration and temperature.

Often these values derive from steel samples that have been left for a long period undisturbed in a non-charged and static liquid medium.

Any producer of phosphoric acid knows that it is his pump impellers that disappear first of all, and that, consequently, movement has an important effect. This factor has been noted in the literature (2). We therefore sought a test which would take account of the kinetic energies, which are comparable to those which act in an industrial plant.

Furthermore, an acid that is chemically at rest may be much less aggressive than an acid during its formation. Thus we discovered that corrosion was greater in the reaction slurry.

We carry out our tests in a pilot plant which produces phosphoric acid by attacking phosphate as in a full-scale plant, with the same operating rates, that is, adding the raw materials in the same ratio (Fig. 1 and 1 b). It is not however necessary to keep to this ratio exactly since we did not observe variations in corrosion when this ratio was varied by $\pm 50\%$ (phosphate added in proportion to the volume of the slurry).

The steel samples tested form the agitator blades on which we measure corrosion by weight loss. We measured the weight loss in spite of the fact that this method demands a lot of time and effort: at least 3 hours' preparation work and 5 hours' operation of the pilot plant for a set of 4 values of weight loss in a given medium. We are in the process of collaborating with IFDC in seeking a more flexible method which would enable us to find the corrosion value more quickly, but more time still needs to be spent on this research.

With the agitator, there was a slight problem of extrapolation. Abrasive corrosion is a function of the differential speed between the metal and the slurry, consequently of the peripheral speed, or the product of $n \times d$, where n = speed of rotation in rev/sec,
 d = diameter of the impeller in metres

On the other hand, for a good filterable grade of slurry, the agitation, which requires a certain energy threshold by volume of the slurry, follows the relationship $n^3 d^2$.

Thus, a small 0.11 m agitator at 436 rpm and a large 1.8 m one at 80 rpm have the same $n^3 d^2$ of 4.64 and therefore the same specific energy transmission in the direction of the slurry. In contrast, their peripheral speeds are 150 m/min and 352 m/min respectively.

To be able to work with peripheral speeds comparable to large agitators, we developed a special agitator with a small surface area but a large diameter, transmitting the same specific energy as normal agitators, that is, around 1.5 - 2 kW/m³.

The energy transmitted was verified by the PRONY brake method, placing the tank on a rotating plate and measuring the tangential force when the agitator is operating (fig. 2).

D) RESULTS

1. Checking the results

As far as possible we sought the same results on the pilot plant and full-scale plant by weighing the pump impellers or agitator blades. The values we obtained agreed fairly well on the whole. We did of course verify whether, over a range of surface/volume ratios, the small tank underwent degasification of fluorine or chlorine but the analytical results reassured us; the change, if there is one, is not analytically detectable.

2. Corrosion factors

The quantitative value of the corrosion or the threshold of harmful corrosive action is the result of chemical and physical factors, and the relation between them is always very complex.

Phosphoric acid, on its own, is not very corrosive; it is the impurities concentrated in it that make it aggressive. These impurities or chemical factors are essentially:

H₂SO₄
F
Cl

The physical factors which increase the action of the chemical factors are mechanical wear or abrasion by the movement of the metal in the liquids loaded with crystals: a function of the differential or peripheral speed and the temperature which, when it rises, increases the reaction rate, and consequently the aggressiveness of the medium.

The physical factors only increase the existing aggressiveness. They do not reverse or modify an existing order between two different types of material.

a) peripheral speed

First of all we studied the speed function in the case of abrasion corrosion. The agitators in the reaction tank work at 250-450 m/min, the pumps at 1,000 - 2,000 m/min. We studied corrosion according to speeds, working in our pilot plant at between 120 and 350 m/min, and made comparisons with the same metals on pumps working in the same media.

It emerges from these studies that abrasion corrosion is an exponential function of the peripheral speed, frequently of the type:

$$Co = K (nd)^x \quad \text{with } x \approx 2.4 \quad (\text{fig. 3})$$

This equation underlines the importance of the kinetic tests: a metal on a small slow agitator 0.5 m in diameter at 120 rpm (= 188 m/min) corrodes 0.5 mm, a very small amount; on a pump impeller of 0.4m diameter at 1,500 rpm (= 1,884) m/min) the same metal could lose, in the ratio

$$0.5 \left(\frac{1,884}{188} \right)^{2.4} = 126 \text{ mm, which is an enormous amount.}$$

We can see here that the results of static tests will not be much help when choosing a material for fast speeds. Of course, the exponential 2.4 is not always valid, but we frequently came across it. I believe that it varies from one material to another.

b) temperature

No-one will be surprised to learn that temperature greatly accelerates corrosion. Its effect becomes particularly visible beyond 80°. Often the value for 85° is twice that for 70°. On reviewing the information in the specialist literature (3) and our own results, we found that the variation in the corrosion according to temperature seems to be a relation of the type

$$\frac{C_{t1}}{C_{t0}} = \Delta(t)^x$$

Between 70 and 85°, temperatures which are particularly of interest in the dihydrate process, the value $x(t)$ approaches $\frac{1}{4}$.

c) sulphuric acid

Sulphuric acid is an extremely active corrosion agent (fig. 4). Since it is always found in phosphoric acid, owing to the nature of the process and its content depends on the quality of the crystallisation, it can constitute the major determinant of the degree of corrosion.

At 10 g per litre, expressed in total H₂SO₄, it is not very aggressive, probably because the SO₄⁻ ions are in equilibrium, principally with metal cations such as Ca⁺⁺, Al⁺⁺⁺, Fe⁺⁺⁺, etc. In general, the sum of these cations is roughly equivalent to 20 to 30 g/litre of H₂SO₄, but we also have to take account of the presence of H₂SiF₆ which is equivalent to 17-25 g of H₂SO₄. This could explain the virulence of the sulphuric acid beyond 15-20 g/litre.

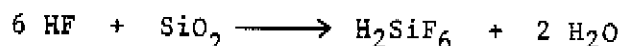
Whatever the reason, the sulphuric acid always increases all aspects of corrosion, most especially when the medium at the start, that is, without notable excess of H₂SO₄, already shows some degree of aggressiveness.

Increasing the sulphuric acid from + 20 g/l to + 40 g/l can multiply the corrosion by a factor which may be anything from 4 to 10. The graph provided is only one example, from which a rule cannot be made. It corresponds to an initially aggressive phosphate.

d) Fluorine

Fluorine is present in all phosphates in the proportion of 10 to 14% of the P₂O₅.

When the phosphate is attacked by sulphuric and phosphoric acids, it passes into solution in the form of hydrofluoric acid which has a great avidity for silica.



HF is a weak acid, PK_a = 3.2, while fluosilicic acid is a strong acid. However, as regards corrosion, we have found in practice that hydrofluoric acid is much more aggressive than fluosilicic acid.

This is very fortunate since it is easy to push the reaction towards H_2SiF_6 simply by feeding enough reactive silica into the attack medium. The action of the Al^{+++} ions in forming AlF_6^{---} , which is also less corrosive than F^- , should also be noted. We have not yet carried out systematic tests with Al^{+++} .

The presence of sulphuric acid greatly enhances the aggressiveness of the fluorine.

The $H_2SO_4 - SiO_2$ diagram for a constant fluorine content of 3.7% in the phosphate shows the correlations well. SiO_2 reduces the aggressiveness of the fluorine but H_2SO_4 strongly reinforces it (fig. 5). According to the concentration required by the reaction, which should supply a readily filterable gypsum, there must be compensation by a greater or smaller quantity of reactive silica (preferably combined or else SiO_2 with a very large surface area).

The pilot plant values were checked by weighing the pump impeller in the plant to verify the correlation between the laboratory and the plant.

e) chlorine

For a long time, the idea of accepting chlorine in the presence of phosphoric acid was totally rejected.

Different authors gave 0.01, or even 0.05, as the maximum content with respect to the phosphate. However, the arrival on the market of a certain number of phosphates containing more chlorine than has been accepted until now makes this problem topical again. It is a problem that can also be linked with that of the chlorine contained in the process water in areas where pure water is not available. We therefore examined what happens when chlorine is present.

Chlorine-induced corrosion is of a different appearance from that found with fluorine and phosphoric acid. Chlorine attacks more in pin points, known as pitting.

The action of the chlorine is also intensified by the presence of sulphuric acid; the increase is often more than tenfold when the level of sulphuric acid is doubled.

On the other hand, the effect of the physical factor of "speed" greatly surprised us; instead of increasing by the power of 2 or 2.5, for example, corrosion decreases with the peripheral speed at high chlorine concentrations (fig. 6). This indicates or even emphasises the difference between the mechanism of chlorine attack and that of normal abrasion corrosion.

The chlorine diagram for Florida phosphate (fig. 7), thanks to its numerous measurement points, defines fairly clearly the zones of strong and weak corrosion and, consequently, the acceptable tolerances for the chlorine according to the materials used. The acceleration of corrosion due to the presence of a greater excess of sulphuric acid (40 g/l instead of 20 g/l) can also be very clearly seen.

At certain points, we checked the extent of the effect of temperature which remains an important multiplier (1.54 for Hastelloy; 2.40 for 316 L when it is raised from 70° to 85°).

At 0.01 of Cl the speed relationship returns to normal. Certainly different corrosive functions superimpose one upon the other.

The chlorine diagram for Florida phosphate shows that with 316 L and moderate excess of sulphuric acid, 0.1% of chlorine can be accepted but the presence of sulphuric acid (40 g/l) will already cause problems: this justifies the accepted limit in the region of 0.05%.

On the other hand, Uranus B6 allows 0.4% or even more, at least in the range of speeds studied.

Hastelloy C is completely protected since it is difficult to imagine a Florida phosphate where the chlorine additives reach 2% of the phosphate.

However, this only refers to Florida phosphate.

Once the phosphate is changed, the tests have to be done again. On a more aggressive phosphate, which we will call A, we plotted points where corrosion of Uranus B6 is significantly higher (fig. 8).

The threshold of chlorine attack is much lower for Uranus B6 and for all the other steels tested. The combined action of $F-H_2SO_4-Cl$ is extremely severe.

3. Conclusions

The parallel drawn between the results from our pilot plant and the results found in plants which use the same phosphates in similar conditions allow us to give a realistic picture of the degree of corrosion that can be expected from a given steel in a given medium using the operating method described with the pilot plant.

It would however be unwise to draw conclusions of a general nature from an individual diagram. The multiplicity of factors acting, and the extreme sensitivity of the exponential functions, leave us to anticipate a large scattering of the results due to small differences when passing from one raw material to another.

E) APPENDICES

APPENDIX 1 - TECHNICAL CHARACTERISTICS OF THE PILOT PLANT

Stainless steel tank: 200 x 200 x 400 external dimensions

Overflow height: 215 mm

Internal rubber lining: (185 x 185)

Stainless steel evaporation-proof cover

All submerged in a bath of water or oil so that the temperature can be maintained up to 85 or 90°

Variable speed motor 0.5 kW. Speeds up to 750 rpm
(peripheral speed of plates: around 350 m/min)

Power requirement at this speed: 2 watt/litre

Surface area of metal exposed per plate: around 5 cm² each

APPENDIX 2 - OPERATING CONDITIONS OF THE PILOT PLANT

Useful volume used: 7.4 litres

Phosphate feed rate, 500 g/hr, corresponding to approximately 2 m³ of reaction volume per tonne of P₂O₅ produced per day.

Temperature 80° except where otherwise stated for Florida phosphate; 76° except where otherwise stated for Asian phosphate.

Water evaporation/hr: around 125 cm³/hr

Returned recycled acid: 1.1 litres/hr, 190 g/l P₂O₅, density 1.17

H₂SO₄ level monitored every 30 minutes

Method: total H₂SO₄ by BaSO₄

P₂O₅ monitoring: volumetrically every 30 minutes

Degree of corrosion determined by weight loss from the plates - agitator blades.

APPENDIX 3 - CORROSION MEASUREMENT PROCEDURE

Generally, a plate is only used once. Repeated tests, especially in the case of pitting, are likely not to offer identical surfaces from one test to the next.

The corrosion value is determined by the difference in weight of a plate before and after the corrosion test.

The average duration of a test is 4 to 5 hours. For a less corrosive medium the test may be longer.

Before each test, the plates are subjected to a surface preparation treatment by soaking them for 20 minutes at 60°C in an acid bath of the following composition:

HNO ₃	40 Be	12.5%
HF		3%
water		remainder

APPENDIX 4 - ANALYSIS OF THE STAINLESS STEEL SAMPLES USED

	Cr	Ni	Mo	Cu	C max	Others
316L	18	13	2.5		0.03	
Hastelloy C	15.5	54	16		0.08	W. Co
Sanicro 28	26	30	3.6	1	0.015	
Uranus B6	20	25	4.5	1.5	0.02	

F) REFERENCES

- 1) FONTANA M.G Chem. Eng. Progr. 53 (11) 525/1957
- 2) Méthodes d'essais et études des phénomènes de corrosion-abrasion.
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Minerale - 15 mars 1976
- 3a) Corrosion-abrasion en milieux phosphoriques industriels
D DUBERTRAND - Industrie Minerale - 15 mars 1976
- 3b) Les aciers inoxydables dans la fabrication de H_3PO_4 par voie humide
A BORGHESE - Information chimie - novembre 1975 No 189
- 3c) Un acier spécial destiné à la concentration de H_3PO_4
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avril 1978

KEY TO FIGURE 1

- 1 Sulphuric acid reservoir with weight indication
- 2 Return acid reservoir, graduated
- 3 Peristaltic pumps
- 4 Constant temperature bath
- 5 Pilot scale reactor
- 6 Agitator
- 7 Variable speed motor
- 8 Vibrating hopper, phosphate feed
- 9 Prepared phosphate charges
- 10 Slurry reservoir for possible filtration tests
- 11 Gaseous effluents

Fig 1

CORROSION PILOT PLANT

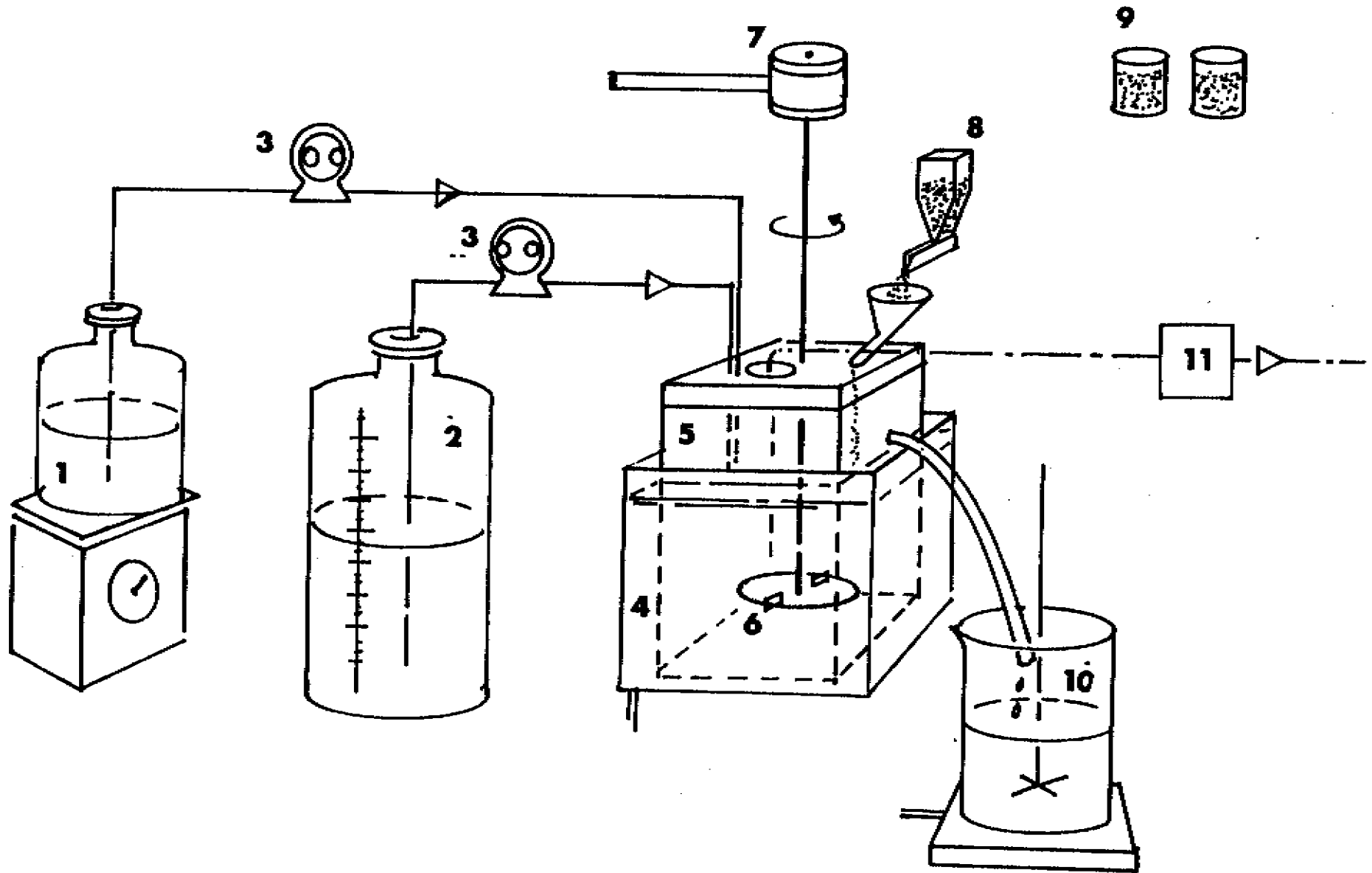
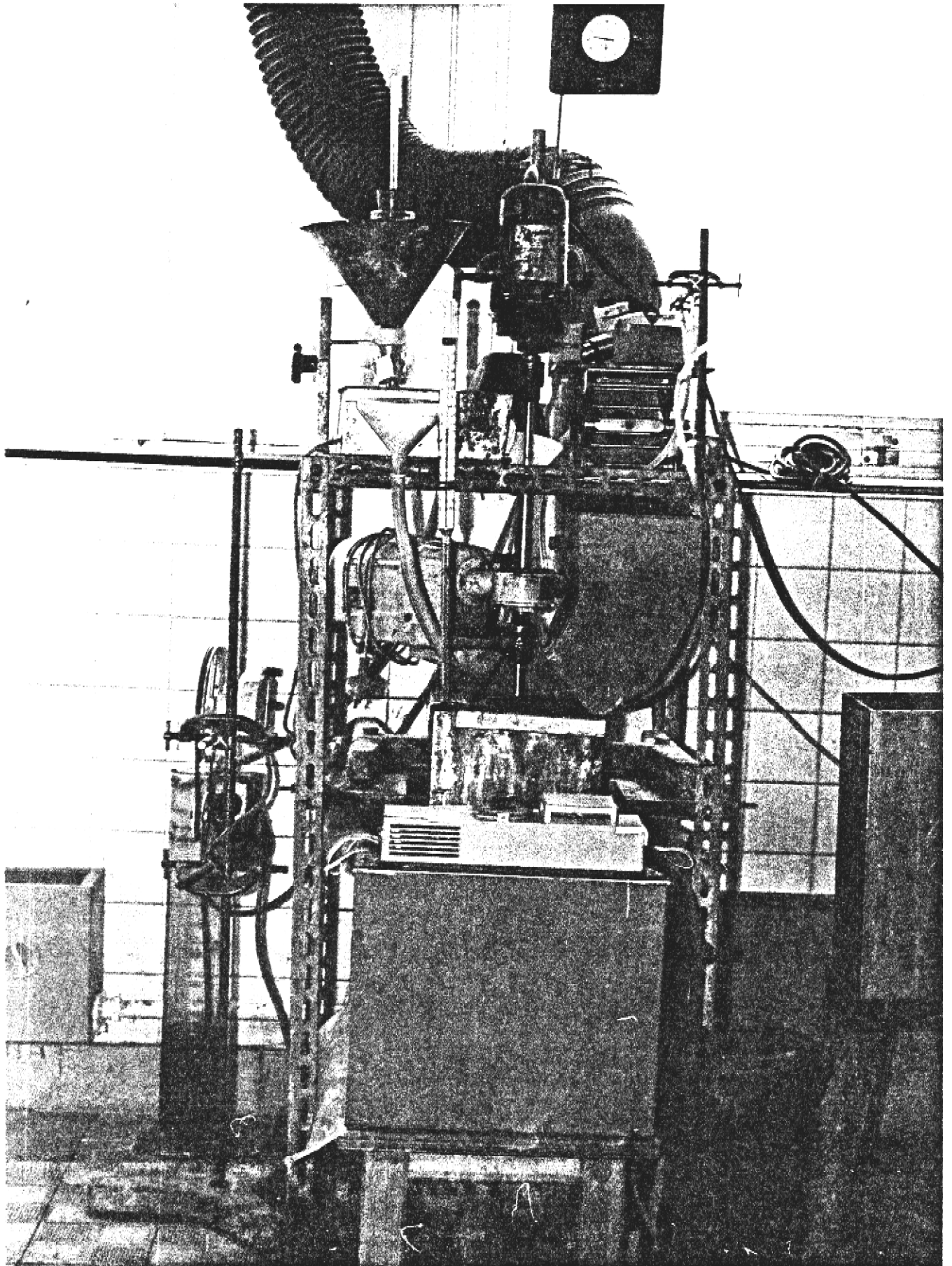


Fig. 1 Bis.

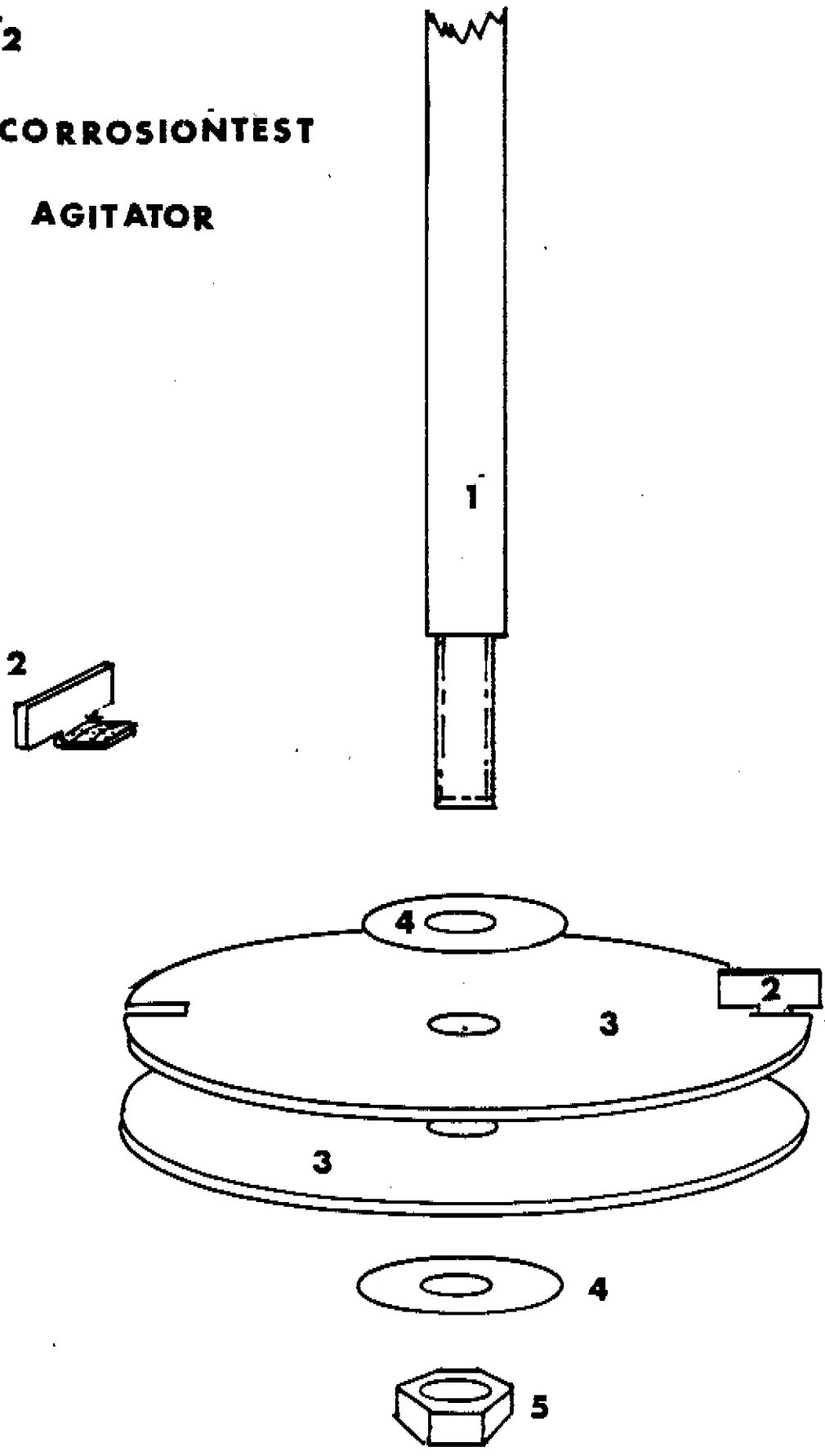


KEY TO FIGURE 2

- 1 Shaft
- 2 Sample, agitator plate of metal to be tested, fixing plate isolated by teflon band
- 3 Plastic discs supporting blades
- 4 Stainless steel washer
- 5 Securing nut

fig 2

**CORROSION TEST
AGITATOR**



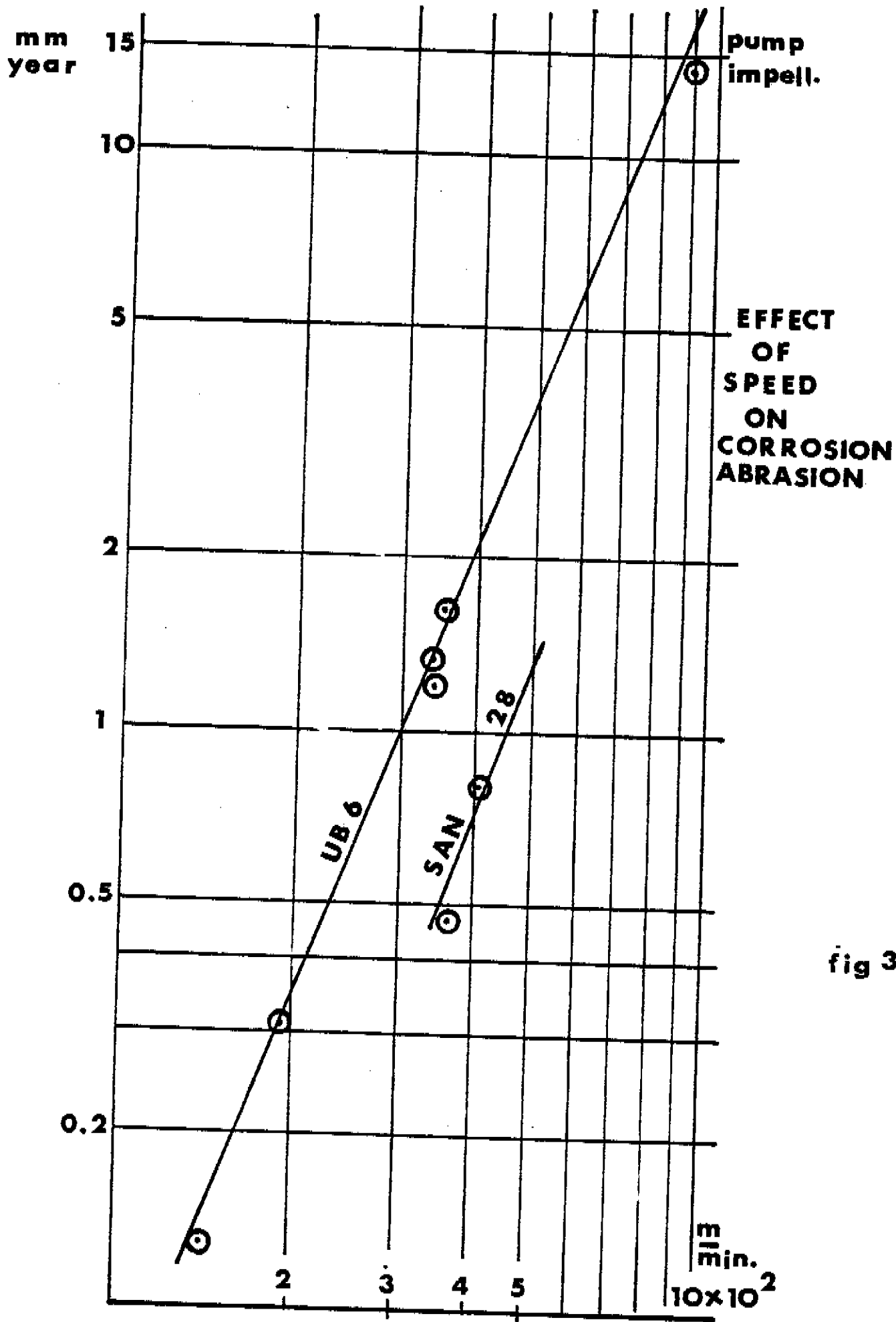


fig 3

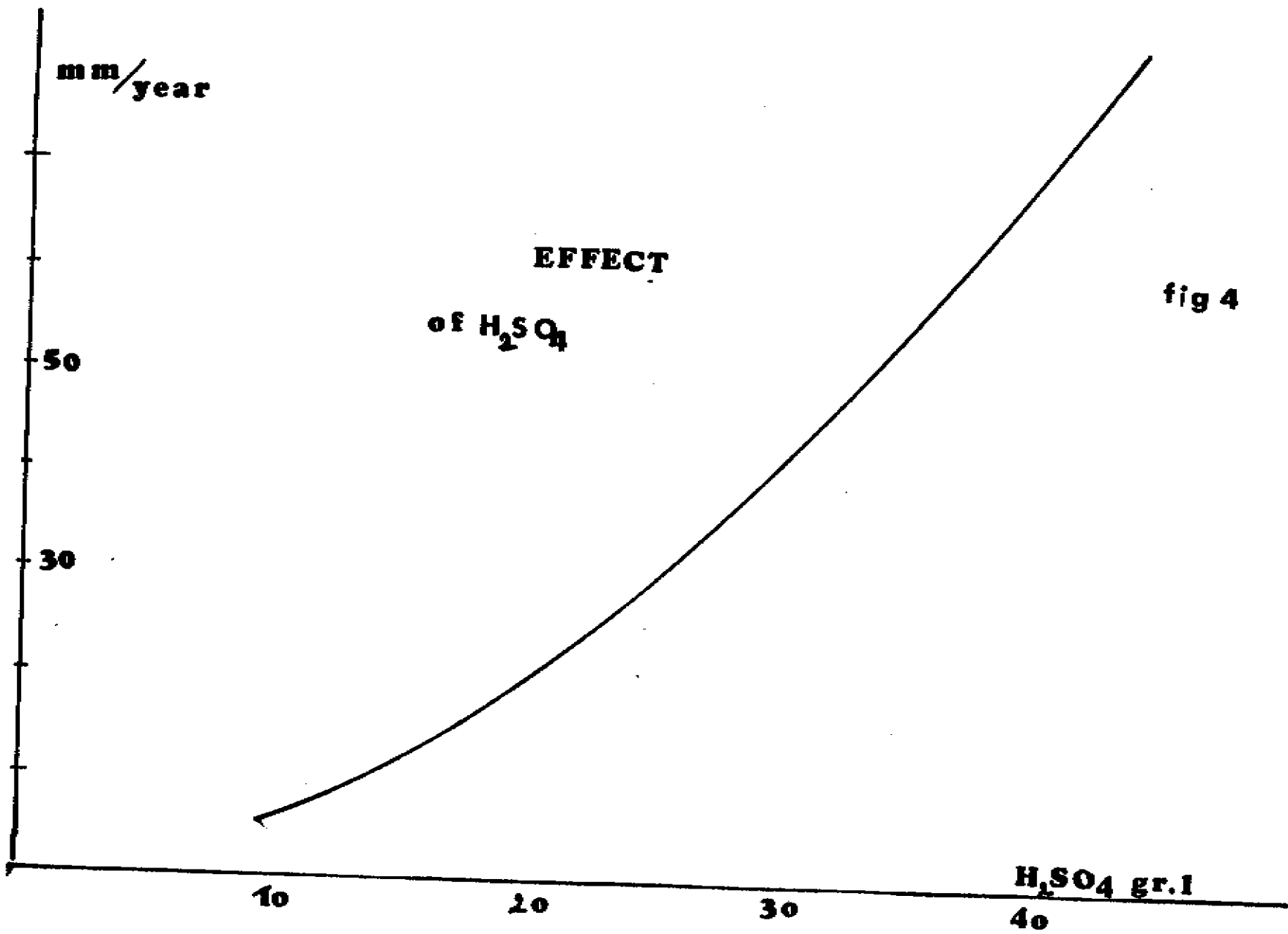


fig 5

COMBINED EFFECT of H_2SO_4 - F- and SiO_2 on CORROSION ABRASION

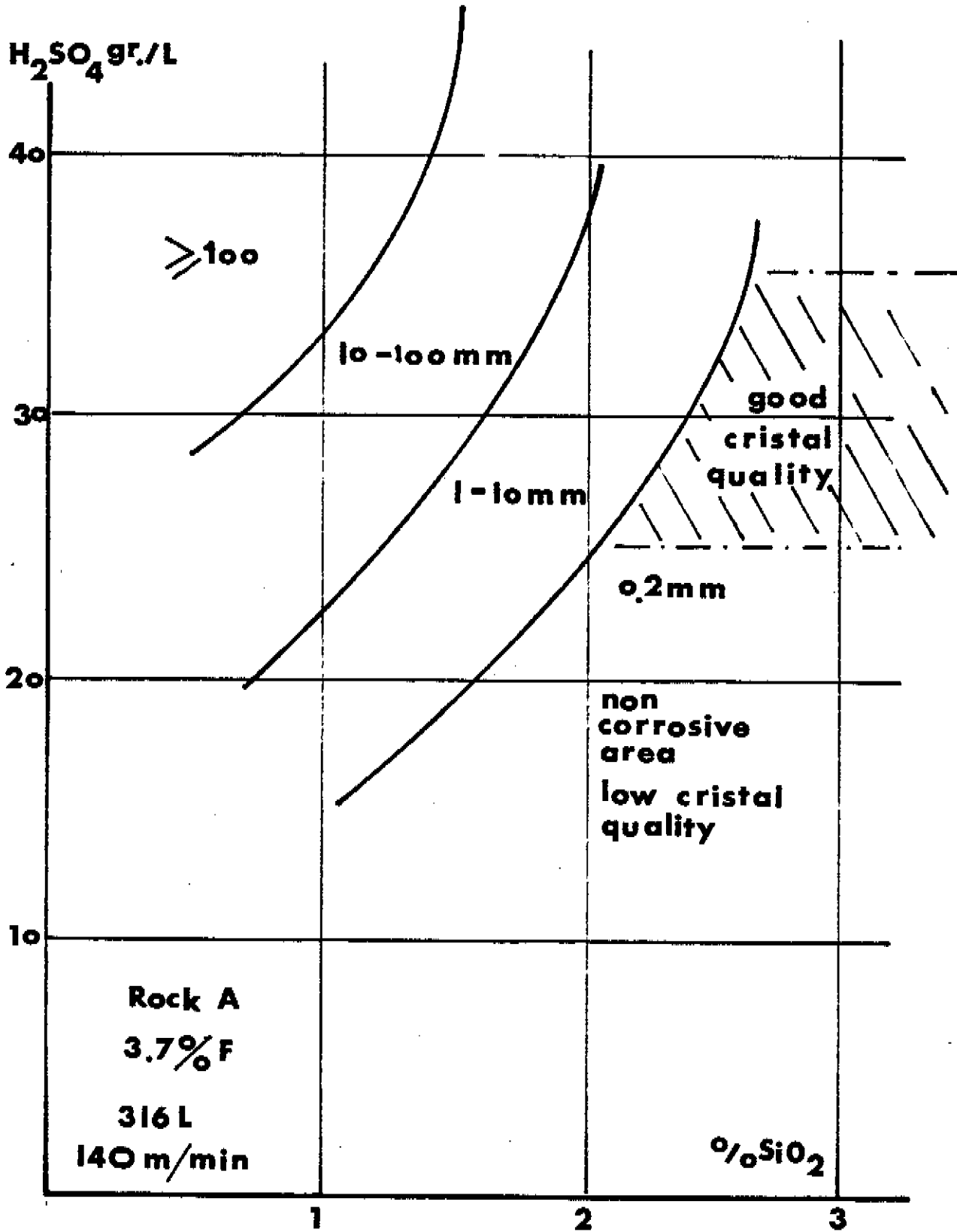
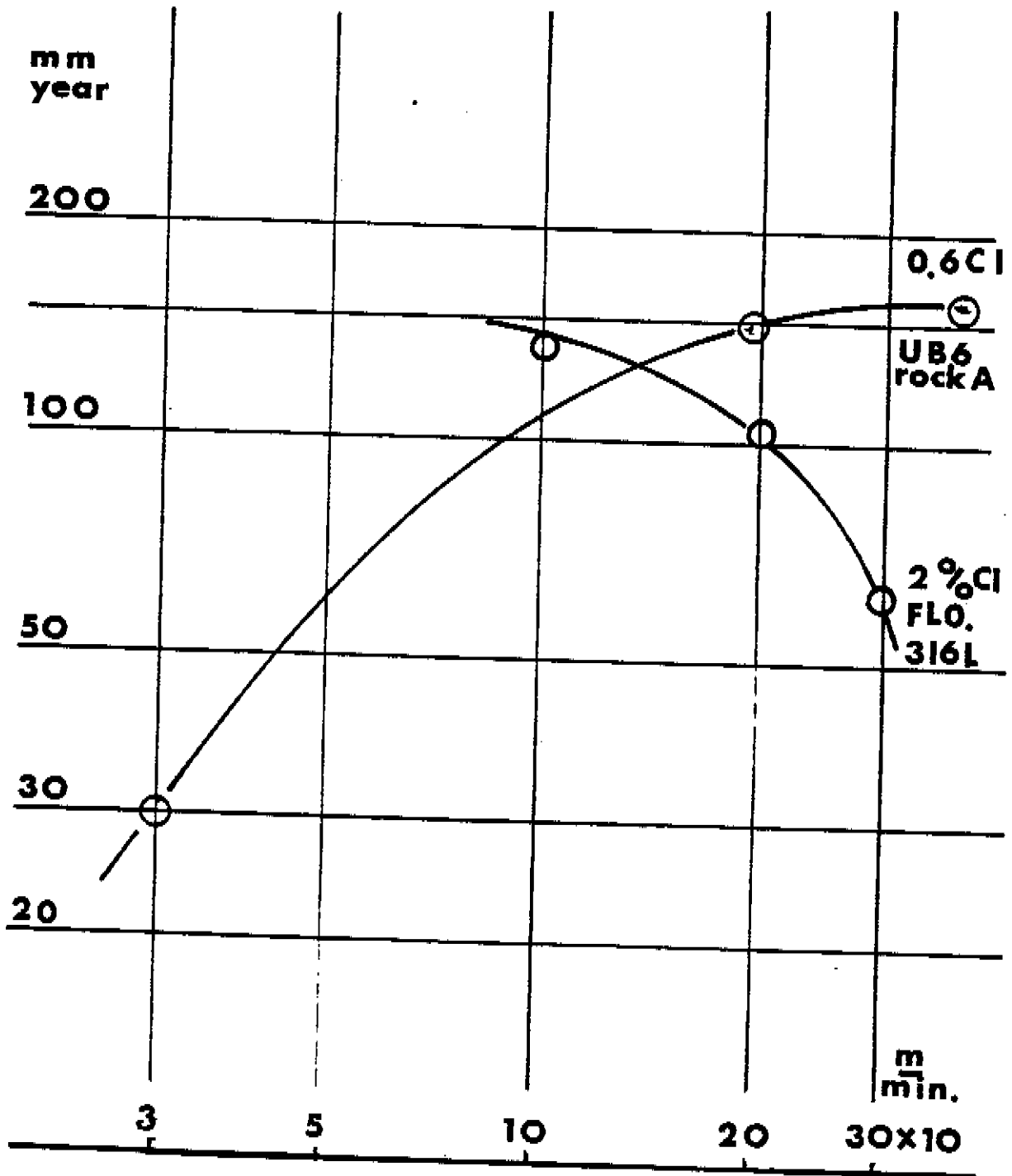


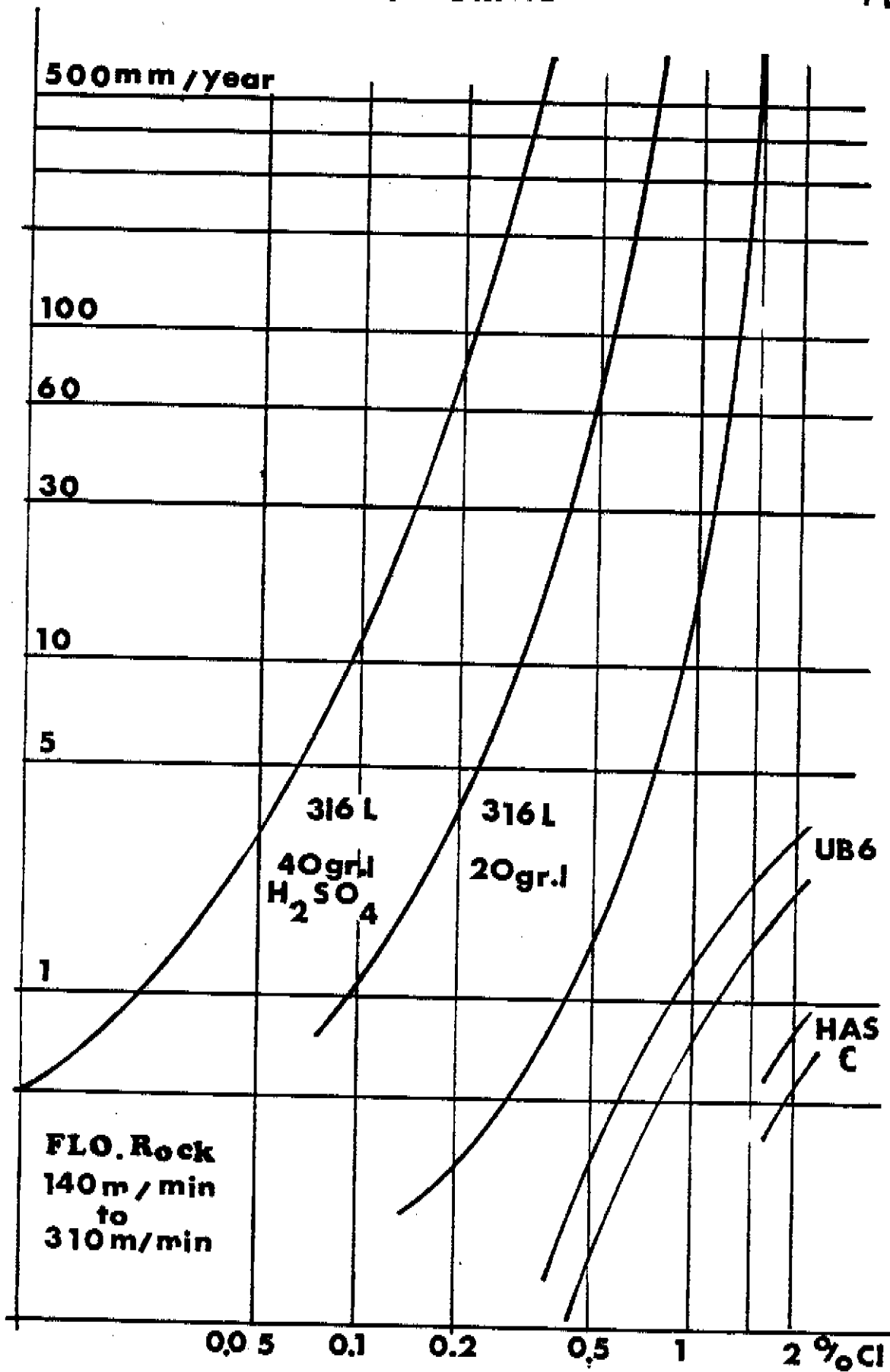
FIG 6

EFFECT OF SPEED ON CHLORINE PITTING



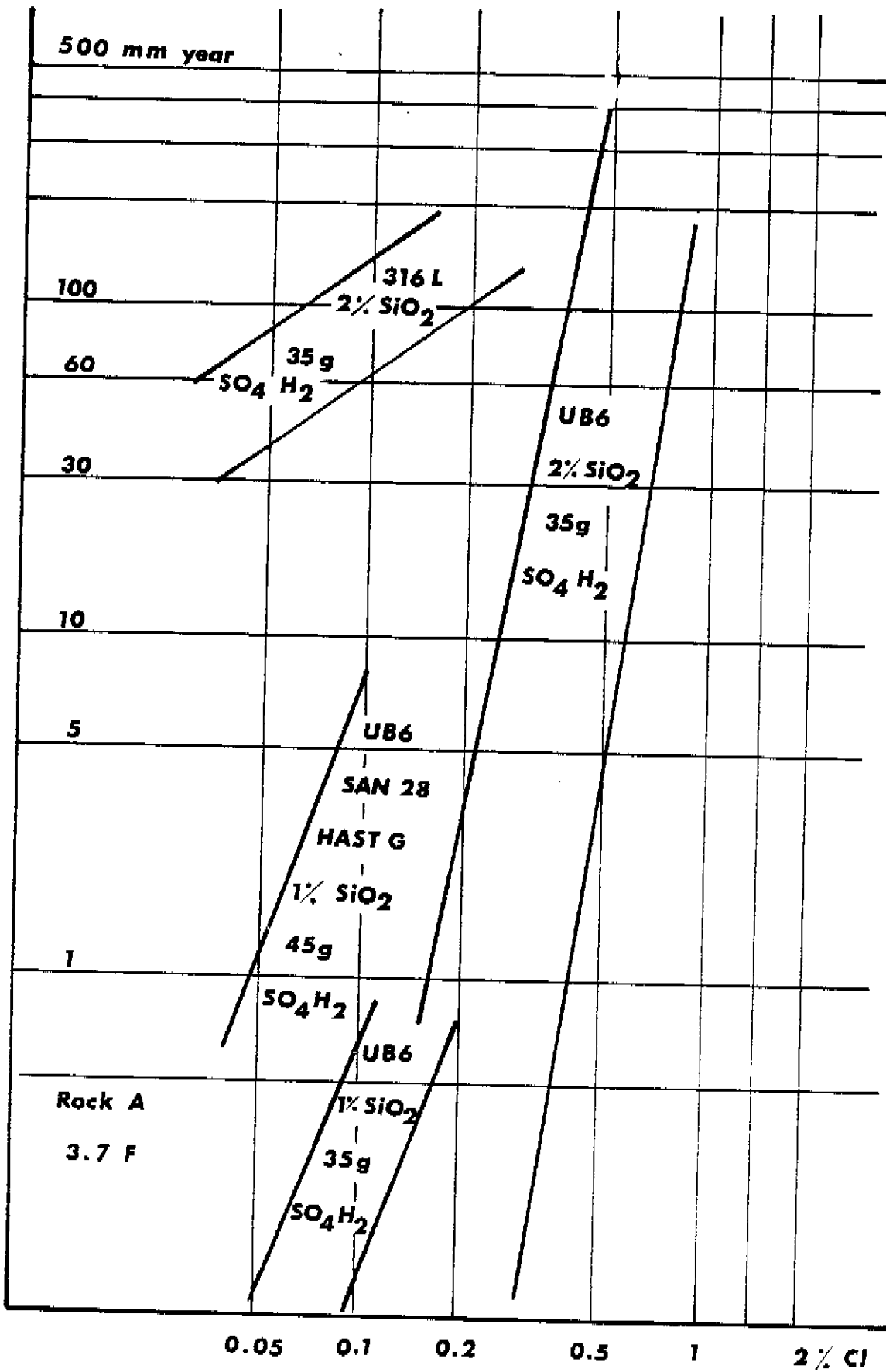
EFFECT of CHLORINE

FIG 7



EFFECT of CHLORINE

FIG. 8



TA/80/1 Factors governing the rate of corrosion of stainless steels during the production of wet process phosphoric acid by P. Becker, M. Duthoit, M. Gauron, H. de Villele, Compagnie Française de l'Azote, France

DISCUSSION : (Rapporteur F. Thirion, Société Industrielle de Prayon, Belgium)

Q - Mr. M. Barloy, CERMI, France

- 1) Did you study the influence of scaling on the corrosion and, more specifically, the speed of establishment of an equilibrium between scaling and erosion?
- 2) The exponential 2.4 you refer to page 1.3 and 1.4 varies certainly according to the quality of the stainless steel. What quality was it obtained with?

A - 1) No

- 2) The exponent varies certainly according to the quality of the stainless steel. Those which gave 2.4 are UB6 and Sanicro 28.

Q - Mr. P. MORAILLON, Générale des Engrais, France

- 1) What type of reactive silica do you recommend to reduce corrosion by hydrofluoric acid?
- 2) The agitation power mentioned, $1.5-2 \text{ kW/m}^3$ would correspond, on the basis of an 80% electromechanical efficiency, to an energy consumption of 90-12 kWh/ton P_2O_5 for the agitation alone, if, as indicated, the reaction volume is $2 \text{ m}^3/\text{ton } \text{P}_2\text{O}_5$ per day. Is it not higher than the normal industrial figures?

A - 1) Large area clays (kaolin, bentonite) and silica (Porosil for example)

- 2) The agitation power, $1.5-2 \text{ kW/m}^3$ relates only to the feed sites of the reagents (premixer). Elsewhere, it is sufficient to maintain the slurry uniform and power requirements are lower. In our tests, we could operate at different speeds and thus cover a wide range of power.

Q - Mr. P. BALDWIN, Cremer & Warner, United Kingdom

How is the Cl value on your graphs measured? In the rock or in the slurry?

A - The chlorine content is measured in the rock. It is controlled in the slurry at the corresponding level of the Cl/ P_2O_5 ratio. To obtain the points on the diagram, it is sufficient to introduce the adequate amount of chlorine ions (as HCl for example) in the returned acid.

Q - Mr. T.J. PEARCE, Estech Chem. Corp., United States

How is the amount of reactive silica determined?

A - No analysis method can determine accurately the part of the silica contained in the rock which will react with fluorine in phosphoric acid manufacture. On the other hand, pilot tests as those described indicate if the rock contains enough reactive silica or if an addition is necessary.

Q - Mr. J.H. FOURIE, Foskor, South Africa

The problem of corrosion we found is not increasing when the grade of rock is going down, therefore impurities increase. We are at present producing a 39.8% P_2O_5 (86.5 BPL) rock but have found the low SiO_2 content lead to severe attack on stainless more than before with our previous 80 BPL rock.

Could you perhaps give us an indication of the acceptable F: SiO_2 ratio?

A - The acceptable F/ SiO_2 is indicated on the diagram, figure 5. Combined effect of H_2SO_4 -F-and SiO_2 on corrosion abrasion. F/ SiO_2 (reactive SiO_2) must be lower than 1.4.

Q - Mr. R. LUDEMANN, Occidental Chem. Co., United States

The Cl pitting has implications relative to the practice of washing tanks of sea going tankers (nGA and/or SPA) with sea water. Would you comment?

A - Our work concerns the effect of chlorine present in phosphoric acid reactors. The question is too far away from that context for us to be able to answer.

Q - Mr. J. LE PAGE, SIES, Senegal

In the manufacture of pump impellers Uranus B6 is not, to my knowledge, in great use. Why have the authors not studied the behaviour of various "chromized irons"?

A - To study the behaviour of chromized irons for using them in pump turbines, it would be useful to make a test with a small pilot pump allowing to operate at peripheral speeds comparable to those of the pump. If not, errors due to too big extropolations are to be expected (Peripheral pump speed 1500 m/min., agitators 300 m/min.).

Q - Mr. R.F. BARUT, Heurtey Industries, France

1) Your results show that the variation in the corrosion between 70 and 85° C follows an exponential relation with an exponent of 1/4. Can you indicate the variation you accept between 50, 60 and 70° C?

2) Your tests stress the role of impurities; in the case you want to simulate a 54% acid for corrosion tests, what are, in your opinion, the most important factors to pay attention to in that simulation (form of constituents, buffer effect, ...)?

3) You mention a surface area of 5 cm² for each plate. Does it relate to the total exposed area?

4) Can you indicate if your tests were also made with welded plates, made of the same metal or different metals, since the welded points are often subject to corrosion?

5) With your results, you could establish a correlation of weight losses between the pilot plant and pump impellers. Did you establish a similar relation for chlorine induced pitting?

- A -
- 1) We did not study the corrosion below 70° C.
 - 2) One needs to build a concentration pilot, each stage operating continuously and feed it with unpurified acid. Corrosion could be studied on a small pilot circulation plant.
 - 3) Yes
 - 4) No, but it can be done
 - 5) Yes, only for low chlorine contents.

Q - Mr. R. MCNALDI, Montedison SpA, Italy

We are going to ask if you made experiments with phosphate rocks containing more than 150 ppm of sulphides? What is in this case the action in reference to pitting corrosion?

A - Corrosion by sulphides was not studied.

Q - Mr. I. EZAHR, O.C.P., Morocco

- 1) The corrosion measurements of weight loss you made give only an idea on the homogeneous corrosion. Have you another experimental method to assess a corrosion by pitting? These weight loss measurements have only a comparative interest (comparison of different steel qualities) but can in no case describe the mechanism of corrosion.
- 2) How did you draw the curve on figure 4 about the effect H_2SO_4 ?

- A -
- 1) Corrosion by pitting can be followed with an optical microscope or, preferably, a sweeping electronic microscope. The rate and intensity of chlorine corrosion in relation to speed show clearly that it is a phenomenon other than corrosion abrasion (Compare fig. 3 and 6).
 - 2) Experimental conditions of the curve fig. 4: 316 L steel, phosphate A, 1% SiO_2 , peripheral agitator speed 140 m/min.