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#### SUMMARY

The fluorine recycle in the manufacture of superphosphate is an original Montedison process and was first presented at the ISMA Technical Conference in The Hague in 1976.

Studies were carried out in the Fertilizer Research Center in Porto Marghera and the know-how was applied by Agrimont in the revamping of numerous superphosphate plants and in the construction of new plants in Italy and abroad.

Studies were continued in order to extend the technique of the fluorine recycling to the phosphoric acid processing. The first mention of this was given at the IFA/CNCCC Technical Conference in Peking in 1983.

The process chemistry was examined thoroughly and the basic operations were developed and improved in the utilization of several phosphate rocks. The main advantages of the process are :

- the solution of various ecological problems due to the total re-utilization of the wastes in the production cycle;
- reduction in the consumption of sulphuric acid to attack the phosphate rocks;
- improvement of the process efficiency.

The fluorine recycling process was started up industrially in the phosphoric acid plant in Porto Marghera in 1977 and in the ISAF plant at Gela in 1981.

#### INTRODUCTION

The fluorine recycling process in the manufacture of superphosphate was developed and set up by Agrimont in 1973-1975. A technical report regarding this was presented at the ISMA Technical Conference in The Hague in 1976 (1).

The recycling of fluorine in superphosphate has had a great success and has been applied by Montedison in the revamping of many plants and in the construction of new ones in Italy and abroad. The new plant built by the Phosphate Co-operative Company of Australia Ltd. in Celong having a 3000 t/d capacity employs the Montedison know-how.

The ecological problem which gave rise to the research, considering the difficulty of marketing compounds containing fluorine, became increasingly more urgent and severe. One only has to look at the ecological regulations in the various countries concerning this problem in order to understand the situation.

In Italy, the concentration of fluorine based compounds, expressed as F, must not exceed  $0.02 \text{ mg/m}^3$  around the perimeters of the plants (in the work place the maximum allowable value is  $2 \text{ mg/m}^3$ ).

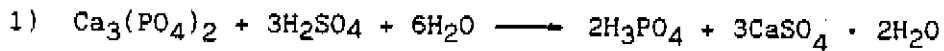
The situation regarding discharge of the wastes is therefore particularly burdensome in the phosphoric acid plants due to the fact that the hydrofluosilicic acid either neutralized with lime or non-neutralized is usually discharged with the gypsum, which may represent a problem. This is the main reason which drove Agrimont to continue research aimed at the total recycle of fluorine in the phosphoric acid plants.

The process was first industrially applied in the Porto Marghera plant in 1977 and secondly was set up in the Gela plant in 1981 as reported at the IFA/CNCCC Technical Conference held in Peking in 1983 (2).

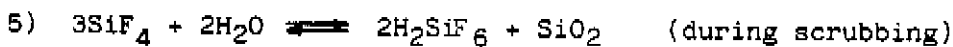
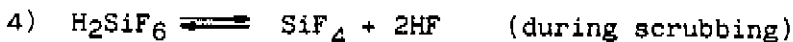
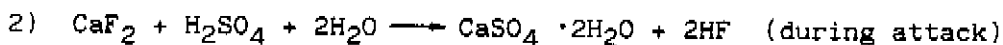
## PROCESS THEORY

### 1. Process Chemistry

The main reaction taking place in the phosphoric acid production process can be expressed by the following equation :



All phosphate rocks have a defined F/P<sub>2</sub>O<sub>5</sub> ratio which determines the chemical structure of the fluoroapatite molecule. The main reactions occurring in phosphoric acid production in which fluorine - containing compounds also participate, can be concisely represented as follows :



The released HF (reaction 2) rapidly reacts with silica, forming H<sub>2</sub>SiF<sub>6</sub> (reaction 3).

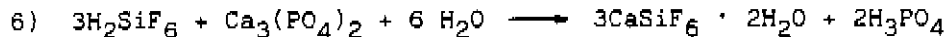
Silica is always present in phosphate rocks as quartz silica (α quartz) and as various silicates of different origin. This silica is usually called soluble silica or active silica, because it participates in reaction 3.

Sodium and potassium are always present in phosphate rocks and react with hydrofluosilicic acid formed by reaction 3 and 5, obtaining sodium and potassium fluosilicates and other slightly soluble salts.

Fluorine distribution among the various flows of the dihydrate process (gypsum, attack gas, sedimentation sludge, vapors from concentration and produced acid) depends on the chemical characteristics of the phosphate rock utilized and; in particular, on the fluorine, active silica and sodium content, as well as on the concentration of phosphoric acid produced. The H<sub>2</sub>SiF<sub>6</sub> solution obtained

by scrubbing out the vapors from the rock attack and acid concentration sections is recycled to the reactor together with the recycled phosphoric acid (or through the gypsum washing loop).

The reaction mechanism of the  $\text{H}_2\text{SiF}_6$  recycled in attack can be stoichiometrically expressed by the following reaction :



(Other less important reactions are neglected)

For each mole of  $\text{H}_2\text{SiF}_6$ ,  $2\text{H}^+$  participate in the attacking reaction. By recycling fluorine, it is possible to reduce the amount of  $\text{H}_2\text{SO}_4$  by an equivalent amount of hydrofluosilicic acid recycled.

## 2. Gypsum Morphology

The morphology of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  crystals is not affected by the use of the fluorine recycle technique, provided that the phosphate rock attacked has an active silica/fluorine ratio high enough to complex all the fluorine to  $\text{SiF}_6^{2-}$  ion.

If the phosphate rocks have a ratio lower than 0.526, corresponding to the stoichiometric value, then kieselguhr or bentonite should be added during the attack, in order to prevent that part of the fluorine is recycled as HF. Should this happen, the attack slurry will contain a high level of  $\text{F}^-$  ions, which could only deteriorate the morphological characteristics of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  crystals, by preventing growth along the z crystallographic axis. In this case, the gypsum crystals will be thinner and longer, thus being more difficult to filter and wash.

Upon addition of active silica and aluminum, the morphology of the gypsum crystals takes on the typical "rose" shape. Consequently, the rate of filtration and washing increases by some 15-20%.

The use of surfactants remarkably improves the morphology of the crystals obtained from phosphate rocks containing high levels of organic matters.

For each type of phosphate rock a specific surfactant has been identified, which offsets the negative effects caused by organic matters. Figure 1 shows a photograph, 100 times magnified, of gypsums obtained from Morocco phosphate having a weight ratio of active  $\text{SiO}_2/\text{F} = 0.2$ , without any addition of bentonite or surfactant. Figure 2 shows those gypsums which were obtained by adding bentonite up to a ratio active  $\text{SiO}_2/\text{F} = 0.526$  and the employment of a specific surfactant. The results so obtained are self evident.

## 3. Corrosion Control

It should be noted that fluorine recycling in the  $\text{H}_3\text{PO}_4$  production generates systematic corrosion phenomena above standard on stainless steel type AISI 316.

The other metals and alloys commonly used in  $\text{H}_3\text{PO}_4$  production units, such as ALLOYS 20, SANICRO 28 (\*), etc. do not show any remarkably different beha-

(\*) trade mark of SANDVIK

viator, with or without fluorine recycling.

A research study was carried out at the Agrimont Fertilizer Research Center in order to determine both the influence of individual parameters on corrosion, and to control corrosion on AISI 316. The work consisted in performing anodic polarization measurements in order to study how individual chemical species interact with each other in generating phosphoric acid corrosion (3).

It is well known that this latter type of phenomenon is linked with the presence of particular substances contained in the original phosphate rock (chlorides, fluorides, etc.) or originated by the attack reaction (sulphate ions).

In our investigation we examined the effects of both fluorides by themselves and also together with chlorides. The possibility of offsetting the aggression was also examined.

### 3.1. Experimental

Tests were performed in phosphoric acid solutions (28%  $P_2O_5$ ) prepared by mixing distilled water,  $H_3PO_4$  85%, with additions of  $H_2SO_4$  96%, NaCl, HF,  $Fe_2(SO_4)_3$  and  $H_4SiO_4$  (all reagent grades). The measurements were performed in a PVC cell, immersed in a thermostatically controlled bath, so as to maintain a constant temperature of 80°C. An AMEL apparatus was used, consisting of a potentiostat, function generator, interface unit, and an X-Y recorder.

Specimen polarization was started at -500 mV (S.C.E.) and was performed at a scanning rate of 60 mV/min in the anodic direction.

Cylindrical-shaped AISI 316 specimens were used (height = 15 mm, diameter = 8 mm). Their chemical composition was C = 0.034%, Cr = 18.06%, Ni = 10.60%, Mo = 2.26%.

### 3.2. Corrosion Test Results and Evaluation

The plots of current density vs. potential, obtained through the procedure above, are reported in Figures 3, 4 and 5.

Figure 3 shows the curves measured in solutions containing phosphoric acid 28%  $P_2O_5$ , with  $H_2SO_4$  (2%), chlorides (0.1%) and ferric ions (0.5%) additions. It can be clearly seen that the chlorides cause an increase of the current density in the active range while no remarkable variations occur in the passive range. This means that the chlorides hinder the formation of a passivation oxide layer. On the other hand, once this oxide has developed, it is stable enough to protect stainless steel from corrosion.

Consequently, in order to offset the chloride effect, the oxidizing characteristic of the solution must be enhanced by adding substances capable of raising the potential.

Indeed, the addition of an oxidizing agent such as ferric ion results in

the disappearance of the current density peak in the active zone, thus helping the passivation of AISI 316.

The amount of ferric ions to be added depends, of course, on the chloride content; in experiments carried out with 0.1 % chlorides, the resulting minimum concentration of  $Fe^{3+}$  required was 0.5 %.

This picture is altered by the presence of fluorides (Figure 4). In this case the current density is remarkably higher also in the passive zone. As a consequence, the passivation oxide layer is shown to be unstable, and unable to protect the alloy.

This implies that moving the solution potential to the passive zone of AISI 316 is not sufficient to prevent corrosion.

Thus, the aggressive agent must be removed.

This result will be easily attained by complexing the fluoride ion, e.g. as fluosilicate, by means of adding reactive silica to the solution. This was verified by electrochemical measurements (Figure 4, for comparison).

These measurements were made with 0.5 %  $F^-$  and 0.30 %  $SiO_2$  corresponding to a weight ratio  $SiO_2/F = 0.60$ .

The contemporary presence of chlorides and fluorides results in a combination of the individual effects (Figure 5). Hence, oxidizing and complexing agents must be simultaneously present in order to prevent corrosion.

In the industrial practice, it is possible to reduce the corrosive effect of phosphoric acid in the presence of high concentrations of chlorides and fluorides by adding a raw material such as bentonite during the attack phase. This material contains silica and ferric ions, but also moderate amounts of aluminum and magnesium (Table 2) which can complex fluorides, even though not to the same extent as silica.

As far as corrosion is concerned, the addition of bentonite is required only for those phosphate rocks lacking sufficient amounts of iron and silica.

When the fluorine recycling process is employed, then the use of phosphate rock with a ratio of active  $SiO_2/F$  under 0.526 brings about a higher fluoride concentration during the attack phase. This results in a greater corrosion rate, according to the mechanism explained above.

The addition of bentonite lowers the concentration of free fluoride and greatly reduces the corrosive effects on equipment made of AISI 316, still in use in several existing plants.

The addition of bentonite is also beneficial to higher alloyed grades (ALLOY 20, SANICRO 28, etc.), although not so much as before, as phosphoric acid-induced corrosion is lower in this case.

Corrosion tests carried out on plant equipment confirm these findings (Table 1).

## INDUSTRIAL APPLICATIONS

### 1. Equipment for the recovery of fluorine

In the phosphoric acid plants the fluorine emissions occur in the attack and concentration sections as HF and  $\text{SiF}_4$  together with other gases and vapors. Thus it is necessary to purify the vapors of the pollutant elements which develop in these two sections of the plant before they are discharged outside the plant so as to comply with the regulations in force. These compounds are recovered through absorption in water.

The equipment utilized for scrubbing the fluorine is reported in literature by various authors (4) (7).

Usually the equipment is steel lined with ebonite or ALLOY 20 and can be with or without polyethylene or polypropylene packing.

On applying the recycle of fluorine in attack to an existing plant, it was found that the content of fluorine in the vapors, that develop in concentration, is considerably higher than without the fluorine recycle and the scrubber must operate at a higher load.

In the case of a new plant, the bigger load of fluorine necessitates a bigger scrubbing column in order to comply with the amounts allowed in the effluents.

The process design of the scrubbers is made according to the same methods usually applied (5) (6) (7); table 3 shows some typical operating parameters of the scrubber equipment.

Figure 6 gives mass transfer coefficients, vapor pressure and power consumptions.

In the case of an existing plant the performance of the existing scrubbers must be improved; in our case the fluorine content in the effluents remained the same by simply installing sprayers in appropriate positions.

In our towers, we worked with a gas capacity of  $50 \text{ kmoles/m}^2\text{h}$  and a flow of circulating liquid of  $20 \text{ kmoles/m}^2\text{h}$  obtaining 93-96 % scrubbing efficiency.

### 2. Description of the attack recycling scheme

The fluorine recycle process was applied to the Agrimont phosphoric acid plant in Porto Marghera, based on a conventional dihydrate process (Figure 7).

The scrubbing systems consist of spray towers, endowed with special pre-washing and spraying systems for the concentration section, and a Venturi scrubber for the attack section.

The fluorine content in the cooling air of the attack reactors and in the concentration vapors is absorbed in a solution of  $\text{H}_2\text{SiF}_6$  5-15 %.

The scrubber fluorine is collected in the tank D6.

The concentration of the solution is controlled through a densimeter and a level regulator.

All the scrubbed fluorine obtained in the attack and concentration sections is fed to the tank containing acid 22 %  $P_2O_5$  or is sent to filters, in the second washing step. From the tank containing acid 22 %  $P_2O_5$  the fluorine recycles to the attack tanks, carried by the same medium acid.

In the attack section a hopper with a weighing feeder for the bentonite or kieselguhr was installed in order to regulate, when required, the  $SiO_2/F$  ratio.

Therefore, it may be concluded that the installation of the fluorine recycle process in a phosphoric acid plant based on the classical di-hydrate process does not give any particular problem nor does it require large investments: indeed, the plant only requires some small modifications on the piping and the addition of equipment for feeding the bentonite or kieselguhr.

Due to the increased fluorine content of the gas, a performance control of the scrubbers is required; however, usually the existing equipment with small modifications is enough, even under the new conditions.

### 3. Operating Parameters

The operating conditions described below apply to the Porto Marghera production plant having a capacity of 180 t/d of  $P_2O_5$ .

Four different sets of conditions are considered :

Arrangement no. 1: Khouribga phosphate 70 BPL is used. No fluorine recycle.

Arrangement no. 2: Khouribga phosphate 70 BPL is used with fluorine recycle and bentonite addition so that the active  $SiO_2/F$  weight ratio equals 0.526.

Arrangement no. 3: Khouribga phosphate 70 BPL is used with fluorine recycle and kieselguhr addition so that the active  $SiO_2/F$  weight ratio equals 0.526.

Arrangement no. 4: Florida phosphate 70 BPL is used with fluorine recycle, without the addition of active  $SiO_2$ , since the silica content in phosphate is sufficient to ensure that the ratio is 0.526.

The characteristics of the raw materials are reported in Table 2.

Table 3 shows the amounts of raw materials actually consumed, the optimal operating conditions found for each arrangement, and the results obtained.

Table 4 shows the fluorine balance for each arrangement.

The residual fluorine in solution ( $H_2SiF_6$  plus HF) in the concentrated acid



is given in the diagram of Figure 8.

Figure 9 shows a plot of fluorine percentage in concentration vapors vs. acid concentration.

The following observations ensue from a critical examination of these tables and figures, and in short from other mass balance flows which are not detailed here :

- a) Reduction in the amount of  $H_2SO_4$  used varies between 2 and 6 % in comparison to the process with no recycle.

This reduction is due to :

- the type of phosphate rock used and, more precisely, ratio of active  $SiO_2 / F$  content in phosphate;
- the addition of active  $SiO_2$ , if the silica content in the phosphate rock is low;
- concentration of phosphoric acid produced. This directly affects the amount of  $H_2SiF_6$  evaporated and thus recycled.

- b) Fluorine content in diluted phosphoric acid (28-30 % wt  $P_2O_5$ ) depends on the type of phosphate rock and on the operating conditions used.

If Khouribga phosphate rock 70 BPL is used, fluorine content is 1,8 %, provided no additions of materials containing active  $SiO_2$  is made and can exceed 3.0 % if kieselguhr is employed.

- c) Fluorine content in gypsum does not depend on the amount of  $H_2SiF_6$  solution recycled to the attack, but on the active silica/fluorine ratio employed.

For gypsum obtained with the addition of kieselguhr or bentonite, it is possible to entirely remove the fluorine which was transformed into  $SiF_6^{2-}$  ion by washing the gypsum exhaustively. Whereas, for those gypsums which were obtained without any additions, and with phosphate rock having a low ratio of active silica/fluorine, the fluorine content is not substantially modified by washing exhaustively. In this case, the fluorine content is around 1-1.2 % of the gypsum mainly present in the form of unattacked  $CaF_2$ .

- d) Temperature and pressure being the same, the fluorine content in the concentrated phosphoric acid depends on the concentration and the arrangement employed (Figure 8).

At a concentration of 52 % of  $P_2O_5$ , fluorine content as  $H_2SiF_6$  is 0.95 % and, as HF is 0.15 % (Arrangement no. 3).

The F/ $SiO_2$  molar ratio in the gas phase ranges between 4.9 and 5.2 ( $HF/SiF_4 > 2$ ).

As shown in Figure 7, the fluorine content in the gas phase depends on the arrangement employed as well as on the  $P_2O_5$  concentration.

The presence of  $SiO_2$  in the condensate reveals that, by using the fluorine recycle process, only  $H_2SiF_6$  is brought back in the attack phase and not HF.

- e) The sedimentation sludge so obtained has a higher fluorine content than resulting from traditional processes which do not adopt the recycle of  $H_2SiF_6$ .  
If additives containing active silica, aluminum and iron are utilized, then the fluorine content in the sludge is even higher due to the presence of fluorine compounds having the isometric crystal structure of "ralstonite",  $NaMgAl_5F_{12}(OH)_6 \cdot 3H_2O$ , and various silicates. On the other hand the amount of sludge sedimented per unit of  $P_2O_5$  produced is reduced, as well as the amount of complex salts such as  $(Fe, Al)_3 KH_{14}(PO_4)_8 \cdot 4H_2O$ , etc.
- f) The concentration of  $H_2SiF_6$  that is recovered and recycled usually varies between 5 and 15 %.  
A higher concentration of  $H_2SiF_6$  in solution would be obtained if the water balance is too limited (using low concentration  $H_2SO_4$ , recycled water streams, etc.).  
Should the water balance be too limited it would be advisable to send the  $H_2SiF_6$  solution together with the wash water to the gypsum filter.  
On the other hand, if  $H_2SO_4$  is available at a higher concentration (e.g.  $H_2SO_4$  98 %) then  $H_2SiF_6$  can be recycled in a more diluted solution, with the consequent improvement of scrubbing efficiency.
- g) The total  $P_2O_5$  yield increases by at least one percent than that resulting from a process which does not utilize the recycle process. Indeed, by recovering the  $H_2SiF_6$  solution, all the phosphoric acid entrained by the vapors in the concentration unit can be recovered and reprocessed.
- h) The major economic benefits deriving from the use of the fluorine recycle process in phosphoric acid production, can be obtained with those phosphate rocks which do not require active silica-based additives for fluorine complexing.  
In such cases the variable cost of  $P_2O_5$  is reduced to a saving of 3 %.  
The phosphate rocks tested in phosphoric acid plants are the following: Khouribga 70-72 BPL; calcined Djebel-Onk 72 BPL; Jordan 73 BPL; Land Pebble 70 BPL; Negev-Zin 70 BPL; Taiba 80 BPL; Togo 80 BPL; Palfos 86 BPL.

#### REFERENCES

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- 2) G. Brusasco and R. Monaldi "Improvement of the Montedison Process for recycling hydrofluosilicic acid in simple phosphatic fertilizer plants", Presented at the IFA/CNCCC Technical Seminar held in Peking in 1983.
- 3) Sydberger T., Nordin S. "Corrosivity of Wet Process Phosphoric Acid", Corrosion, Vol. 34, n° 1 January 1978, 16-22.

- 4) P. Becker, Phosphates and Phosphoric Acid, Vol. 3, Marcel Dekker, New York, 1983.
- 5) Strauss W. "Industrial Gas Cleaning", 2<sup>nd</sup> Edition, Pergamon Press, 1975, pag. 114.
- 6) Lunde, K.E. Ind. Eng. Chem. 50, 293 (1985).
- 7) A. Hansen and R.S. Danos, Scrubber for phosphoric acid plants, CEP March, 1982.

Table 1 - Results of the tests of corrosion by immersion carried out in industrial plants (values expressed in mm/year)

Test No.	Material	Without Fluorine recycle	With fluorine recycle	
			without Bentonite	with Bentonite
1	AISI 316	1.58	3.83	N.E.**
	ALLOY 20	0.031	0,088	N.E.
	SANICRO 28	0.020	0.021	N.E.
2	AISI 316	0.10	0.93	N.E.
	ALLOY 20	0.031	0.037	N.E.
	SANICRO 28	0.019	0.023	N.E.
3 *	AISI 316	2.79	7,78	0.038
	ALLOY 20	0.031	0.43	0.015
	SANICRO 28	0.020	0.38	0.002

\* Phosphoric acid from Morocco phosphate rock having a weight ratio  $\text{SiO}_2/\text{F} = 0.2$ .

\*\* N.E. = not executed

Table 2 - Chemical characteristics of the raw materials employed

		Khouribga phosphatite rock 70 BPL	Land Pebble phosphatite rock 70 BPL	Kieselguhr	Bentonite
Moisture	% wt	1.10	1.40	6.80	8.40
P <sub>2</sub> O <sub>5</sub>	"	32.00	31.70	-	-
CaO	"	51.15	46.40	-	-
SO <sub>4</sub>	"	1.36	1.10	-	-
F	"	3.85	3.50	-	-
SiO <sub>2</sub> (total)	"	2.20	5.70	68.00	46.90
SiO <sub>2</sub> (active)	"	0.70	1.90	-	-
CO <sub>2</sub>	"	5.85	3.20	-	-
Al <sub>2</sub> O <sub>3</sub>	"	0.45	1.42	6.60	13.30
Fe <sub>2</sub> O <sub>3</sub>	"	0.20	1.00	4.30	13.60
MgO	"	0.40	0.49	-	7.30
Na <sub>2</sub> O	"	0.88	0.94	0.48	0.11
K <sub>2</sub> O	"	0.06	0.11	0.97	0.32
Organic matter, as C	"	0.20	0.30	-	-
Cl (from chlorides)	ppm	230	100	-	-
S (From sulphides)	"	120	80	-	-

TABLE 3: NTU Values for Typical Scrubbing Systems

Scrubber type	Speed of gas (m/sec)	Liters of water per m <sup>3</sup> effluent gas	NTU per equipment unit or meter of tower	Mass transfer kg F (At) <sup>-1</sup> (m <sup>3</sup> ) <sup>-1</sup> (hr) <sup>-1</sup>	Approximate power requirement in kWh for 100,000 m <sup>3</sup> and 1 transfer unit
Spray tower	0.25	1.7	0.55/m tower	315	4
	0.50	1.7	0.25/m tower	315	9
	1.0	1.7	0.13/m tower	315	18
Packed tower	0.45	1.6	0.9/m packing	1100	7
	0.95	1.6	0.5/m packing	1100	18
	1.90	1.6	0.35/m packing	1100	50
Spray cross-flow	1.9	5-6	0.12/m	600	50
Packed cross-flow	1.6-1.8	5-6	1.6-2.2/m packing	1400-1600	16-22
Venturi	40 (in throat)	1.5	1.6/unit	—	60
	50	1.7	2.0 unit	—	80
	60	0.5	2.4 unit	—	60
Cyclonic spray	0.7 (superficial velocity)	5	0.47-0.67	800-1000	60

Source : Pierre Becker "Phosphates and Phosphoric Acid" Marcel Dekker, New York, 1983, pag.351.

**Table 4 - Raw material consumptions and operating conditions**

	Unit of Measure	Arrangement 1 without fluorine recycle	Arrangement 2 with fluorine recycle plus bentonite	Arrangement 3 with fluorine recycle plus Kieselguhr	Arrangement 4 with fluorine recycle
<b><u>Raw Materials Consumptions</u></b>					
Phosphate rock type	-	Khouribga 70	Khouribga 70	Khouribga 70	Land Pebble 70
Phosphate rock consumption	t/t P <sub>2</sub> O <sub>5</sub> prod	3.29	3.25	3.25	3.24
H <sub>2</sub> SO <sub>4</sub> as 100%	"	2.79	2.69	2.66	2.58
H <sub>2</sub> SiF <sub>6</sub> as 100%	"	-	0.097	0.14	0.044
H <sub>2</sub> SiF <sub>6</sub> concentration	% wt	-	12	15.5	8.5
Kieselguhr	t/t P <sub>2</sub> O <sub>5</sub> prod	-	-	0.063	-
Bentonite	"	-	0.092	-	-
Montaline surfactant type	-	SP-CV/A1	SP-CV/A1	SP-CV/A1	SP-CV
Surfactant consumption	t/t P <sub>2</sub> O <sub>5</sub> prod	0.0005	0.0005	0.0005	0.0005
<b><u>Operating conditions</u></b>					
Phosphate residual at 100 mesh	% wt	40	40	40	45
Attack temperature	°C	78	78	78	80
Solid contents in the slurry	% wt	34	32	32	36
Free SO <sub>4</sub> <sup>2-</sup> in the slurry	g/dm <sup>3</sup>	22	22	20	32
Weak H <sub>3</sub> PO <sub>4</sub> concentration	% P <sub>2</sub> O <sub>5</sub>	28.5	28	28	28.5
H <sub>3</sub> PO <sub>4</sub> concentration	"	46	52	52	46
<b><u>Results</u></b>					
Total yield	%	95	96	96	96.5
Filtration rate	t P <sub>2</sub> O <sub>5</sub> /m <sup>2</sup> /d	10	12	11.5	12.0

Table 5 - Fluorine balance of streams entering and leaving the plant referred to 100 kg of fluorine fed with the phosphate rock

Incoming and outgoing streams	Arrangement 1	Arrangement 2	Arrangement 3	Arrangement 4
Phosphate rock	100	100	100	100
Gypsum	58.1	51.6	51.1	48.5
Attack vapors	4.1			
Sludge coming from diluted acid	6.3	9.3	9.8	8.8
Concentrated and decanted acid	16.5	15.0	17.6	18.5
Sludge from concentration	3.6	24.1	21.5	24.2
Vapors from concentration	11.4	0	0	0
(recycled)	-	(61.3)	(88.5)	(30.7)



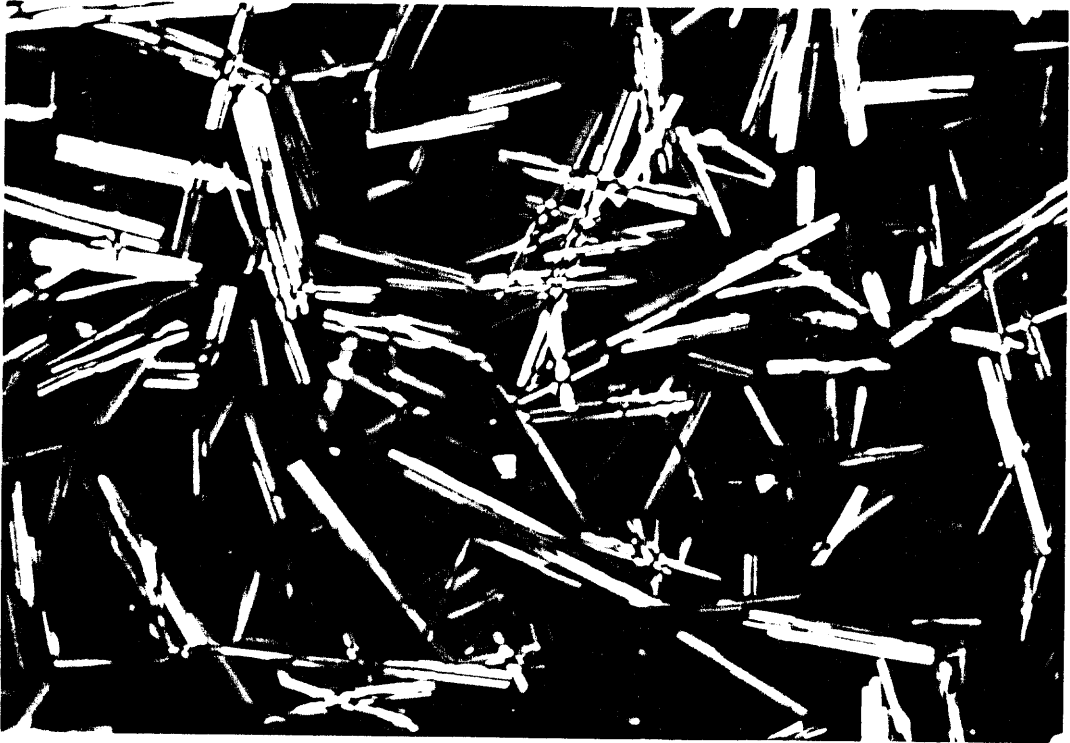


Figure 1 - Gypsum from Morocco phosphate rock without bentonite addition (100 x)

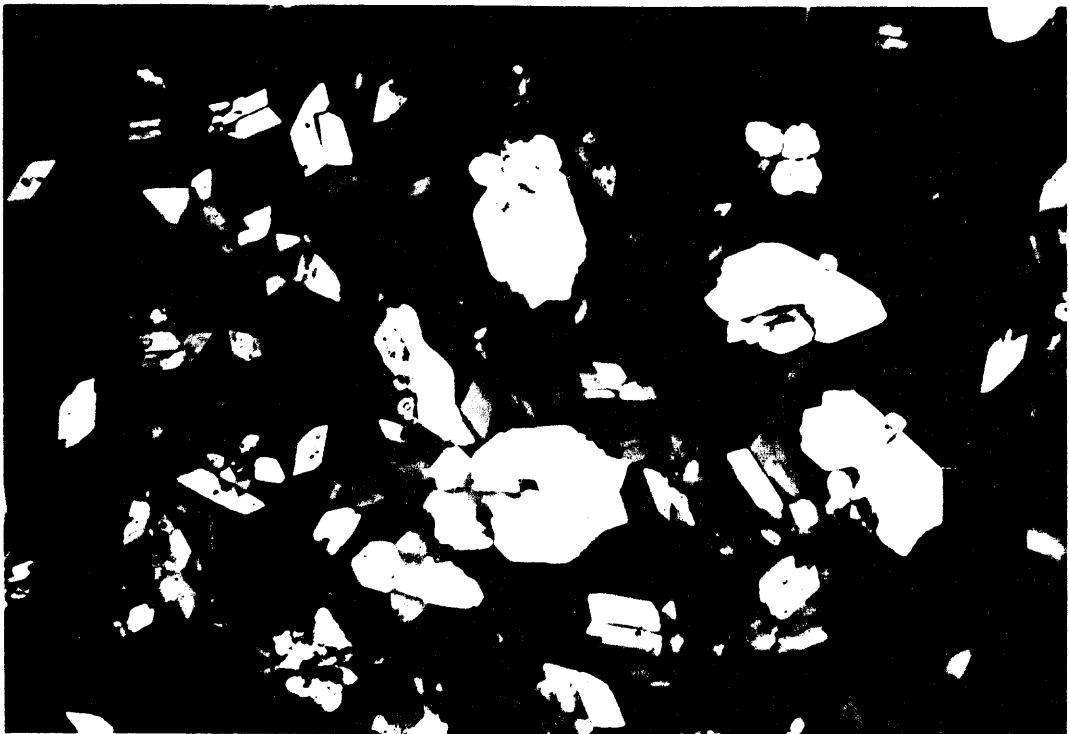


Figure 2 - Gypsum from Morocco phosphate rock with bentonite and surfactant materials addition (100 x)

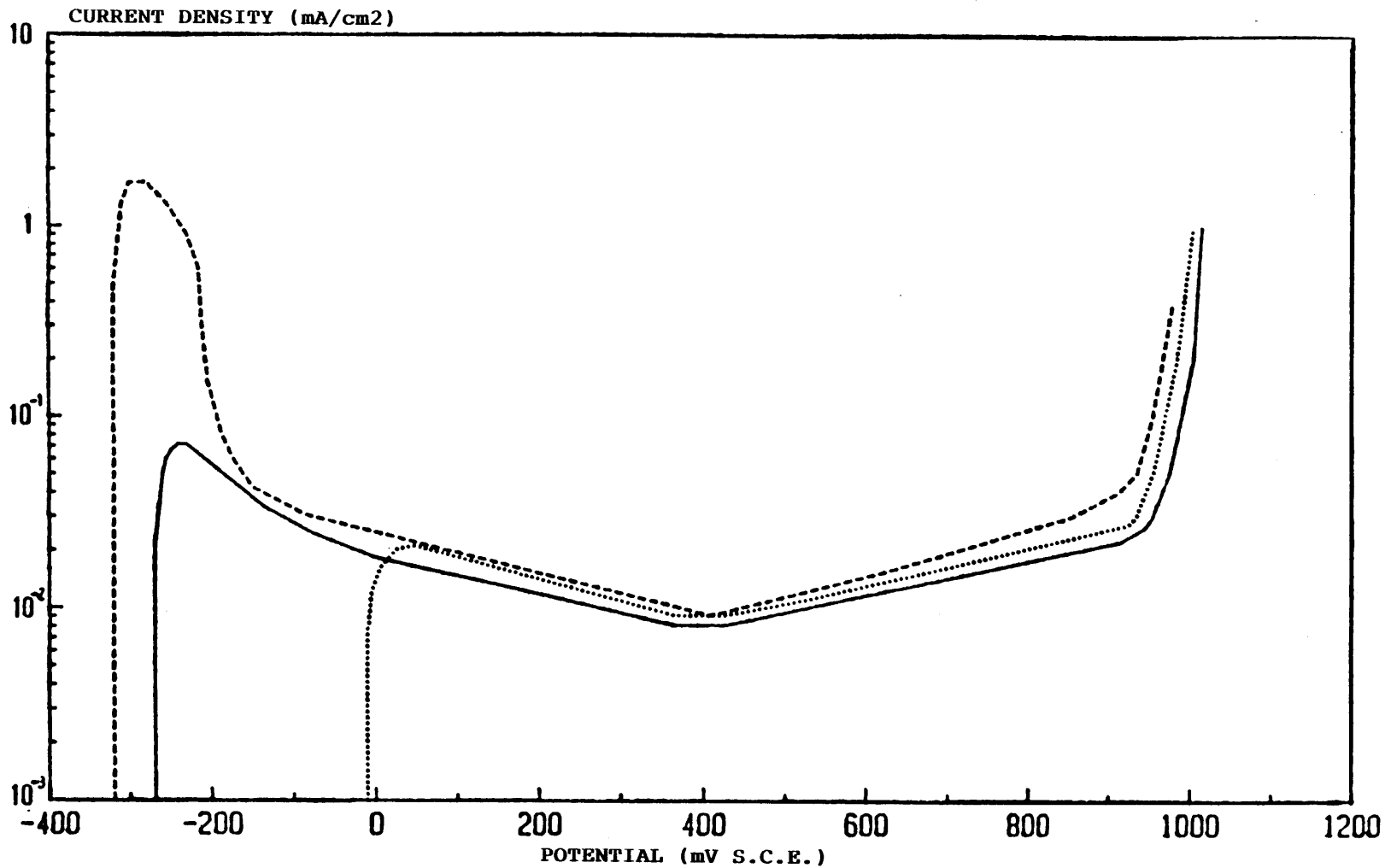


FIGURE 3 - Anodic polarization curve for AISI 316 in phosphoric acid containing  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{Fe}^{3+}$ .  $T = 80^\circ \text{C}$ .  
 — = 28% P2O5+2%  $\text{SO}_4^{2-}$ , ---- = 28% P2O5+2%  $\text{SO}_4^{2-}$ +0.1%  $\text{Cl}^-$ , ...=28% P2O5+2%  $\text{SO}_4^{2-}$ +0.1%  $\text{Cl}^-$ +0.5%  $\text{Fe}^{3+}$ .

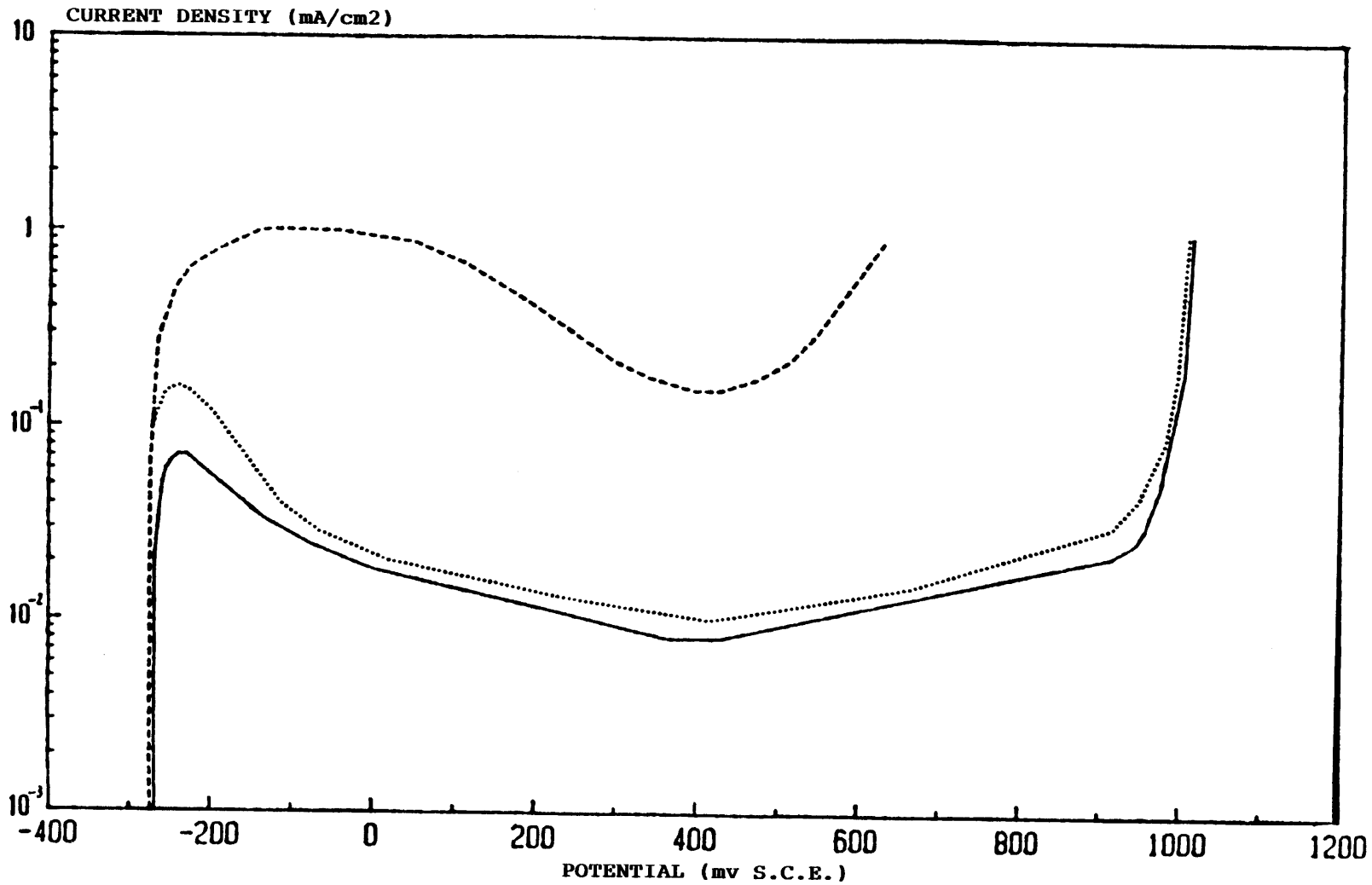


FIGURE 4 - Anodic polarization curve for AISI 316 in phosphoric acid containing  $\text{SO}_4^{2-}$ ,  $\text{F}^-$ ,  $\text{SiO}_2$ .  
 $T = 80^\circ \text{C}$ . — = 28%  $\text{P}_2\text{O}_5$ +2%  $\text{SO}_4^{2-}$ , --- = 28%  $\text{P}_2\text{O}_5$ +2%  $\text{SO}_4^{2-}$ +0.5%  $\text{F}^-$ , ... = 28%  $\text{P}_2\text{O}_5$ +2%  $\text{SO}_4^{2-}$ +0.5%  $\text{F}^-$ +0.3%  $\text{SiO}_2$ .

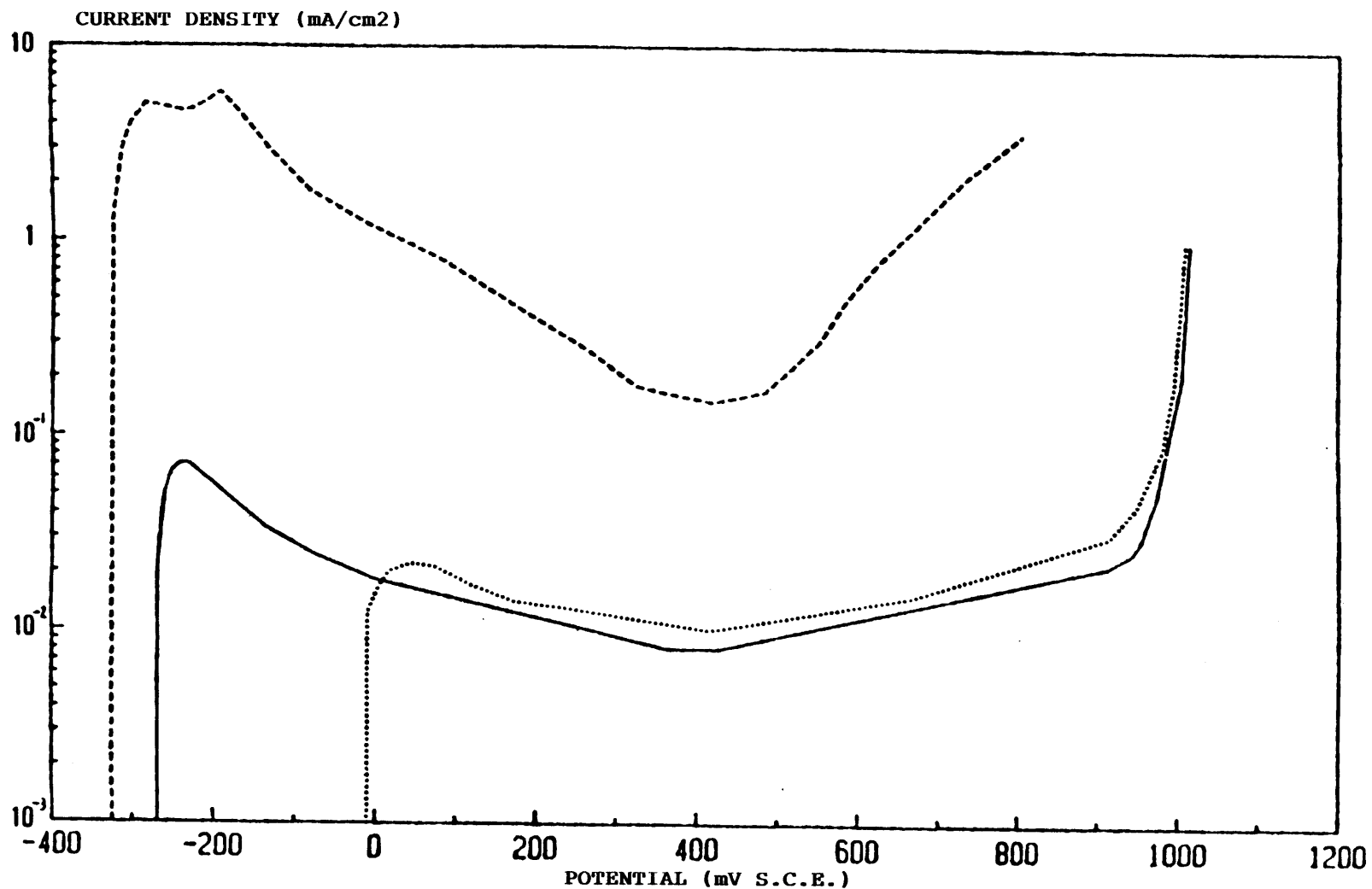


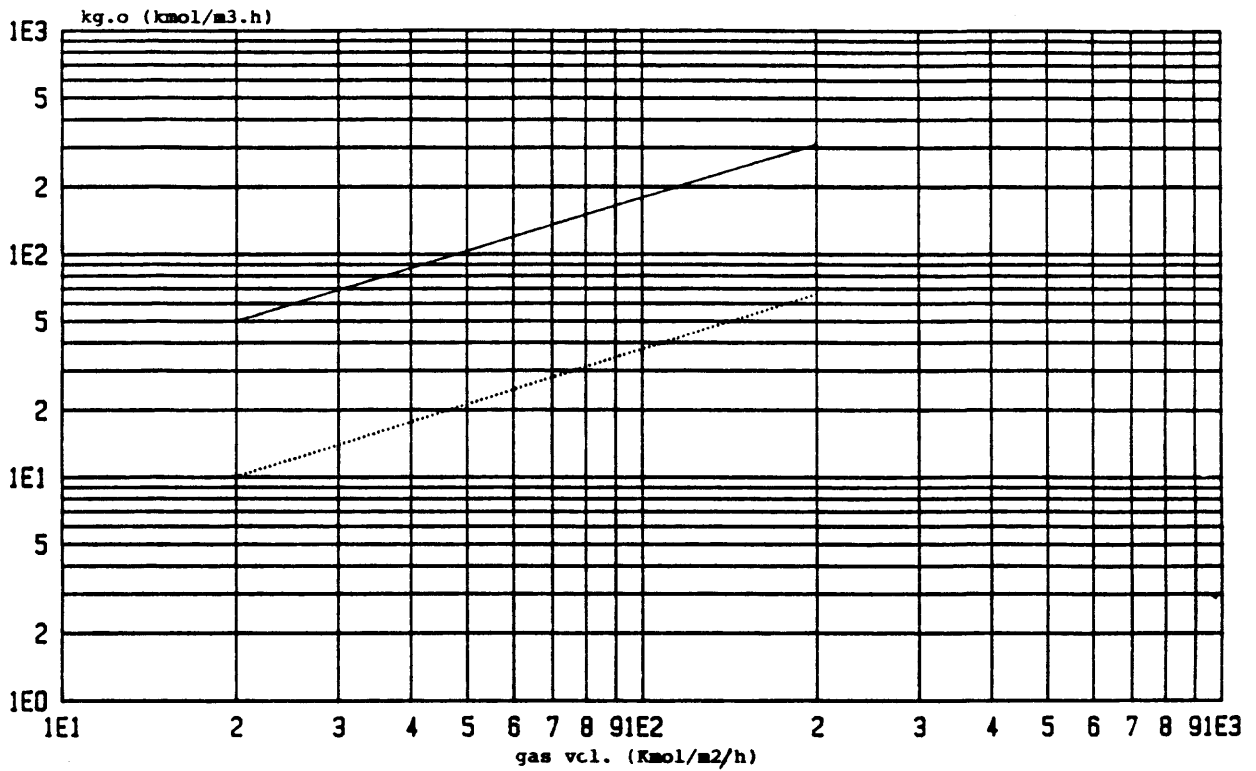
FIGURE 5 - Anodic polarization curve for AISI 316 in phosphoric acid containing  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{F}^-$ ,  $\text{Fe}^{3+}$ ,  $\text{SiO}_2$ .  $T = 80^\circ \text{C}$ . — = 28%  $\text{P}_2\text{O}_5$ +2%  $\text{SO}_4^{2-}$ , ---- = 28%  $\text{P}_2\text{O}_5$ +2%  $\text{SO}_4^{2-}$  +0.1%  $\text{Cl}^-$  +0.5%  $\text{F}^-$ , ... = 28%  $\text{P}_2\text{O}_5$ +2%  $\text{SO}_4^{2-}$  +0.1%  $\text{Cl}^-$  +0.5%  $\text{F}^-$  +0.5%  $\text{Fe}^{3+}$  +0.3%  $\text{SiO}_2$ .

FIGURE 6 (1)

MASS TRANSFER COEFFICIENT (1)

packed  
scrubber

spray  
scrubber



FLUORINE VAPOUR PRESSURE (1)  
ON H<sub>2</sub>SIF<sub>6</sub> SOLUTIONS

50 °C

65 °C

80 °C

F/H<sub>2</sub>O w. ratio in vapour phase

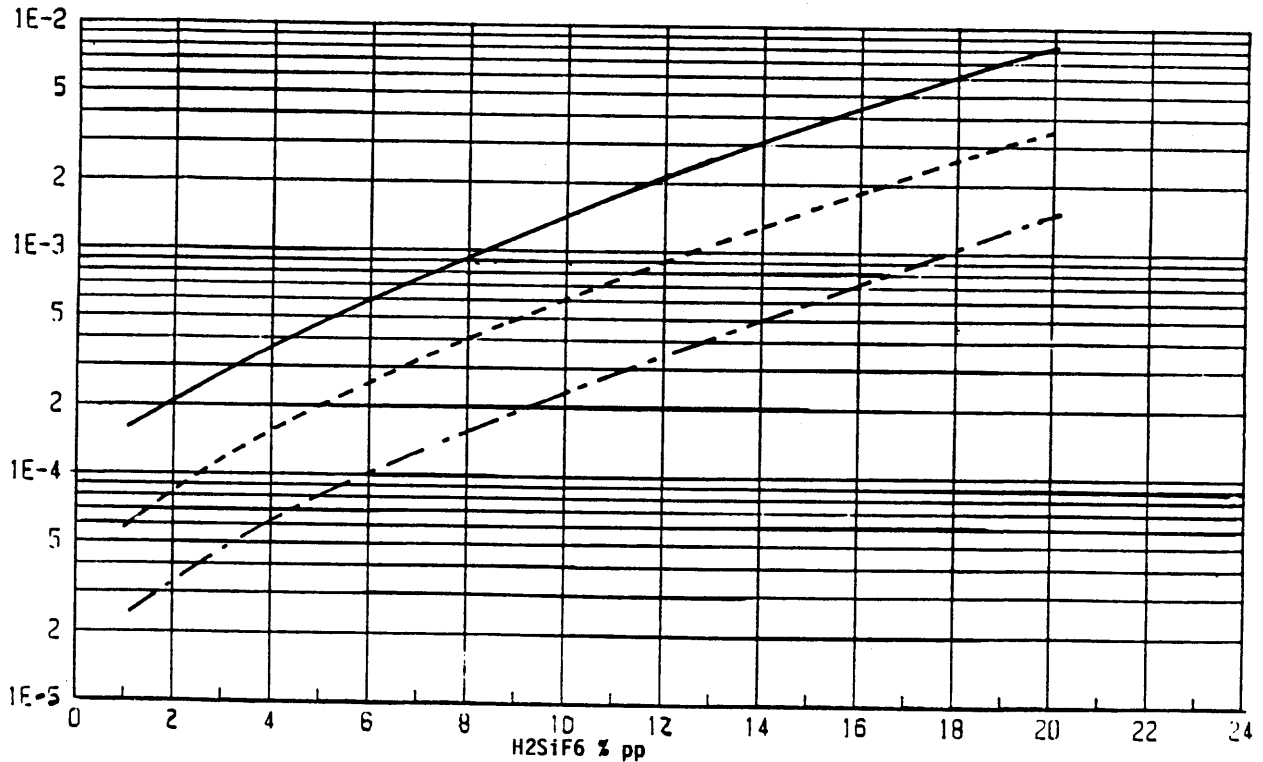
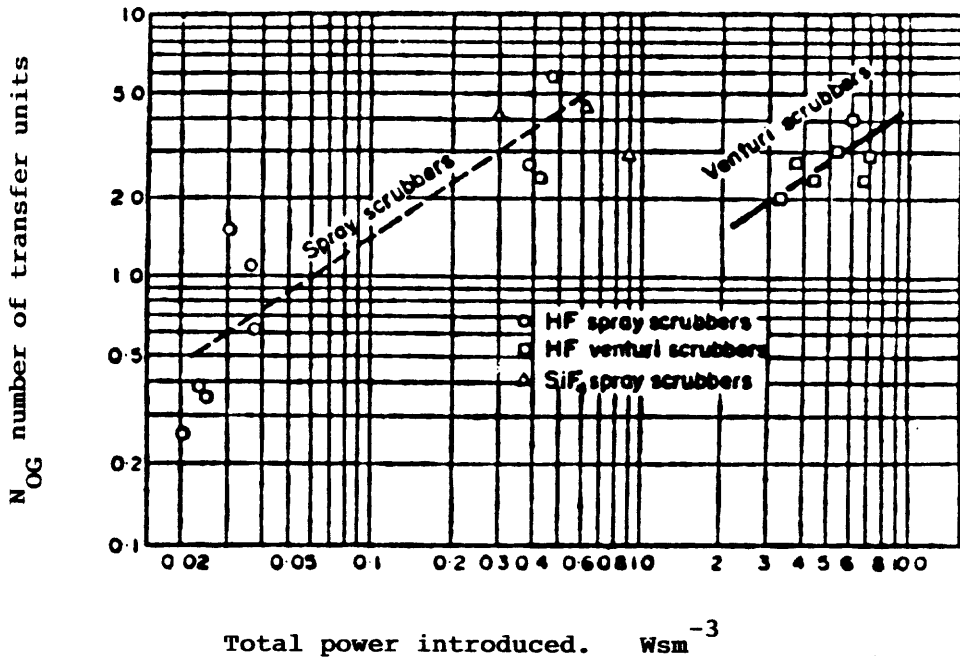


FIGURE 6 (2)

TOTAL POWER INTRODUCED VS. NTU (5,6)



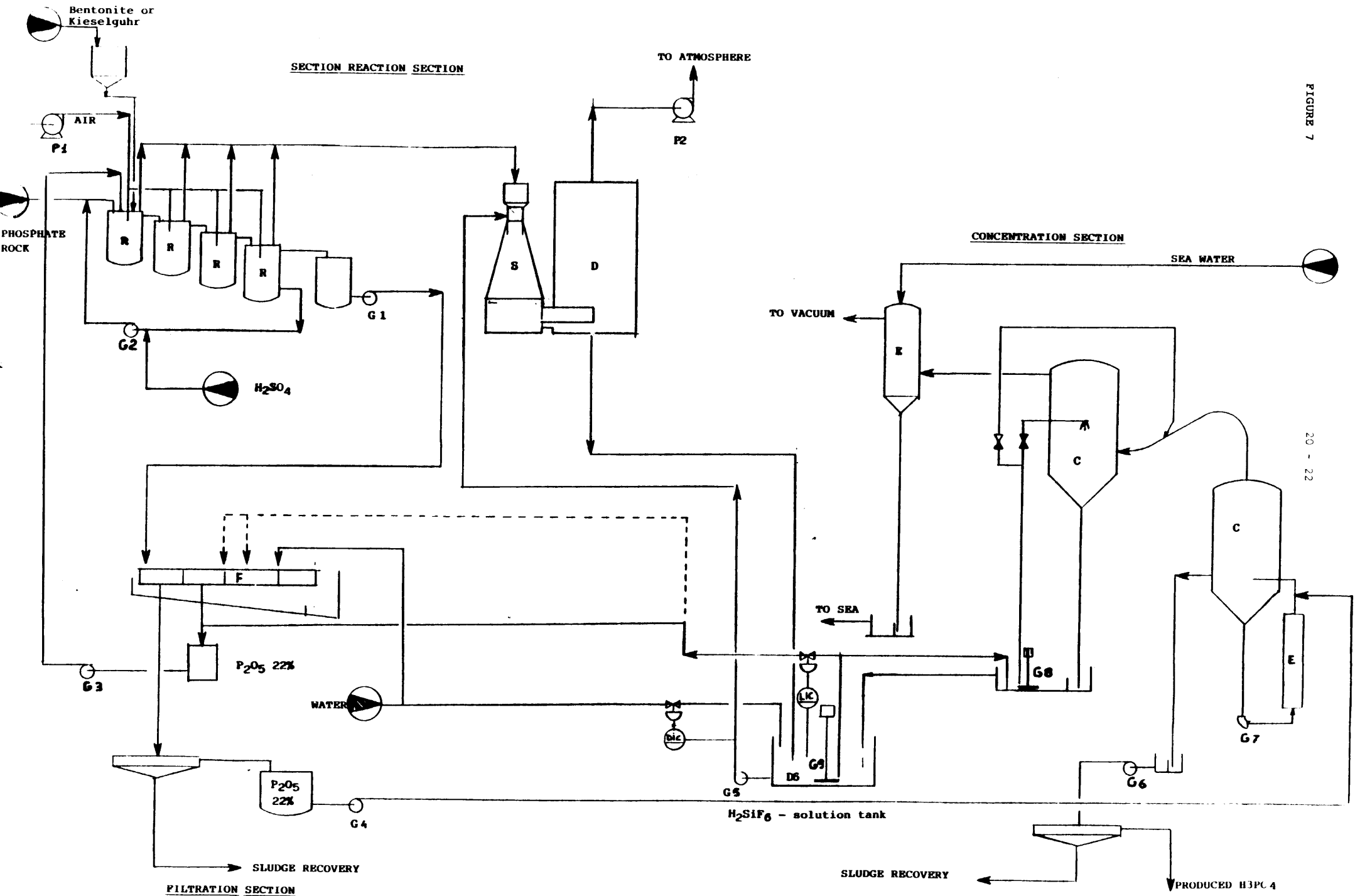


FIGURE 7

# FLUORINE IN THE CONCENTRATED AND SETTLED ACID

FIGURE 8

test 1

test 2

test 3

test 4

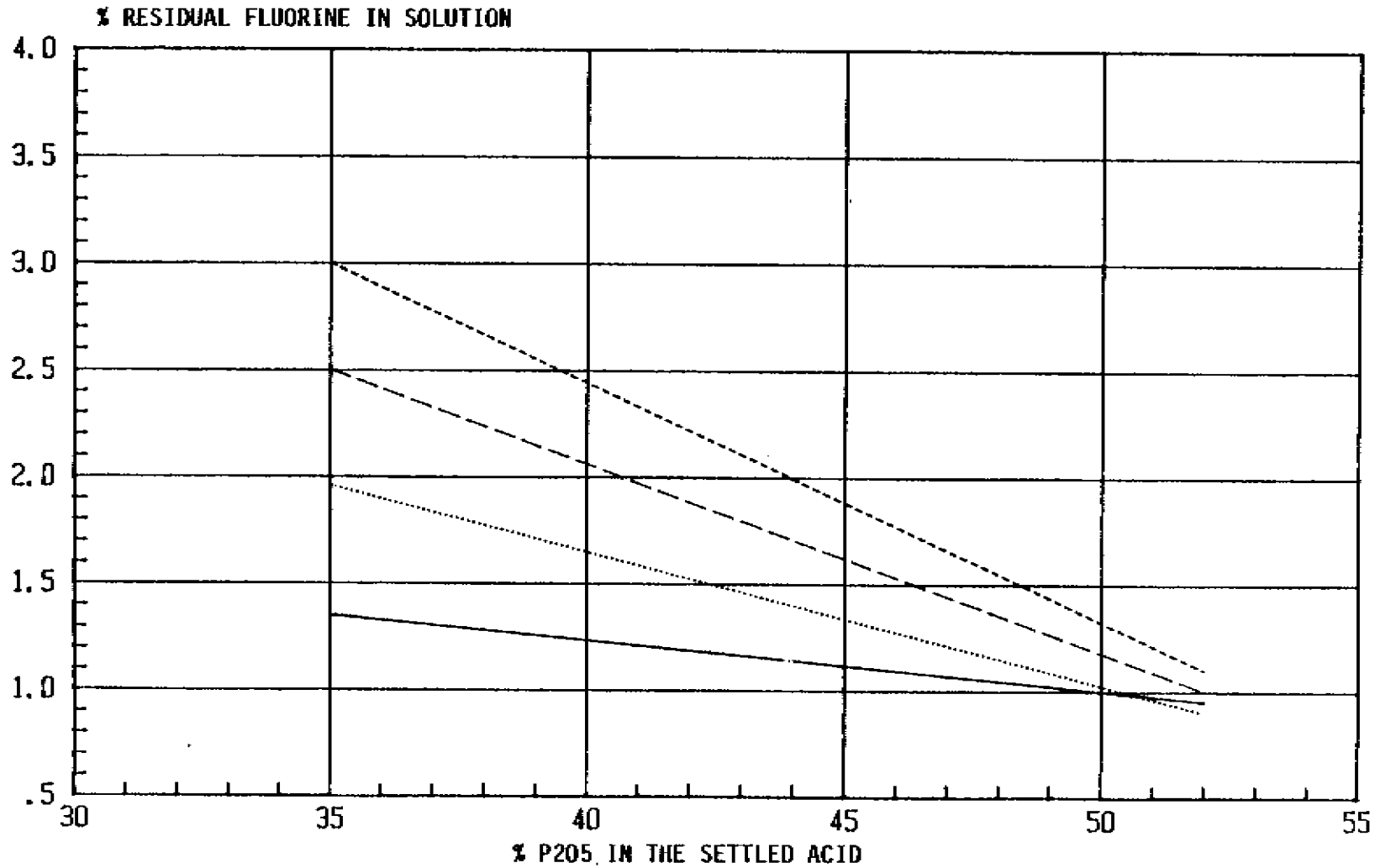
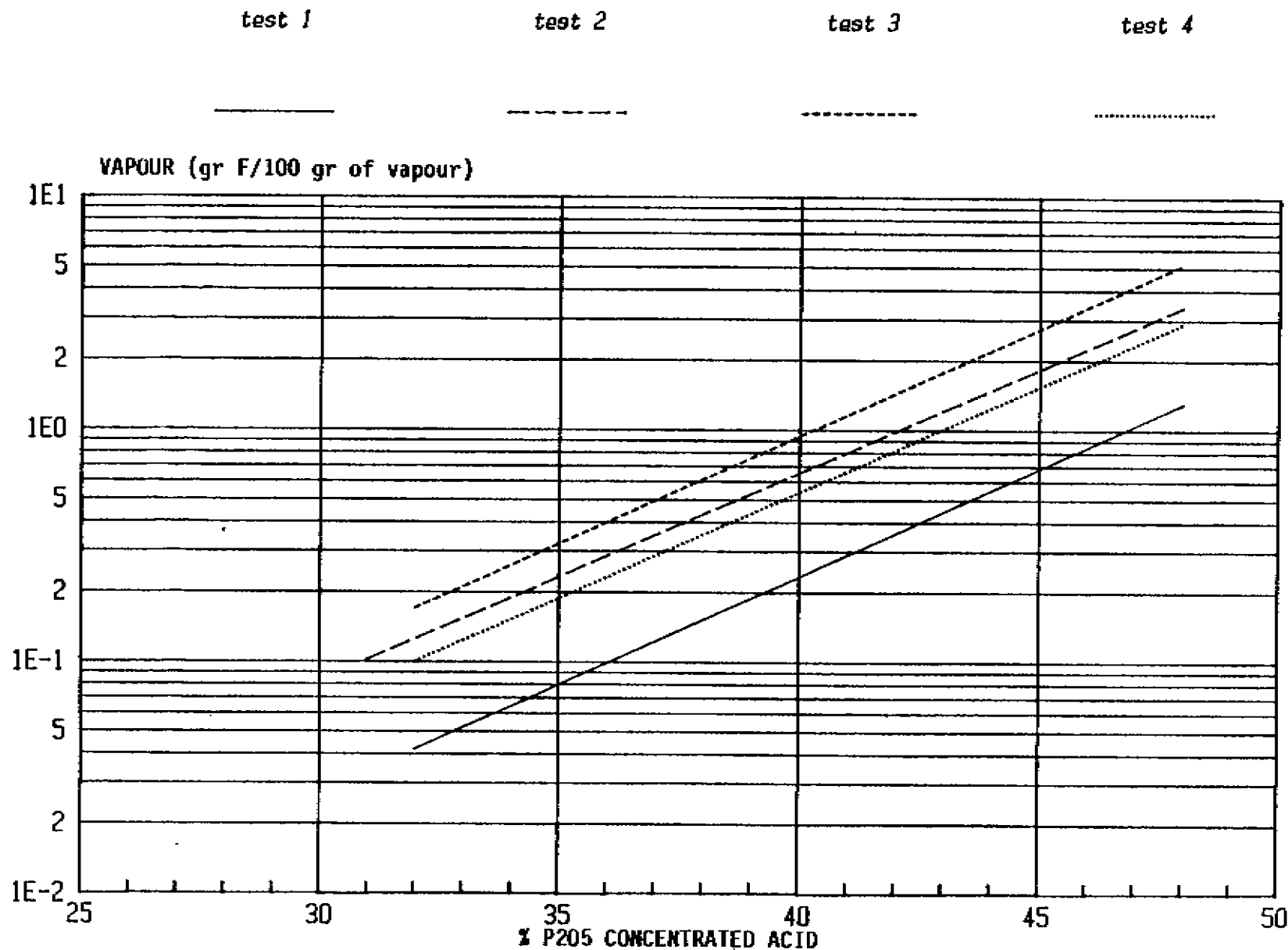




FIGURE 9

COMPOSITION OF VAPOUR AS A FUNCTION OF P2O5 CONTENT



TA/86/20 Fluorine recycle in phosphoric acid plants with the di-hydrate process by R. Monaldi, P. Barraco & E. Tomasello, Agrimont SpA, Italy

DISCUSSION : (Rapporteurs Messrs A. Bourgot & M. Sart, Prayon-Rupel, Belgium)

Q - Mr. G. MARROU, IFC/World Bank, United States

In phosphoric acid production, is fluorine recycling operating at Porto Marghera since 1977 and at Gela since 1981 continuously and for all the fluosilicic acid produced? If so, are consumption figures in table 4 the average industrial results over that period? If not, why?

A - At Porto Marghera fluorine recycling is done on an industrial scale. All fluosilicic acid is recycled.

Table 4 gives industrial results and not theoretical values.

The SiO<sub>2</sub>/F ratio is lower than 0.526.

Q - Mr. CHARFI, ICM, Tunisia

What is the method of analysis of active silica in bentonite and in phosphate?

A - The methods used for these determinations are very similar; in fact active silica is characterized by its solubilization; boron salts are used for the extraction to avoid silica losses due to possible reactions with fluorine resulting in the formation of SiF<sub>4</sub>. Solutions are analyzed by photometry and atomic absorption. We also conduct tests of first and second fusion using potassium and sodium carbonate with a recovery of about 99%.

The quartz content is determined by X ray diffraction. The total silica content is studied by X ray fluorescence.

Q - Mr. P. BECKER, COFAZ SA, France

- How did you prove CaSiF<sub>6</sub> formation in phosphoric acid reaction? (28-30% P<sub>2</sub>O<sub>5</sub>)?

- According to table 5, the fluorine evolved during concentration would be 3 to 9 times higher than without recycling. Is it so?

- What fluorine compound precipitates during concentration?

A - - CaSiF<sub>6</sub> was identified by gypsum washing tests. It is true that the amount of fluorine is good. There is indeed an increase of the values; that depends on the SiO<sub>2</sub>/F ratio in the reaction phase. That is why the final values are fairly high.

- Finally, concerning fluorine compounds, they are found in gypsum and, especially, in concentrated acid sludges.

Much work was done on the nature of these compounds: In particular Mr. Barbera worked on them; he was greatly assisted by radiography in defining the nature of precipitates themselves. The salts we identified are those mentioned on page 20-9: ralstonite and another salt containing potassium aluminium phosphate. In fact no calcium fluosilicate was found by radiography since it is not a crystalline product.

Q - Mr. P. TIBERGHIEU, Rhône Poulenc, France

- Fluorine balance in table 5

In the 2, 3 and 4 arrangements, can you indicate the amount of fluorine in the reaction gases (with  $H_2SiF_6$  recycling)?

- Chlorine balance

As you mention, chlorine follows fluorine in the recycling. Apparently, no chlorine containing complex precipitates: where does it go?

What is the chlorine content in the loop in the case of Khouribga (230 ppm Cl in the rock) and Zn (more than 500 ppm)?

- Does ralstonite precipitating during concentration result in quick scaling of the exchangers?

A - - Table 5 does not mention the F content at the exit of the reaction tank, since all this fluorine is returned to the reaction. We made many analyses during the operation of our plants; our statistics show that the amount of fluorine leaving the reactor is higher than without recycling: 7-8% of the initial fluorine leaves the plant.

- Chlorine does not produce complexes and it is not found in gypsum or in sludges. In phosphoric acid the Cl/P<sub>2</sub>O<sub>5</sub> ratio is the same as in rock phosphate: it is the same for fluorine recycling where the same Cl/P<sub>2</sub>O<sub>5</sub> ratio is to be found. Presently, phosphates used in our plants do not raise great problems with their fluorine content; sometimes there is a little more fluorine in one or the other, but not enough to promote corrosion in the pipes because of recycling.

- We do not have more scaling in the exchangers. At Gela, after five years' operation, we did not find serious scaling problems in the pipes.

Q - Mr. T.J. THOONEN, DSM, Netherlands

a) If the F content in acid of Khouribga 70 BPL (arrangement 2) goes up to 3%, it is our experience that all the Na<sub>2</sub>O precipitates as Na<sub>2</sub>SiF<sub>6</sub>.

b) Do you have a mass-balance on sodium?

c) Where does the precipitate of sodium silicofluoride settle in the plant and how do you deal with it?

A - It is clear that the presence of sodium results in the precipitation of  $\text{Na}_2\text{SiF}_6$ . Precipitation takes place during the reaction stage and depends on the sodium content of the phosphate. I did not bring all the balances with me, but a rapid calculation, for your typical example, may indicate the amount of fluorine trapped by sodium: in general there is a great amount of fluorine in the slurries: 30-35% fluorine is combined as  $\text{H}_2\text{SiF}_6$ , but it obviously depends on the amount of fluorine recycled and on the active  $\text{SiO}_2/\text{F}$  ratio at the reaction stage. We have about 160 kg fluorine and 30 kg sodium in the phosphate. After the reaction we have about 155 kg fluorine of which 2/3 remain; sodium precipitates with the gypsum and everything finally depends on its solubility. (It is not always possible to separate it from gypsum). Most of it precipitates in the different crystallization tanks. In addition, many reactions take place: cations, complex ions, as well as numerous salts and compounds not quoted in the paper.

Q - Mr. M. GAURON, COFAZ SA, France

- If I understood your presentation,  $\text{H}_2\text{SiF}_6$  recycling in the reactor promotes the precipitation of calcium fluosilicate in the gypsum. How do you explain that, in the example of table 5, there is less fluorine in the gypsum with recycling (arrangements 1 and 2)?

- Concerning the use of surfactants to improve the shape of gypsum, did you meet foaming problems with additives such as Montaline which you mention in table 4?

A - - We have several years of experience in that field in the reactions taking place in the attack stages involving  $\text{H}_2\text{SiF}_6$  and HF acids. In the case of a typical phosphate rock attack to produce SSP, fluorine recycling promotes the increase of the calcium fluoride content present: solubility is reduced. It is quite different when fluorine is recycled in phosphoric acid production. In that case, there are more cations and calcium so that reaction stops at a certain moment when  $\text{H}_2\text{SiF}_6$  is formed.

I do not think there is a contradiction in table 5, since silica reactivity plays an important role in determining the formation of  $\text{H}_2\text{SiF}_6$  in a final and non intermediate stage. We come back to the active  $\text{SiO}_2/\text{F}$  ratio.

- The foaming effect depends on certain organic substances, f.ex. those soluble in formic acid. We continue our research on this aspect: foaming effect + effect on crystal shape. But fluorine plays no role in the foaming effect.

Q - Mr. Y. LOUIZI, SIAPE, Tunisia

- A good gypsum crystallization improves the filtrability, i.e. the filtration efficiency; how do you explain that phenomenon?

- Concerning the overall plant efficiency, can you explain in detail the nature of the losses (co-crystallized, unreacted, soluble) in comparison with the reaction without fluorine recovery?

- You use surfactants, how much per ton P<sub>2</sub>O<sub>5</sub> produced? What is their effect on filtration and their influence of fertilizer production?

- What is the fluorine content of the product acid?

- Did you try Gafsa phosphate with fluorine recycling?

A - - The appropriate active SiO<sub>2</sub>/F stoichiometric ratio results in an improved shape as was shown on some slides: we always adjust this ratio which is very important to maintain the plant operational parameters at a constant level; this enables to maintain the filtrability at about 20%. Of course you need more monitoring and control to improve gypsum filtrability.

- The efficiency of our plant at Porto Marghera increased by about 1% and its capacity was improved thanks to other improvements in the control of the process, such as a continuous control of sulphate in the pulp. Sometimes it was possible to reach + 20%.

- I may not have understood well your last question but there is no influence of fluorine on NPK fertilizers since the F content of phosphoric acid remains practically the same.

Q - Mr. B.T. CROZIER, Norsk Hydro Fertilizers Limited, United Kingdom

Does the recycling of fluorine cause an increase in fluorine level in the product acid? And if so, does this increase fluorine evolution in the downstream plant for example DAP or TSP?

A - The increase in the F content in the product acid is negligible when the concentration exceeds 52% P<sub>2</sub>O<sub>5</sub> (see fig. 8). Thus, there is no noticeable effect in the downstream processes.

Q - Mr. P.T. LAMMI, Kemira Oy, Finland

How much does the recycling of H<sub>2</sub>SiF<sub>6</sub> back to the process increase the F-emissions from the waste gypsum area and the water lagoons?

A - The fluorine content in the waste gypsum is even below standard value when H<sub>2</sub>SiF<sub>6</sub> is recycled (see table 5). Thus, there is no ecological problem in the gypsum pond.

Q - Mr. A. EL SAYED, CMRDI, Egypt

1. Does the increase of H<sub>2</sub>SiF<sub>6</sub> concentration and its salts lead to the increase of sodium and potassium fluosilicate hydrolysis during the gypsum washing stage?

2. To what do you attribute the modification of gypsum crystals when you added bentonite and surfactant?

3. What is the type of gypsum shape produced after addition of Kieselguhr?

- Q - 1. During the gypsum washing stage, the dissolved fluosilicates content increases. If the gypsum washing is carried up to neutrality, all the sodium and potassium fluosilicate goes into water solution.
2. The addition of bentonite up to a ratio  $\text{SiO}_2/\text{F}$  of 0.526 eliminates the presence of fluoride ion, that has a harmful effect on the crystal growth along z-axis. The addition of surfactant eliminates negative effect of the organic substances on the crystal morphology.
3. The kieselguhr has the same effect as bentonite; the gypsum shape was shown in slide 5.

Q - Mr. M. BARLOY, SCPA, France

1. Putting together the various information, it seems that during the reaction, the recycled  $\text{H}_2\text{SiF}_6$  is converted to  $\text{CaSiF}_6$ , which would end not in the gypsum, but in the acid and would precipitate in that form or else in diluted acid and concentrated acids. Is it true? In that case, what happens with acid sludges?
2. You say that the addition of bentonite is necessary only for phosphates containing too little iron and silica. Can you indicate the maximum contents in these elements to avoid corrosion?

- A - 1.  $\text{CaSiF}_6 \cdot 2\text{H}_2\text{O}$  forms in the attack reactors. This salt is recovered both in gypsum and in diluted phosphoric acid in connection with the streams flows sent to the filter. A last fluorine increases in concentrated acid decantation sludges; that anyway can be processed as usual.
2. The amounts of silica and iron necessary to prevent corrosion are related respectively to the fluorides and chlorides content in the phosphate rock. As far as silica is concerned, the stoichiometric rate ratio  $\text{SiO}_2/\text{F} = 0.526$  must be respected. On the other hand, the minimum iron level must be defined each time by potential measurements. However interaction between chlorides and fluorides must be considered and it can be estimated and controlled only by experimental test.