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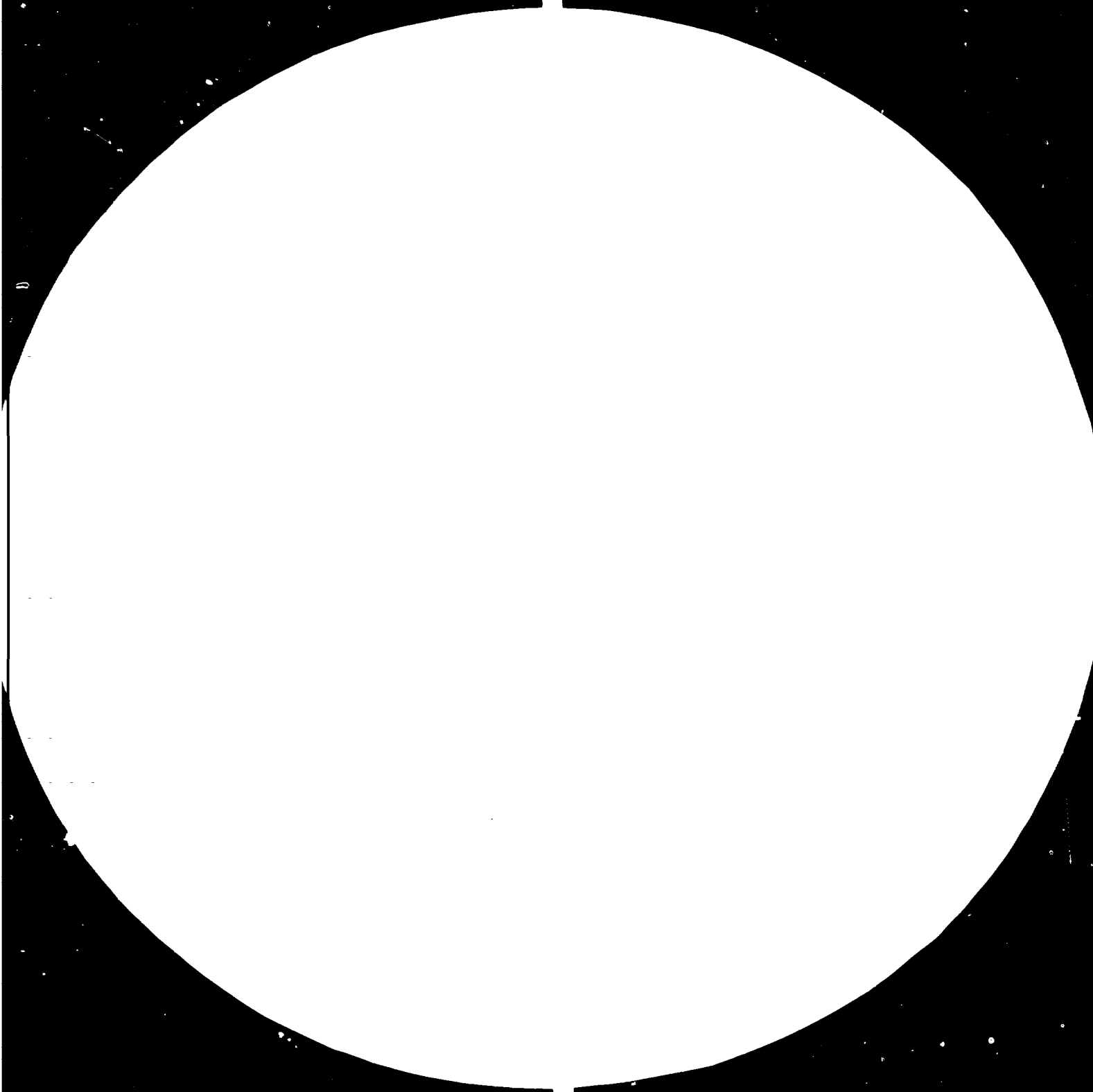
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2.8



2.2



3.6



2.0



1.8



Minimum Resolvable Periodicity (MRP) = $\frac{1}{\lambda \cdot \sin \theta}$

λ = Wavelength of light (m)

θ =



10062



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FACTORS GOVERNING CORROSION DURING THE SAFE PRODUCTION OF
SULPHURIC ACID AND PHOSPHORIC ACID *

by

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001226

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INTRODUCTION

In spite of great developments which have been made in the field of construction materials, corrosion is still a major problem to the fertilizer industry especially in phosphoric acid production, an important intermediate product of the fertilizer industry. One of the major reasons for this is the fact that, the increasing tonnages of raw material needed for the increasing demand has brought many new raw materials with higher corrosion affecting impurity ratios on the market.

(see table 1).

Nevertheless, the phosphoric acid technology is making great progress in developing new corrosion investigation methods which will be a helpful tool for the selection of the most suitable material.

The sulfuric acid technology has achieved a major improvement against corrosion by realising tube and shell acid coolers with anodic protection.

COST OF MAINTENANCE AND CORROSION
WHEN MANUFACTURING 1 T OF DIAMMONIUM PHOSPHATE

	QUANTITY IN M. TON	TOTAL COST OF MAINTENANCE	COST OF CORROSION
Sulfuric acid	1,32	2,9	1,00-1,30
Phosphoric acid (P2O5)	0,49	5,7	0,85-2,85
D.A.P	1	3,6	0,28-0,36
TOTAL PER MT D.A.P		13,9	2,13-4,51

CORROSION WITH SULPHURIC ACID PRODUCTION

Sulphuric acid is a strong acid. When concentrated as high as 98 %, as it comes out of the production unit, the little water still contained in the acid is not enough to dissociate H_2SO_4 and maintain a high acidic aggressivity. At ambient temperature e.g normal steel can be used to build 98 % acid tanks.

It can be seen from fig 1 the great variation within the behaviour of sulphuric acid versus metals at different concentrations and temperatures [1] .

Fig 2 shows a simplified sulphuric acid plant diagram with the different spots where corrosion usually occurs (D = danger of corrosion - HI = high corrosion danger).

These spots, the reasons for corrosion and recommendations, are :

1) Sulphur melting and storing. Free acid in sulphur, corrosion of steel. Prevent by neutralisation with excess of lime followed by sulphur filtration.

2) All boiler type heat exchanger (economiser). They are bricklined. If there will be some humidity with the SO_2/SO_3 gases, oleum will condensate between bricklining and steel shell with consecutive corrosion - Control humidity - no organics with sulphur to be burned.

3) Drying tower - The demister in the upper part - made of 316 - Regular replacement.

4) Heat exchanger - especially after intermediate SO₃ absorption tower because of low temperature and droplet or acid mist entrainment. Install high efficiency demister.

5) Acid cooling section - usually water cooled pipe system. New tube and shell system with anodic protection seems to give promising results.

CORROSION WITH PHOSPHORIC ACID PRODUCTION

Phosphoric acid is one of the stars within the corrosive medium. This behaviour does not belong properly to the phosphoric acid (pure acid is not corrosive) but to the impurities contained in the produced acid. Furthermore the reaction tank works with a mixture of solid and liquid phase : abrasion adds its action to the corrosion, preventing the alloys from any possible passivation.

The type of corrosion occurring with phosphoric acid manufacturing, is called abrasion corrosion and in the presence of chlorides pitting. Abrasion corrosion leads to a regular disappearance of metal : Pitting is a punctual attack of the metal.

Corrosion occurs with the agitators, slurry and acid pumps, with the filter, with the concentrations equipment (circulation pump and heat exchanges if made with stainless steel). (fig 3).

RESPONSIBLE 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.

PHYSICAL FACTOR

Periferical speed

Periferical speed is an important factor because abrasion corrosion increases heavily with it. This can be seen from the equation for a turbine agitator or pump impeller :

$$\text{Corrosion} = K (nd)^X$$

n = speed of revolution

d = diameter

K = constant

X \approx 2.4

It also indicates that statistical tests, submerging a sample into a beaker with acid has is not very representative.

Periferical speed varies enormous by from one equipment to another e.g.

Filter cell	30 m/minute
Pipes	60 m/minute
Agitators	250 - 350 m/minute
Pump impeller	1000 - 1500 m/minute

From the filter cell to the pump impeller the speed ratio is about 30 to 45 and the comparative corrosion rate for a given alloy could be $(30)^{2.4}$ to $(45)^{2.4} = 3\ 000$ to 9 000. (fig 4).

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 [2] and our own results, we found that the variation in the corrosion according to temperature seems to be a relation of the type $\frac{C_{t1}}{C_{t0}} = (\Delta t)^{x(t)}$. Between 70 and 85°, temperatures which are particularly of interest in the dihydrate process, the value $x(t)$ approaches $\frac{1}{4}$.

CHEMICAL FACTORS

Sulphuric acid

Sulphuric acid is an extremely active corrosion agent (Fig 5). 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 H_2SO_4 , it is not very aggressive, probably because the SO_4^- 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 H_2SO_4 , but we also have to take account of the presence of H_2SiF_6 which is equivalent to 17-25 g of H_2SO_4 . 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 H_2SO_4 , 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.

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 be also 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. 6). 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.

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. 7). 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. 8), 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 86 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 86 is significantly higher (fig. 9).

The threshold of chlorine attack is much lower for Uranus 86 and for all the other steels tested. The combined action of $F-H_2SO_4-Cl$ is extremely severe.

ALLOYS TO BE USED WITH PHOSPHORIC ACID PRODUCTION

TYPE	Cr	Ni	Mo	C	COMMENTS
304	18-20	8-12	-	0,08	Only occasionally for splash guards
304 L	18-20	8-12	-	0,03	
316	16-18	10-14	2-3	0,08	At low speed and matured slurry, low corrosive rock
316 L	16-18	10-14	2-3	0,03	
317	18-20	11-15	3-4	0,08	Agitators, valves, filter with low corrosive rock
317 L	18-20	11-15	3-4	0,03	
446	23-17			0,2	Heat exchanger tubes
Hasteloy C	15,5	54	16	0,08	High Cl ⁻ agitator, pump impellers. Evaporators, hot acid
Hasteloy G	22	44	6,5	0,05	
Nionel	21,5	42	3	0,03	Heat exchanger tubes
Sanicro 28	26,0	30,6	3,55	0,015	Pump impeller, agitator turbines when high Cl ⁻
Durimet 20	19-22	27-30	2-3	0,07	Pump, impellers, H2SiF6
Durco 100	24-27	4-6	1,7-2,25	0,04	Pump, valves
U 86 _{PM}	20	20	4,5	0,02	Agitator turbines, pump impellers
U 50 M	22	7-9	2,2-2,8	0,07	Pump impellers
U 55 M	25-27	4,5-6,0	1,5-2,5	0,05	Pump impellers

CORROSION WITH FERTILISER UNITS

Corrosion with fertiliser units is less than with the sulfuric or phosphoric acid units. Most of the equipment of the fertiliser units handle solid granular material which is by far not as aggressive as liquid concentrated acids.

The corrosive spots of a fertiliser plant are located where liquid phases are handled : preneutraliser, effluent gas washing granulation drum, granulation mixer. Corrosion depends on the kind of fertiliser produced : it is obvious that a PK fertiliser, having a low PH and containing chlorides will have a much higher corrosive behaviour than a diammonium phosphate having a high PH and containing no chlorides.

When producing PK fertilisers the granulator drum sometimes has to be lined with very exotic alloys (especially when sulfuric acid is added into the drum as a granulation agent causing high hydrochloric acid release).

When drying PK fertilisers, HCl will evolve during drying and be collected with the effluent gas washing. High corrosive behaviour of the effluent wash liquor is to be expected. But since there are no high temperatures plastic material can be used.

METHODS OF CORROSION INVESTIGATION

The most common but also the most reliable figures are available from the fertilizer industry itself. Those figures result from the practiced results by utilising various alloys with the different kinds of raw materials.

This, of course, is not a method of investigation but it was taken because for a long time corrosion tests were not reliable at all. Those tests usually consisted in just immersing a sample of an alloy into phosphoric acid and weigh it after a certain time. No attention was paid to the fact that the media was not comparable with the media of a reactor in working conditions.

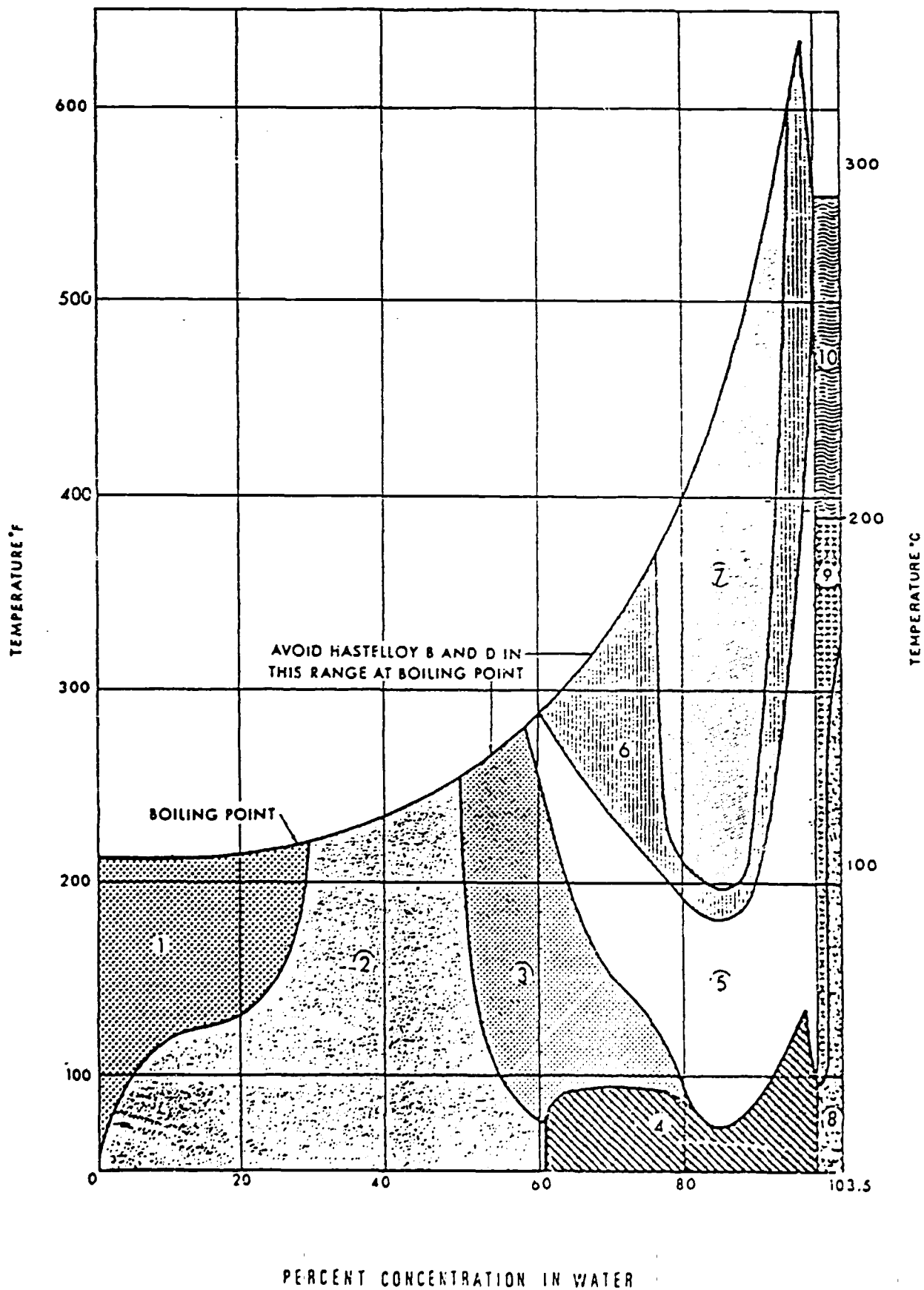
Presently methods are developping. They base on testing in active slurry, that means slurry where the chemical reactions occur and the corrosive impurities like native HF are present. Care is taken about the differential speed between the alloy and the media.

The loss of metal by corrosion or abrasion-corrosion is measured either by the traditionnal weight loss or by more modern potentiometric methods.

Fig 10 shows the diagramm of a bench scale test set which has been experienced successfully for wet process phosphoric acid corrosion tests. It is a real small phosphoric acid reactor, producing slurry as it is in a large industrial reactor. A special agitator had to be developped to meet the power trans-

fer to the slurry and the periferical speed of the large impellers used in industrial plants. This agitator (fig 11) also permits quick exchange of agitation blades which in fact are the testing samples.

FIG 1



CODE FOR SULFURIC ACID GRAPH

Materials in shaded zones have reported corrosion rate <20 mpy

ZONE 1

20Cr 30Ni

66Ni 32Cu¹

62Ni 28Mo

Type 316²

Al bronze 10%¹

Copper¹

Gold

Lead

Molybdenum

Nickel cast iron

Platinum

Silver

Tantalum

Zirconium

ZONE 2

20Cr 30Ni³

66Ni 32Cu¹

62Ni 28Mo

Type 316²

Al bronze 10%¹

Copper¹

Gold

Lead

Molybdenum

Nickel cast iron⁴

Platinum

ZONE 3

20Cr 30Ni³

66Ni 32Cu¹

62Ni 28Mo

Gold

Lead

Molybdenum

Platinum

Silicon iron

Tantalum

Zirconium

Silicon cast iron

Silver

Tantalum

Zirconium

- 1. No air
- 2. < 10% aerated
- 3. < 75 C
- 4. < 20% at 25 C
- 5. < 25% aerated at 25 C
- 6. < 96% concentration
- 7. > 96% concentration
- 8. < 80% aerated
- 9. < 75C, < 96%
- 10. 20 to 50 mpy

ZONE 4

20Cr 30Ni

62Ni 28Mo

Type 316²

Gold

Lead⁶

Nickel cast iron

Platinum

Silicon iron

Steel

Tantalum

Zirconium^{8*}

ZONE 5

20Cr 30Ni¹

62Ni 28Mo

Gold

Lead⁹

Platinum

Silicon iron

Tantalum

ZONE 6

62Ni 28Mo^{1*}

Gold

Platinum

Silicon iron

Tantalum

ZONE 7

Gold

Platinum

Silicon iron

Tantalum

ZONE 8

20Cr 30Ni

18Cr 8Ni

54Ni 15Cr 16Mo

Gold

Platinum

Steel

ZONE 9

20Cr 30Ni

18Cr 8Ni

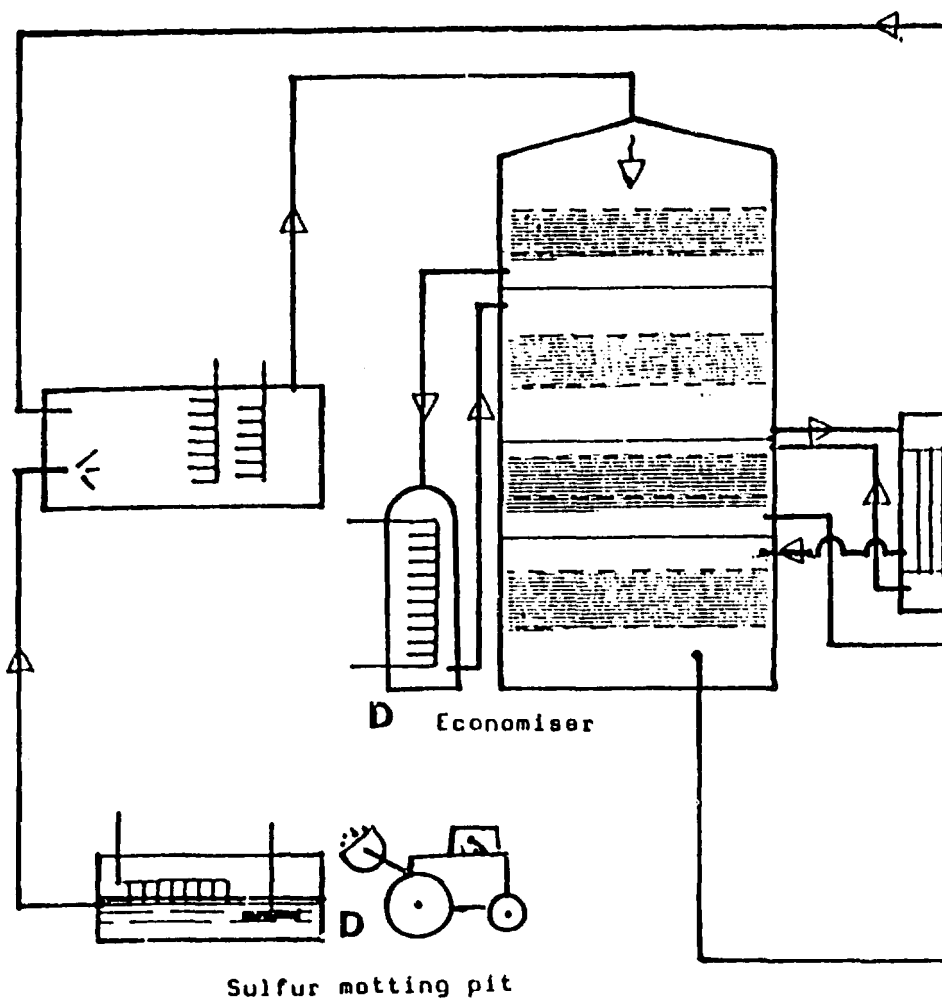
Gold

Platinum

ZONE 10

Gold

Platinum



Simplified diagram for sulfuric acid double absorption system - corrosion spots

FIG 2

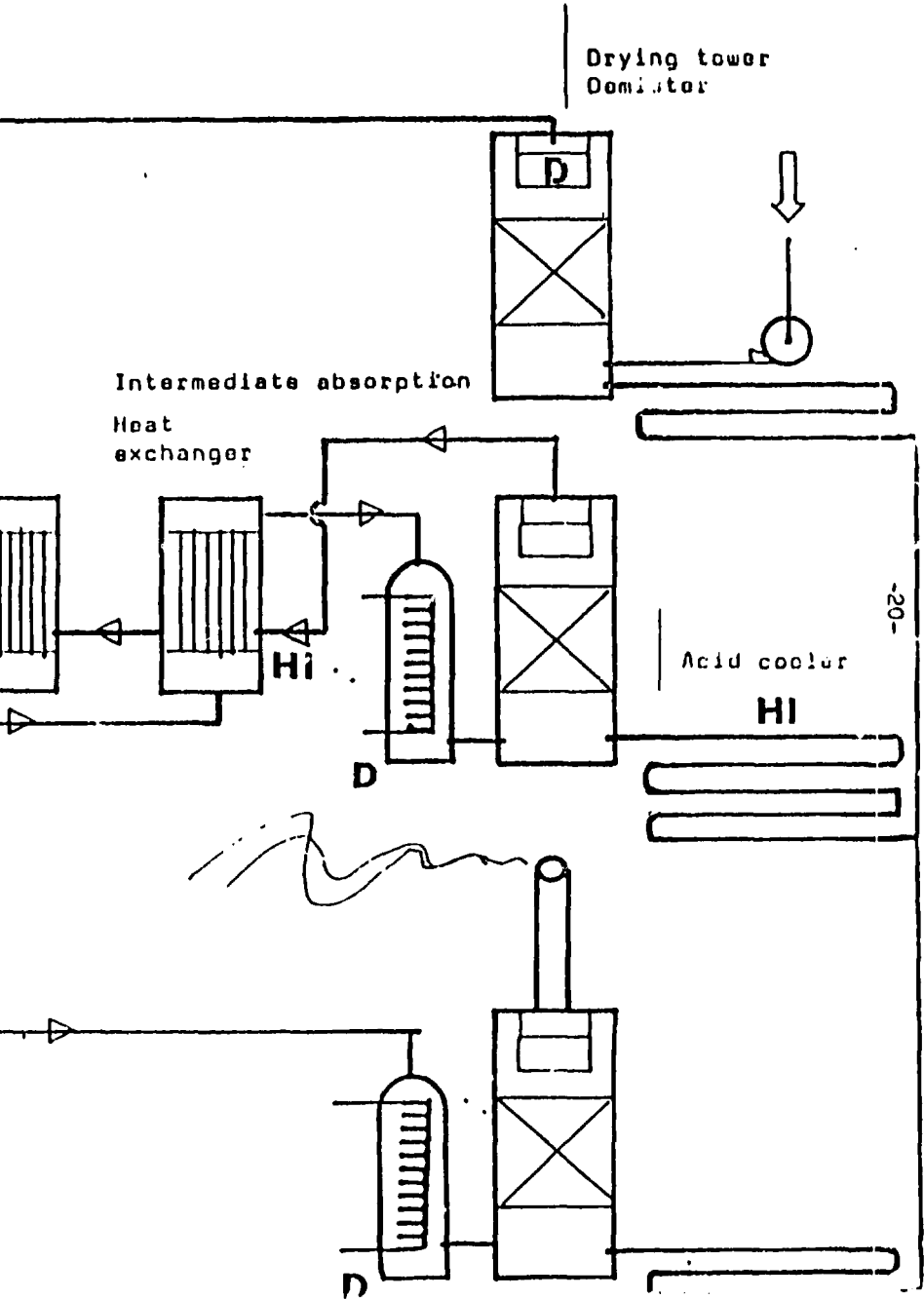
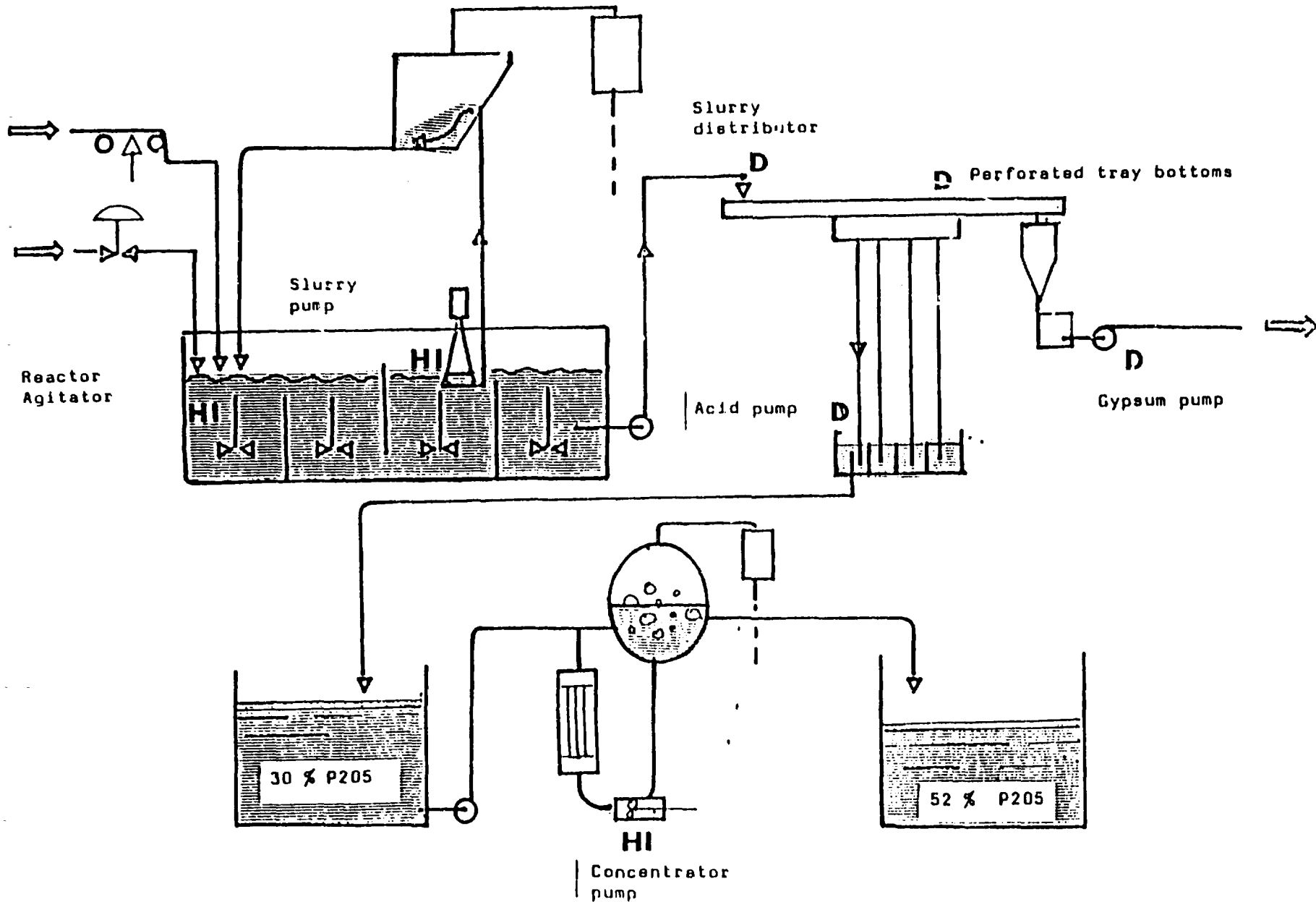


FIG 3

Simplified diagram for phosphoric acid dihydrate system - Corrosion spots



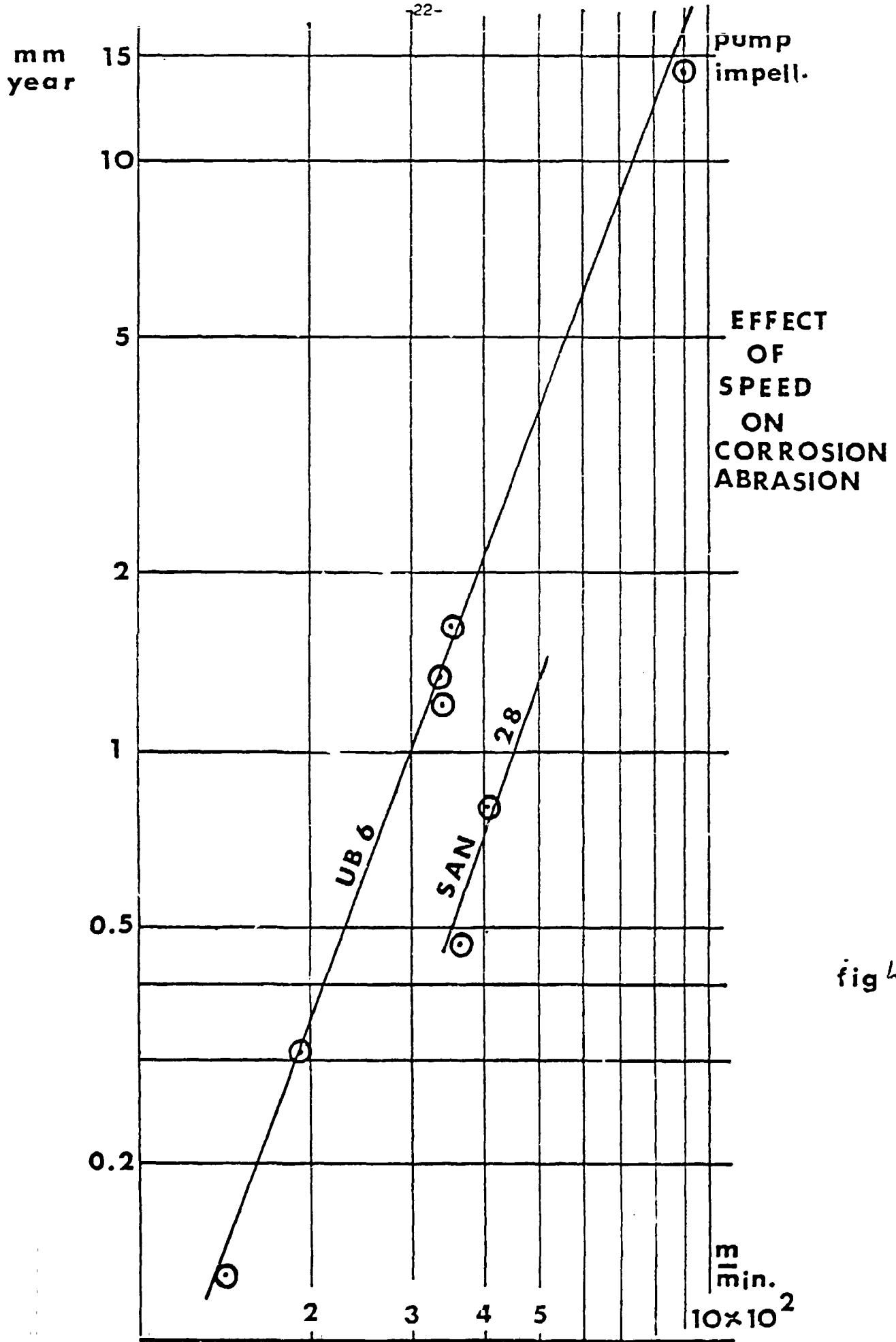
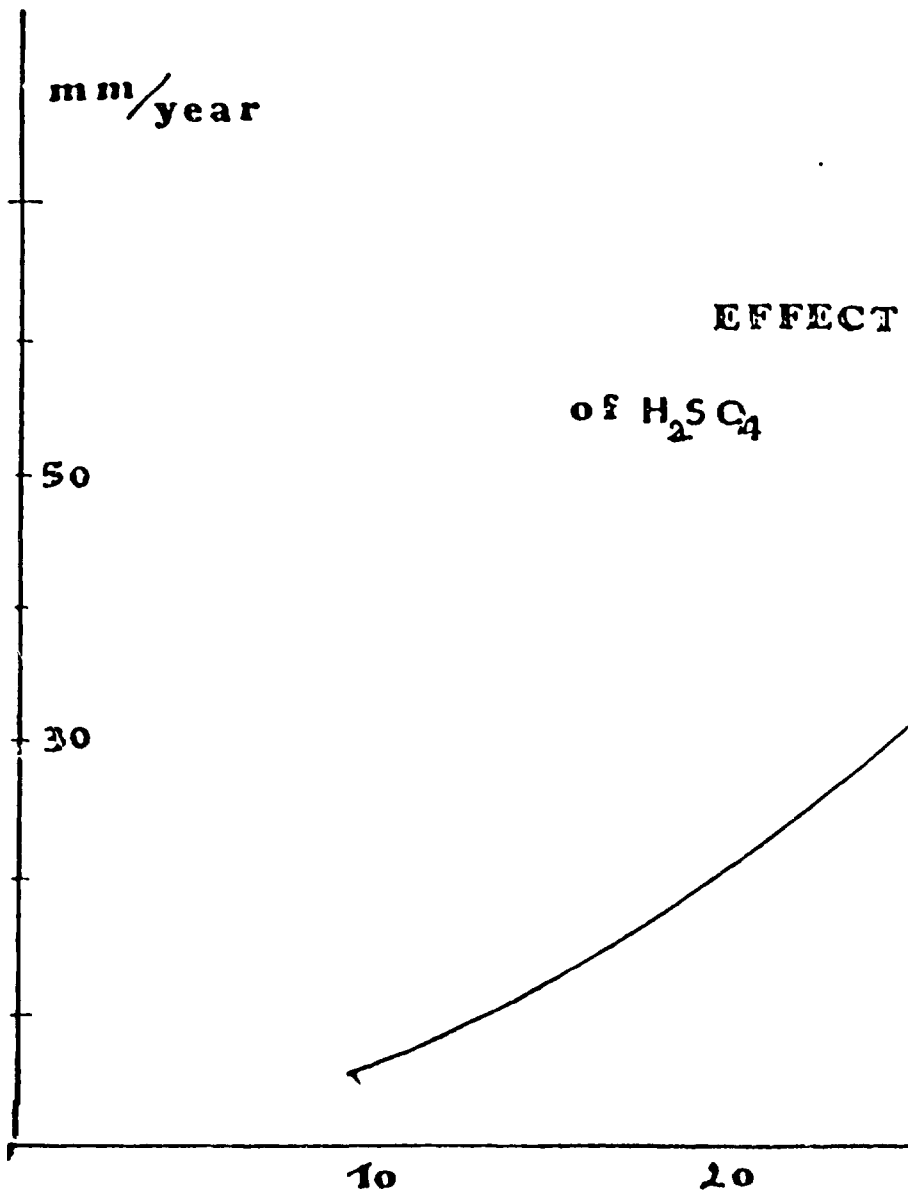


fig 4



mm/year

EFFECT

of H_2SO_4

50

30

10

20

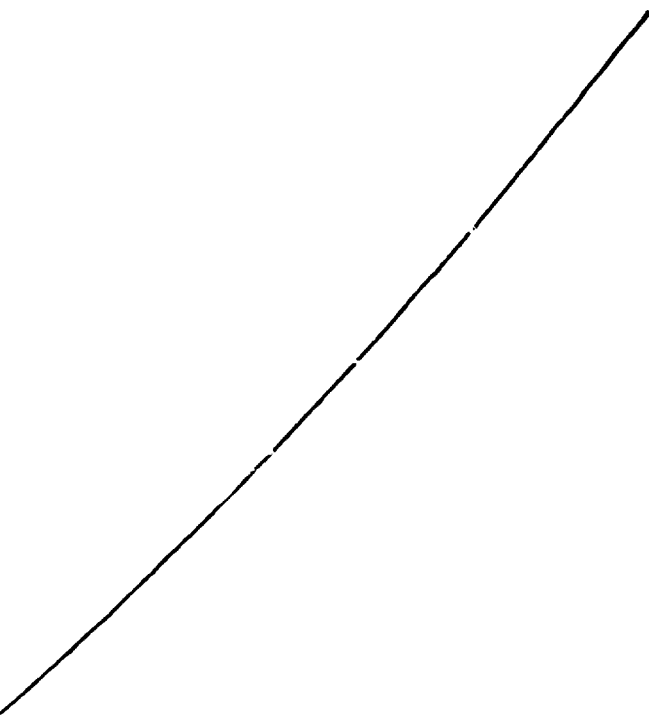


fig 5

H₂SO₄ gr.l

30

40

fig 6

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

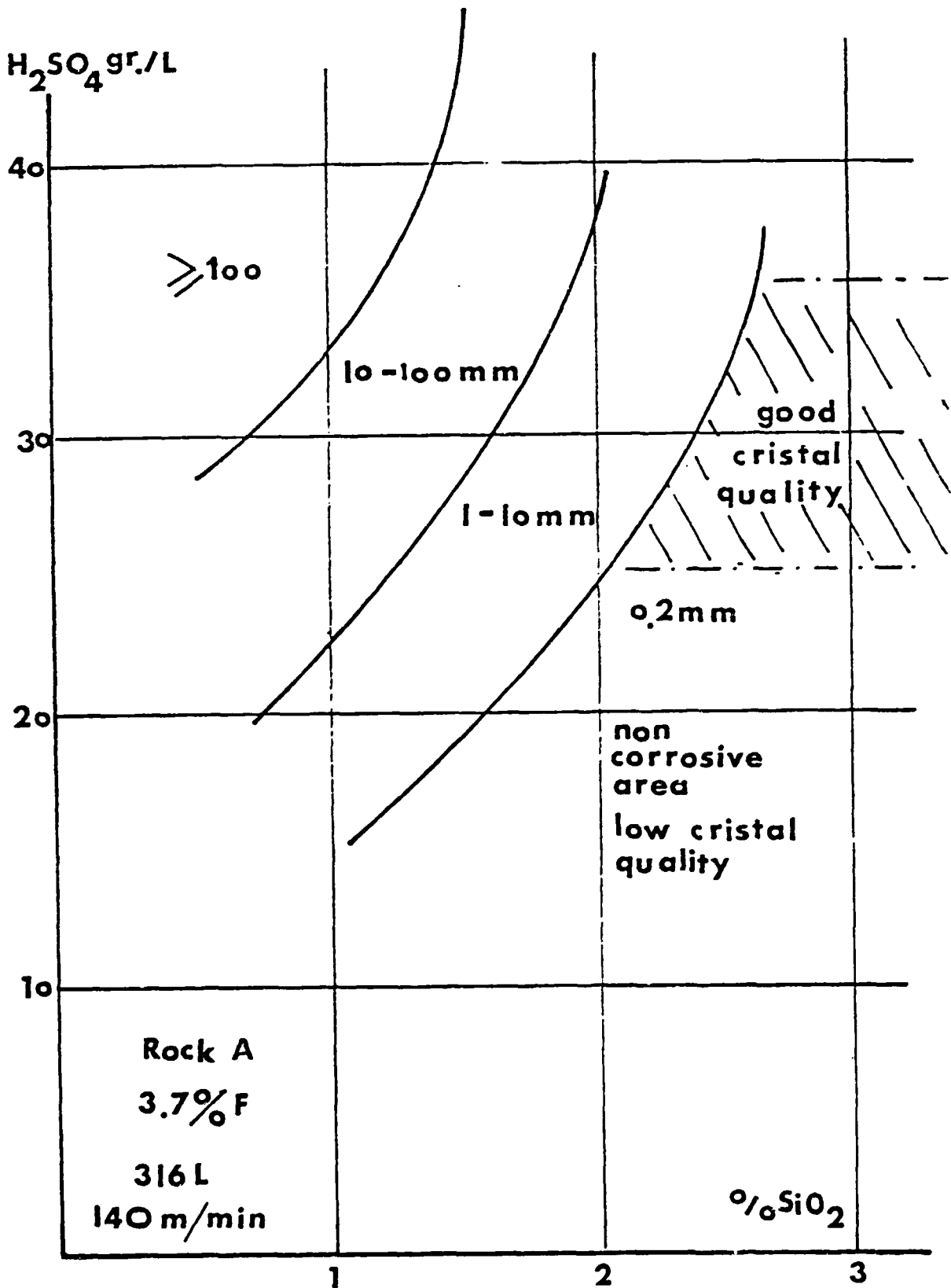
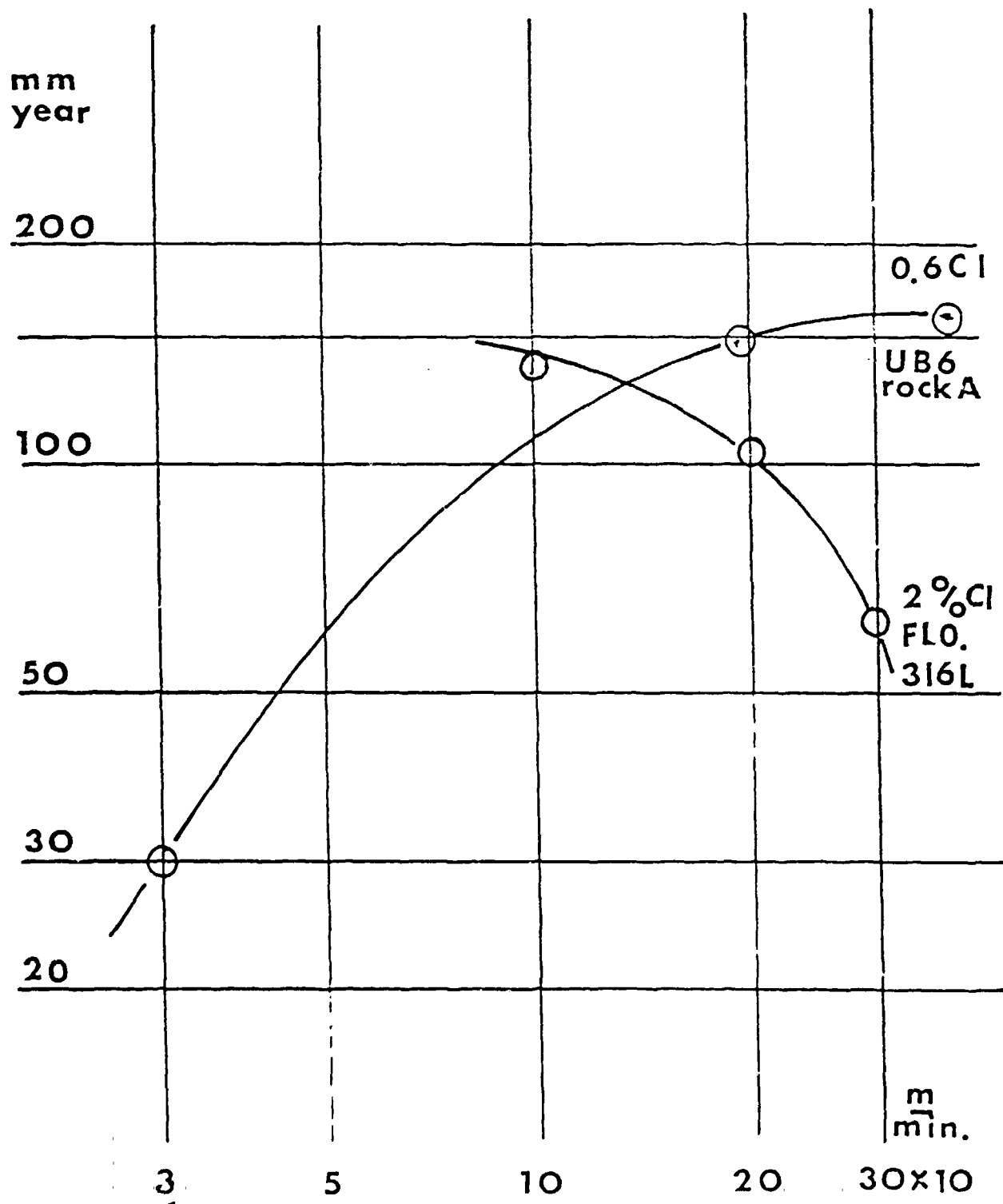


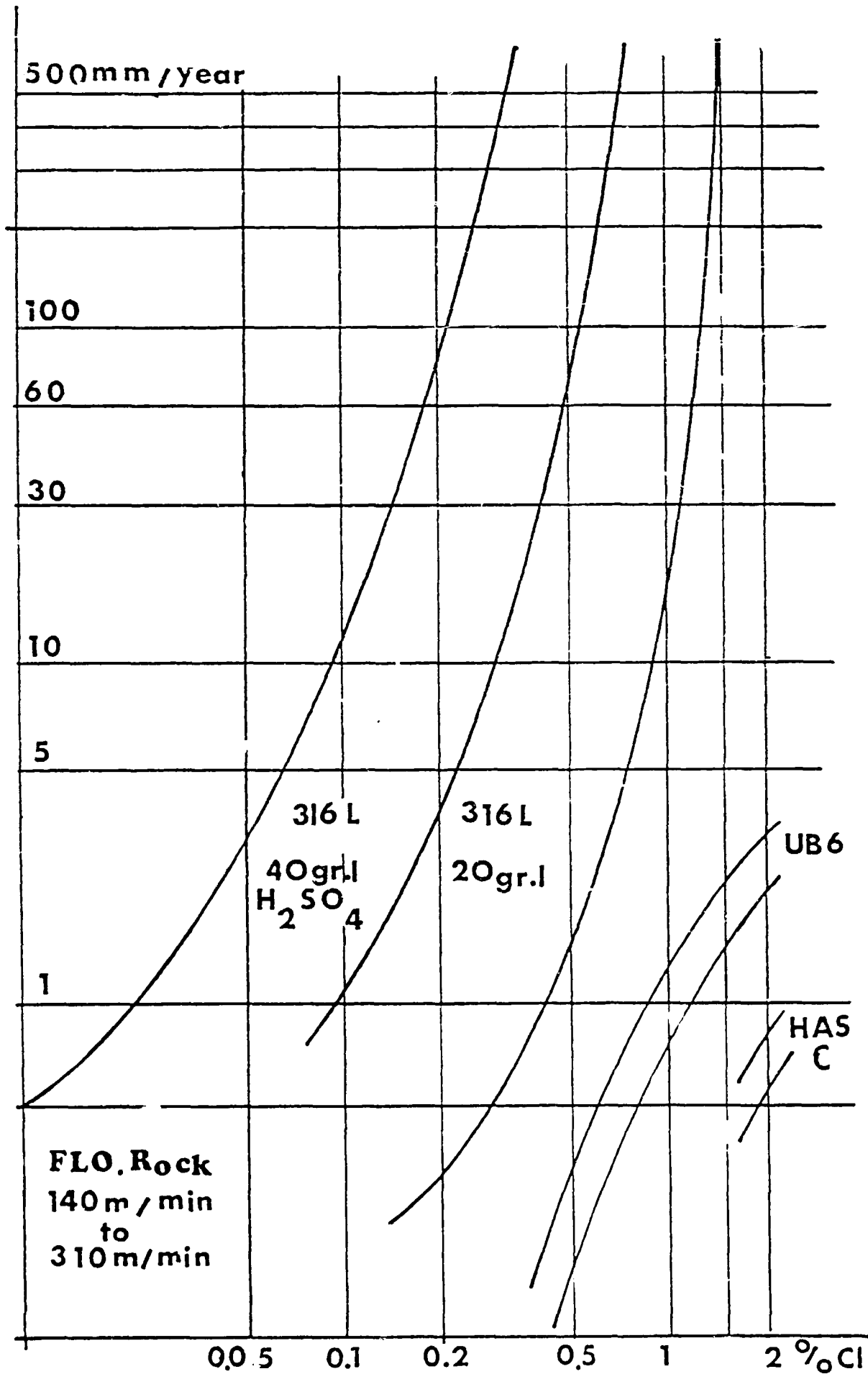
FIG 7

EFFECT OF SPEED ON CHLORIDES PITTING



-26-
EFFECT of CHLORIDES

FIG 8



EFFECT of CHLORIDES

FIG 9

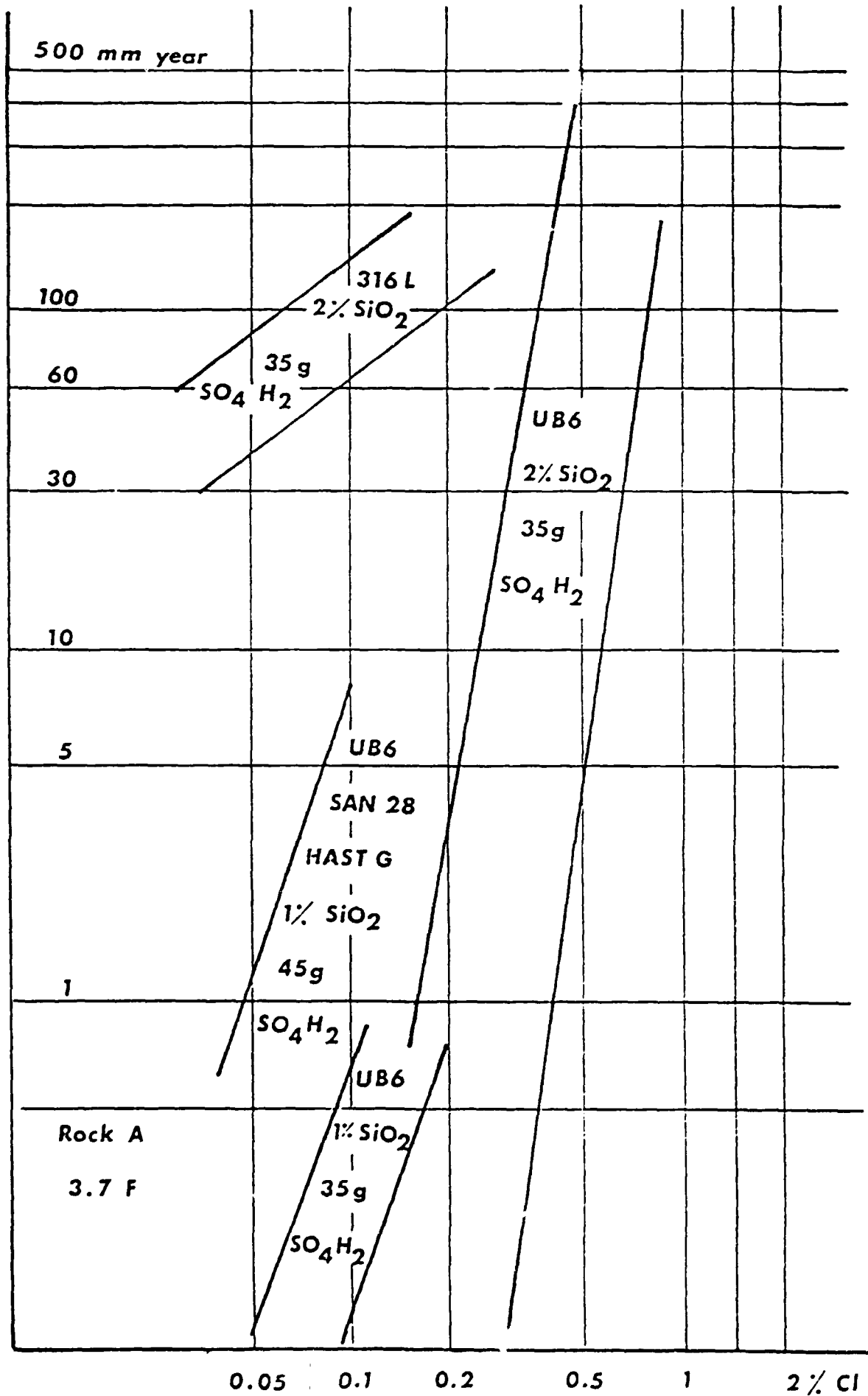
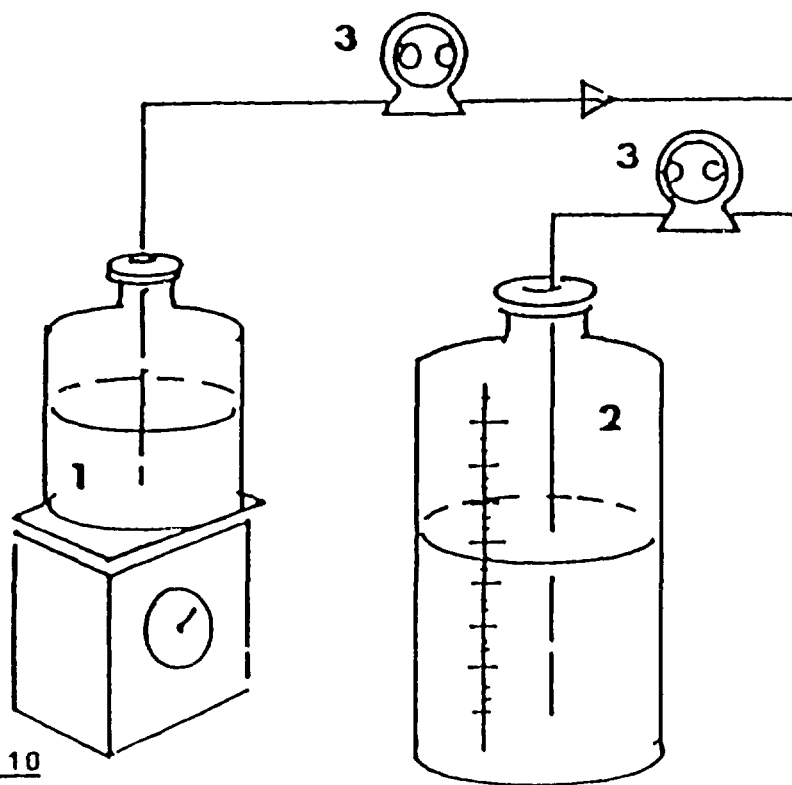


Fig 10

CORROSION PILOT PLANT



KEY TO FIGURE 10

- | | | |
|--------------------|------------------|---------------------|
| 1 Sulphuric acid | 5 Reactor | 9 Phosphate charges |
| 2 Return acid | 6 Agitator | 10 Slurry reservoir |
| 3 Pumps | 7 Motor | 11 Effluents |
| 4 Temperature bath | 8 Phosphate feed | |

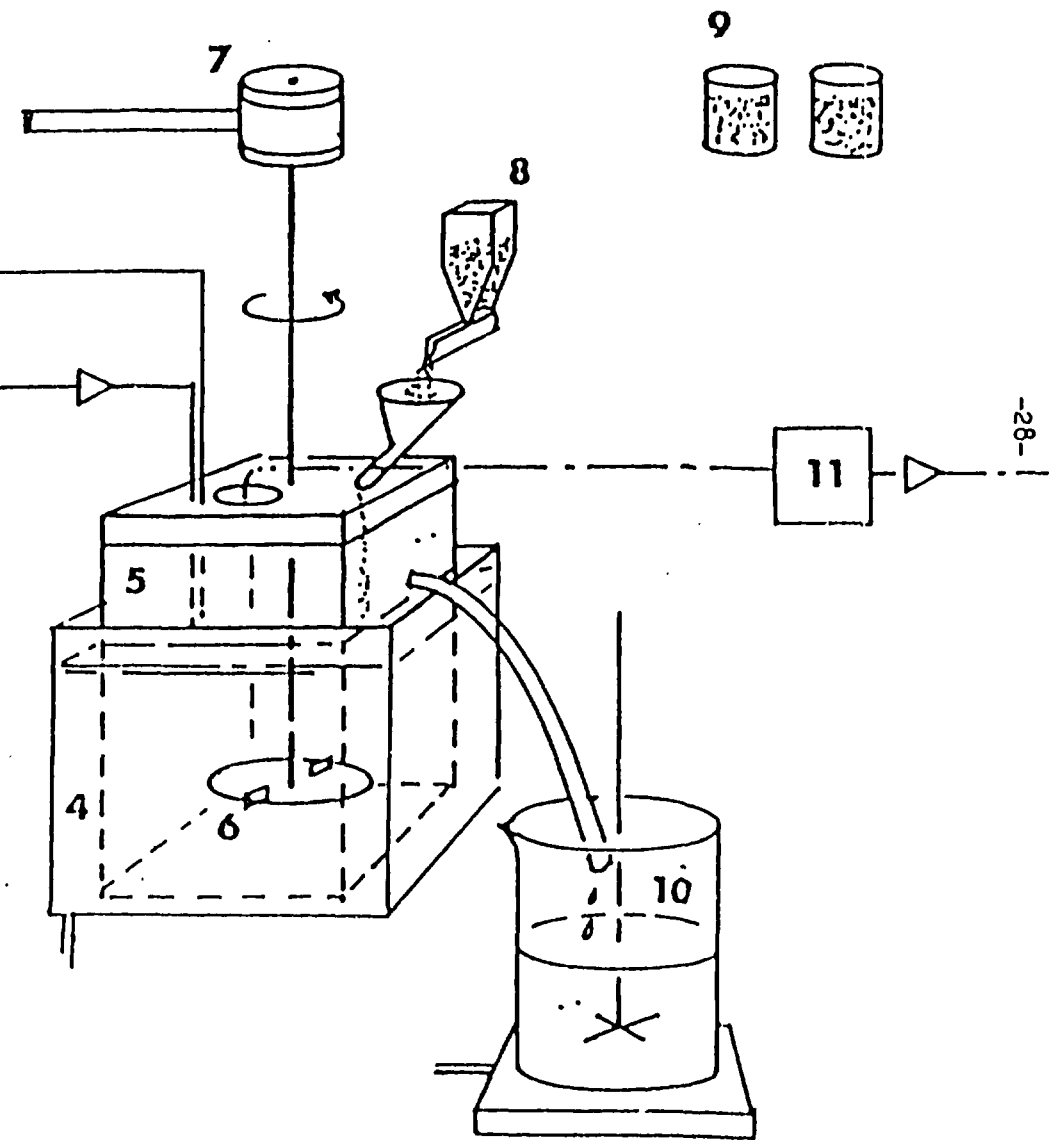


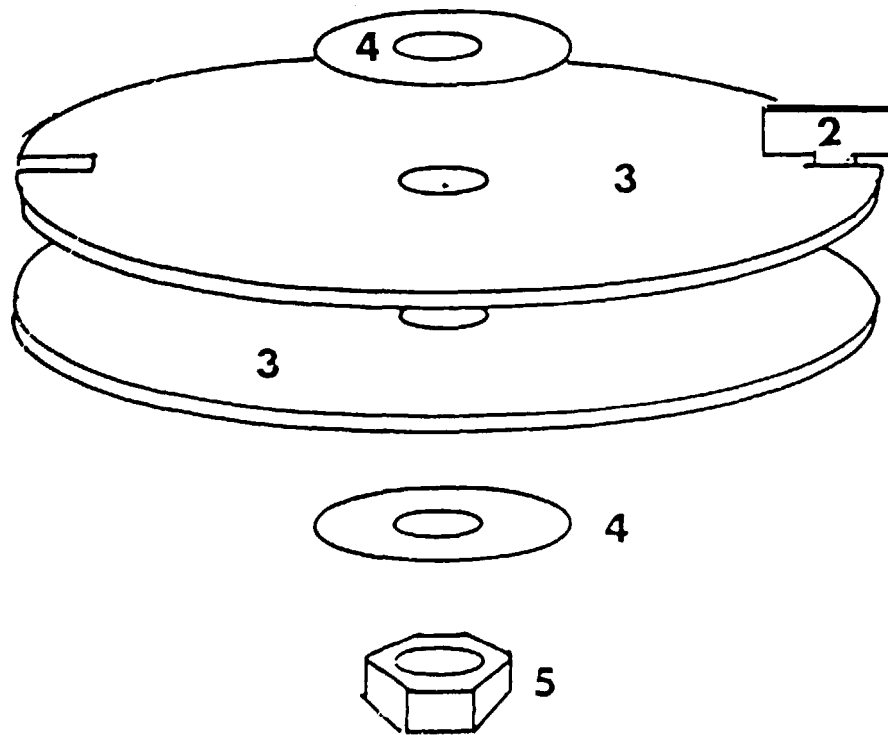
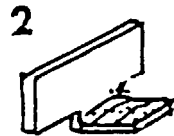
fig 11

CORROSION TEST

AGITATOR

KEY TO FIGURE 11

- 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



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