

PHOSPHATE ROCK TECHNOLOGICAL AND ECONOMICAL CLASSIFICATION

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 **AGRIMONT**

MONTEDISON GROUP

1. INTRODUCTION

Montedison is a holding company composed of over 140 consolidated companies. Montedison is currently ranked twentieth among the world's chemical producers, with sales in excess of 7 billion dollars per year.

Fertilizer production is made by two companies within the Montedison group:

- Agrimont, based in Italy
- Conserv, based in the U.S.A. (Nichols, Florida)

Agrimont's annual production is:

- 1.6 million tons of nitrogen fertilizers
- 0.4 million tons of phosphatic fertilizers
- 1.1 million tons of complex fertilizers (NPK)

Conserv's annual production is 0.5 million tons of DAP

Montedison does not operate phosphate rock mines and one of the criteria for economic success is the ability to buy rock at a better price, through a high degree of flexibility in its final use. For that reason we have been compelled to improve our criteria for rock evaluation. This is required to give our purchasing department all the elements necessary to select from alternatives offered on the international market. The production department also requires these elements for a quick change of operations in production plants, storage, transport etc.

The focal point in the process of collecting all the information is the Research Center where phosphate rock is tested and data sheets are prepared. More than 90 data sheets are presently available, reflecting the variability of the material offered on the market (5), (6). About 400 lb of rock are required to complete a test.

An example of a data sheet is shown in the attachment. When the industrial production summary is available, a new sheet is added to compare the evaluated parameters with the real situation.

In this paper, some tests currently carried out in the Research Center are described.

1. GRINDING

Our experience is limited to dry rock. In Italy, rock is transported by ship and conversion to wet rock grinding is not economically justified. The grinding mills are of roller type. In Nichols, Florida, the Conserv plant is still operated with a rock dryer and the system includes two ball mills.

The evaluation of the industrial mill's rate is made by the following simple equation:

$$Q = M_c * K_f * K_r$$

in which:

Q is the grinding capacity

M_c is a mill constant

K_f and K_r are constants for the ground material.

In a small laboratory mill, with a charge volume of about 2 lb, we compare the different rocks through an evaluation of the rock constants.

Precision is not very good, but sufficient, because the mills never limit the rate of the plants. For example; in the passage from Moroccan to Negev rock, an increase in rate was calculated at a value of 10%. The actual rate increased at a value of 15%, both in the phosphoric acid plant and in the superphosphate plant (complex fertilizers with nitric acid attack don't require grinding). Similar differences were found with other changes in the type of rock used.

2. ACID ATTACK

It is well known that rocks have a varying reactivity, according to their origin. This difference in reactivity has often been claimed to explain the different performances of rocks, but it is not clear if this reactivity is a favorable property or not. The problems related to the gypsum coating of rock particles during the sulfuric acid attack are well described by Becker (1).

We have decided to quantify the reactivity, measuring the reaction rate in conditions in which the gypsum coating doesn't have any effect. Also this measurement is very cheap to make.

The measurement is based on the theoretical basis of the solid-liquid reactions. When the mass transfer coefficient is greater than the kinetics constant the reaction rate can be described by the following equation:

The single superphosphate is a product surviving in Italy and in other countries in which the transportation costs are relatively low (it is a low grade product with 18% P₂O₅) and cheap sulfuric acid is available (spent acid). A batch reactor is used in which the reaction mass is allowed to become solid. After 30 minutes, the reactor is opened and the product is judged with regard to stickiness and friability. This is useful to evaluate the transport and manipulation characteristics in the granulation plant. One sample of the product is stored in an oven and an analysis is done at fixed intervals. This is required because, in the industrial plant, the superphosphate powder is aged before granulation.

We produce NPK fertilizers with a mixed acids rock attack without calcium separation. In the Research Center, we have a small granulation plant with a capacity of about 30 Kg/h of finished product (drum granulation). Usually we don't use this plant to test rocks because the influence of rock on the operations of a granulation plant is not important. We use the granulation plant to study the influence of various parameters on quality and to make large samples of product for agronomic tests or commercial reasons. To evaluate the rock with respect to the NPK production we use a batch test to quantify the antifoaming agent consumption and the nitric acid losses due to the organic content in the rock. A complete chemical analysis is made after the ammoniated slurry is dried in the oven.

3. GRADES AND INSOLUBLE P₂O₅

The influence of rock impurities on DAP grade is well known and our experience is in agreement with the most recent papers (3) (4).

The problems in NPK production are different from the problems in DAP production. Rock attack is made with mixed acids (nitric, sulfuric, phosphoric) and all the rock constituents remain in the finished product (beside CO₂). Increasing the rock P₂O₅ content decreased the rate of phosphoric acid which is an expensive source of P₂O₅. Our production plants are equipped with automatic analyzers, giving a complete analysis every 2 hours (nitric and ammoniacal nitrogen, P₂O₅, K₂O) to correct the rate of the feeds and maintain the grade at the right value and the costs at the minimum value.

Also the insoluble P₂O₅ formation in DAP is widely discussed in technical literature. Our experience can be summarized in the following way:

- In the liquid neutralization step insoluble P₂O₅ appears only if the long residence time permits the growth of well

shaped crystals. The main impurity involved is iron giving insoluble phosphates at low mole ratios. In figure 2, the influence of mole ratio and residence time is shown for a particular phosphoric acid. Insoluble P2O5 can be found in the mole ratio range of 0.5 to 1.0 when the residence time is greater than 1 hour. Also the water content was found to influence the insoluble P2O5 formation.

- At high mole ratio, the insoluble P2O5 has been found to increase with the increase of magnesium content and fluorine has a small beneficial effect. In figure 3 the insoluble P2O5 is diagrammed toward the magnesium content of the DAP at three fluorine contents of the DAP. The diagram has been obtained at the Conserv Co. with the daily analysis covering about two years of DAP production with various rock type feeds.
- In NPK production insoluble P2O5 is due only to tricalcium phosphate when the salt is formed in the liquid phase (long residence times) also at a mole ratio slightly above the mole ratio value 1.1. Some of the ammonia is added in the granulator where insoluble formation never occurs.

4. CORROSION

The use of rock of various origins obliges us to remember the good rules in the corrosion field which at present is well documented thanks to many publications in recent years.

We follow the guidelines to find a chemical correction when chemical analysis of the rock reveals an abnormality. Corrosion problems originating from the rock are present mainly in the phosphoric acid production. In this plant the high acidity can trigger the corrosion activity on metals in certain conditions:

- High chlorine content (Middle East rocks and Togo rock);
- Presence of fluorine not bound to silica (North Africa rocks);
- Erosion from quartz sand (Florida rock).

Usually the rock analysis permits us to calculate the necessary amount of chemicals to feed in order to correct the corrosion activity. If the chlorine content has a greater value than 200 or 300 ppm an oxidizing substance is useful. The effect of a particular oxidizing substance (trivalent iron) is shown in the polarographic diagram of figure 4. Small iron feeds increase the corrosion activity until a critical concentration point is reached at which the corrosion rate is decreased about five times. In this case iron shifted the electrochemical potential

in this passive field. Also nitric acid has been used as an oxidizing substance but it cannot be increased to a high concentration because of problems related to the volatility.

When the soluble silica is not sufficient to bind fluorine some corrosion problems originate from the hydrofluoric acid formed instead of fluosilicic acid. Of course the amount of soluble silica must be specified in the chemical analysis instead of the normal total silica.

Corrosion rates can be estimated calculating the fluorides not bound with soluble silica and using experimental diagrams of which an example is shown in figure 5. Silica is not the only substance inhibiting fluorides. In figure 6 the effectiveness of aluminum is compared with the effectiveness of silica. Usually with rocks such as Negev, we use a feed of bentonite bringing iron to balance chlorine and silica plus aluminum to balance the fluorine corrosion activity.

The corrosion test is performed during the phosphoric acid production test. The small plant mixers are weighted and the obtained corrosion values are compared with the expected values.

References

- 1 - P. Becker. Phosphates and phosphoric acid
- 2 - A. Charfi. Study of the reactivity of the "Washed Metlaoui" phosphate. IFA Technical Conference 1986 (Tunisia)
- 3 - J.A. Hallworth. Influence des impuretes du phosphate sur le titre de l' engrais final. ISMA Congress Technique 1980 (Autriche)
- 4 - M.M. Handley. Effects of impurities on production of diammonium phosphate. IFA Technical Conference 1984 (France)
- 5 - R. Monaldi. ISMA Technical Conference, Orlando 1978
- 6 - A. Barbera. ISMA Technical Conference, Vienna 1980

Reactivity of different rocks

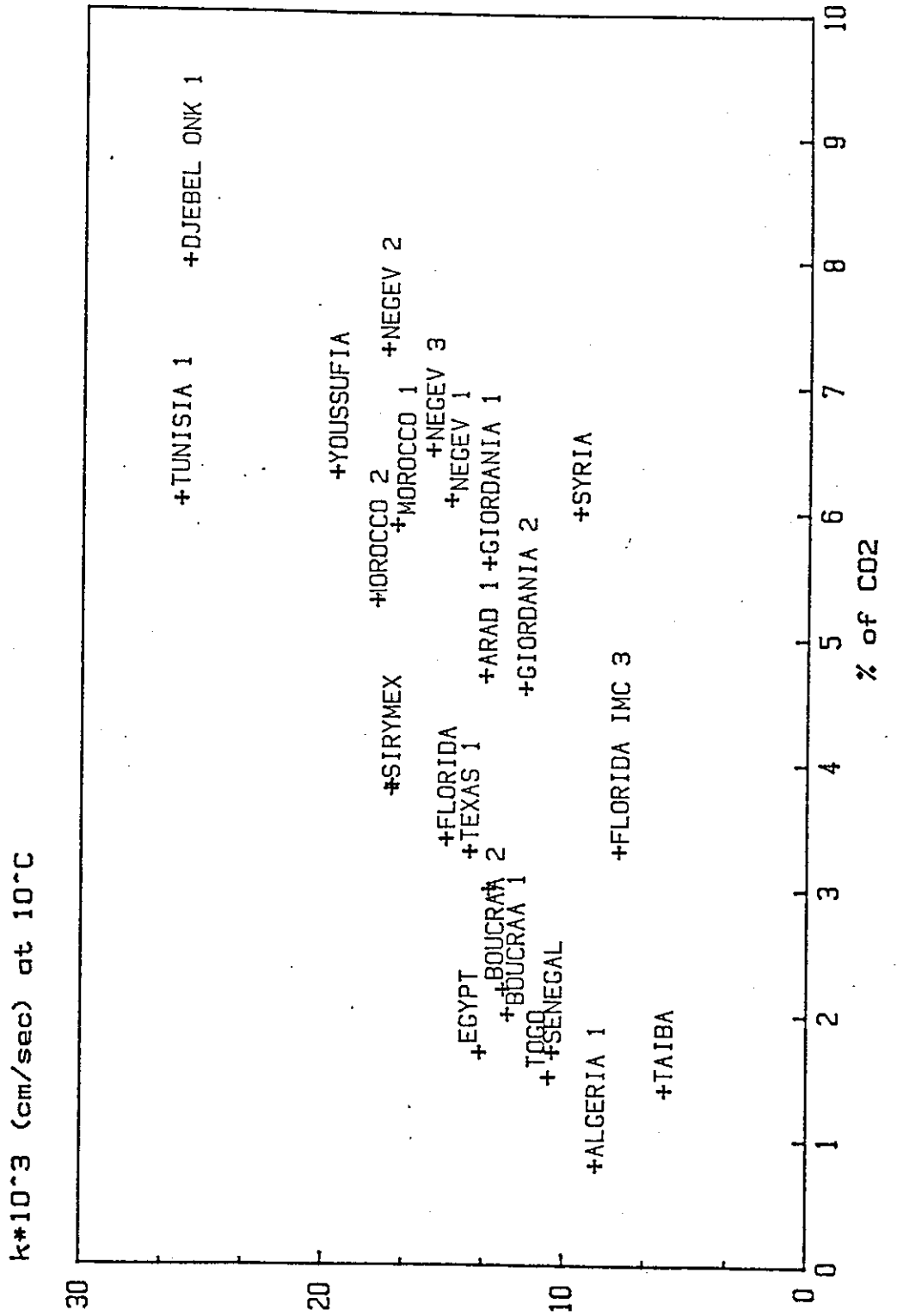


FIGURE 1

INSOLUBLE P205 VS. MOLE RATIO

at different times in liquid

RETENT. TIME
6 HOURS

RETENT. TIME
2 HOURS

RETENT. TIME
0.5 HOURS

INSOLUBLE P205 ON TOTAL P205 %

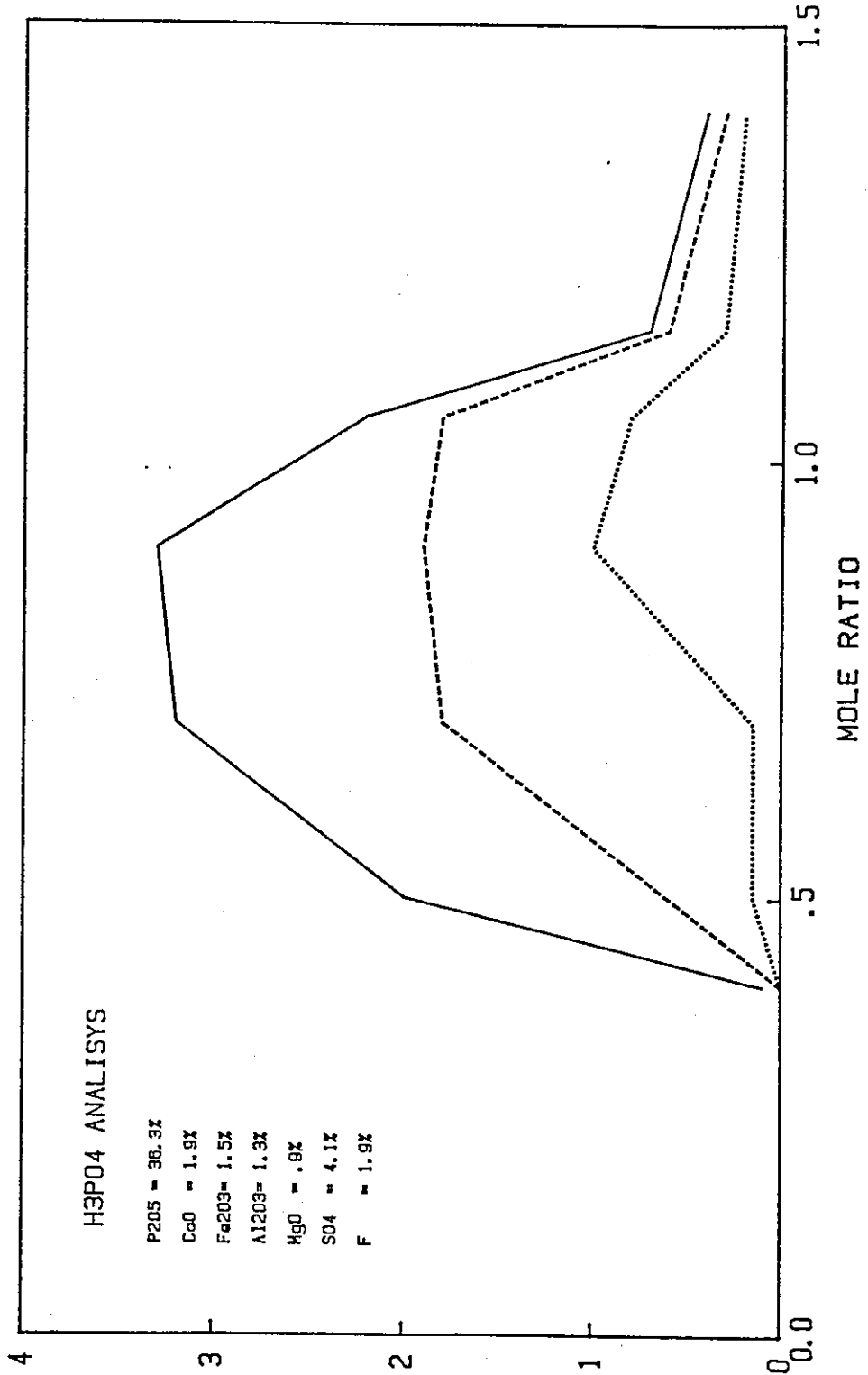


FIGURE 2

P205 LOSSES IN DAP VS. MgO AND FLUORINE CONTENT

MEDIUM FLUORINE LOW FLUORINE HIGH FLUORINE

INSOLUBLE P205 ON TOTAL P205 %

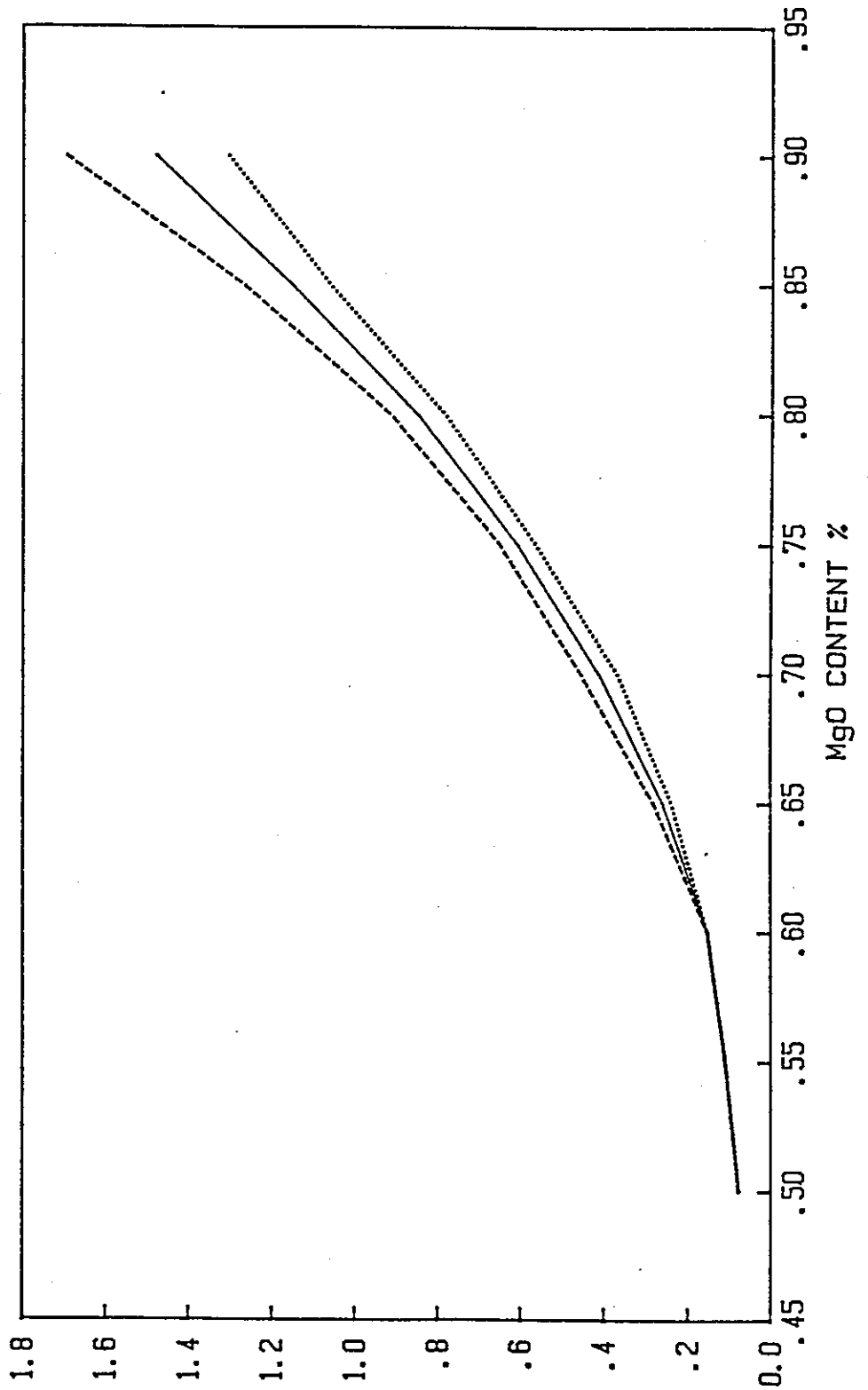


FIGURE 3

Polarization line for AISI 316 in H3PO4 with 5000 ppm Cl

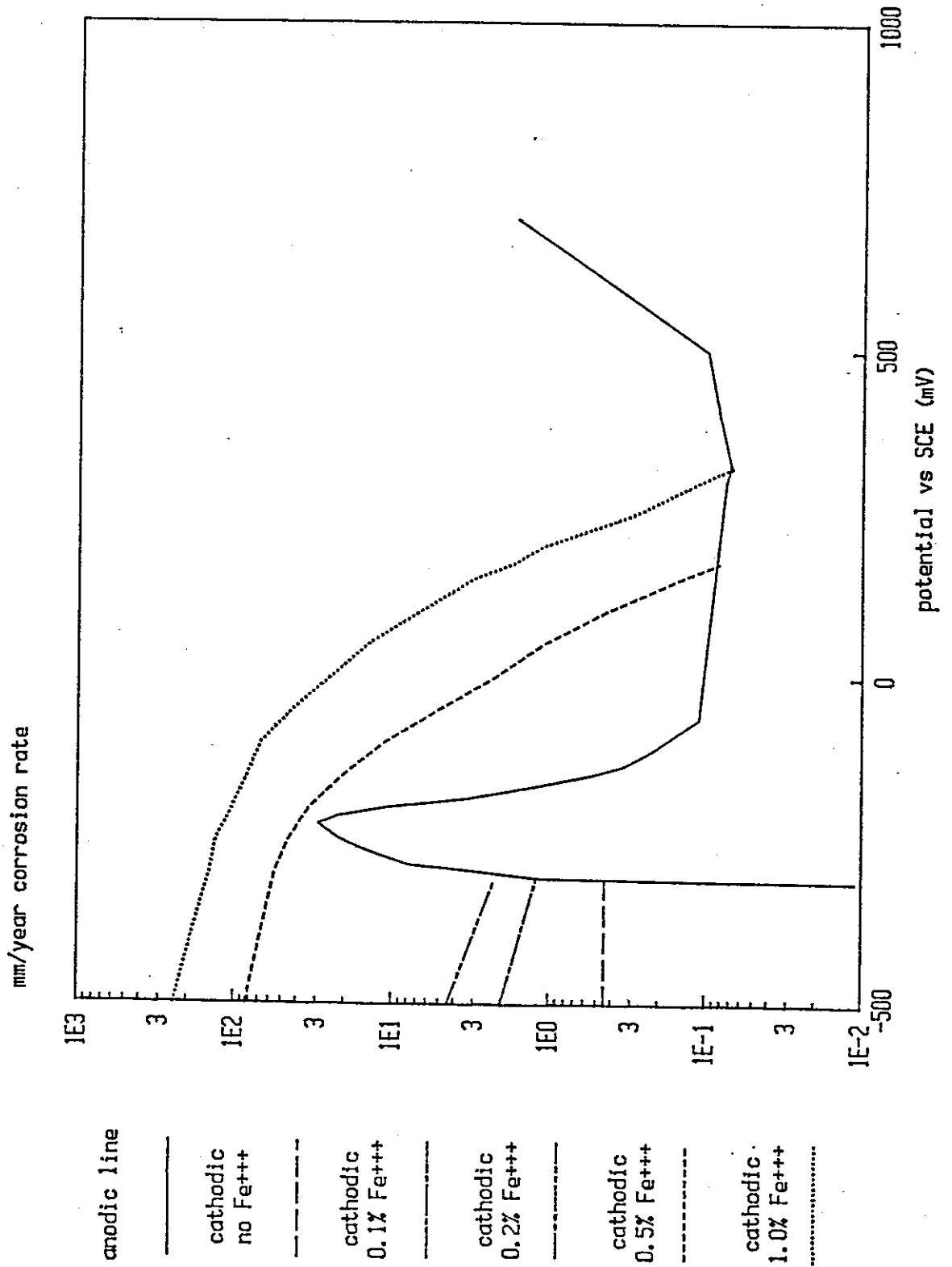


FIGURE 4

Corrosion rate of AISI 316 VS Free fluorides content

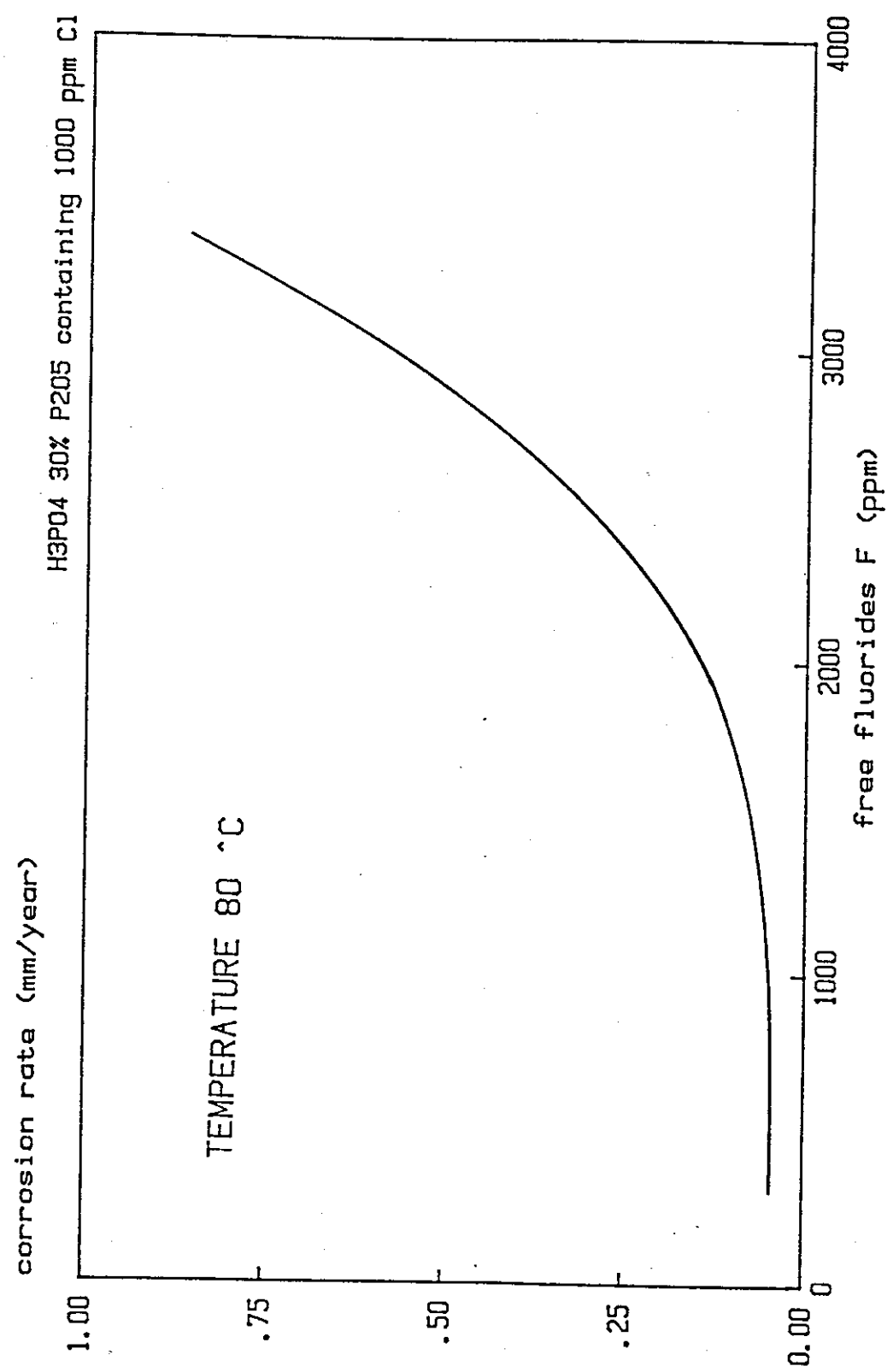


FIGURE 5

Inhibition of fluorides by aluminum and silica

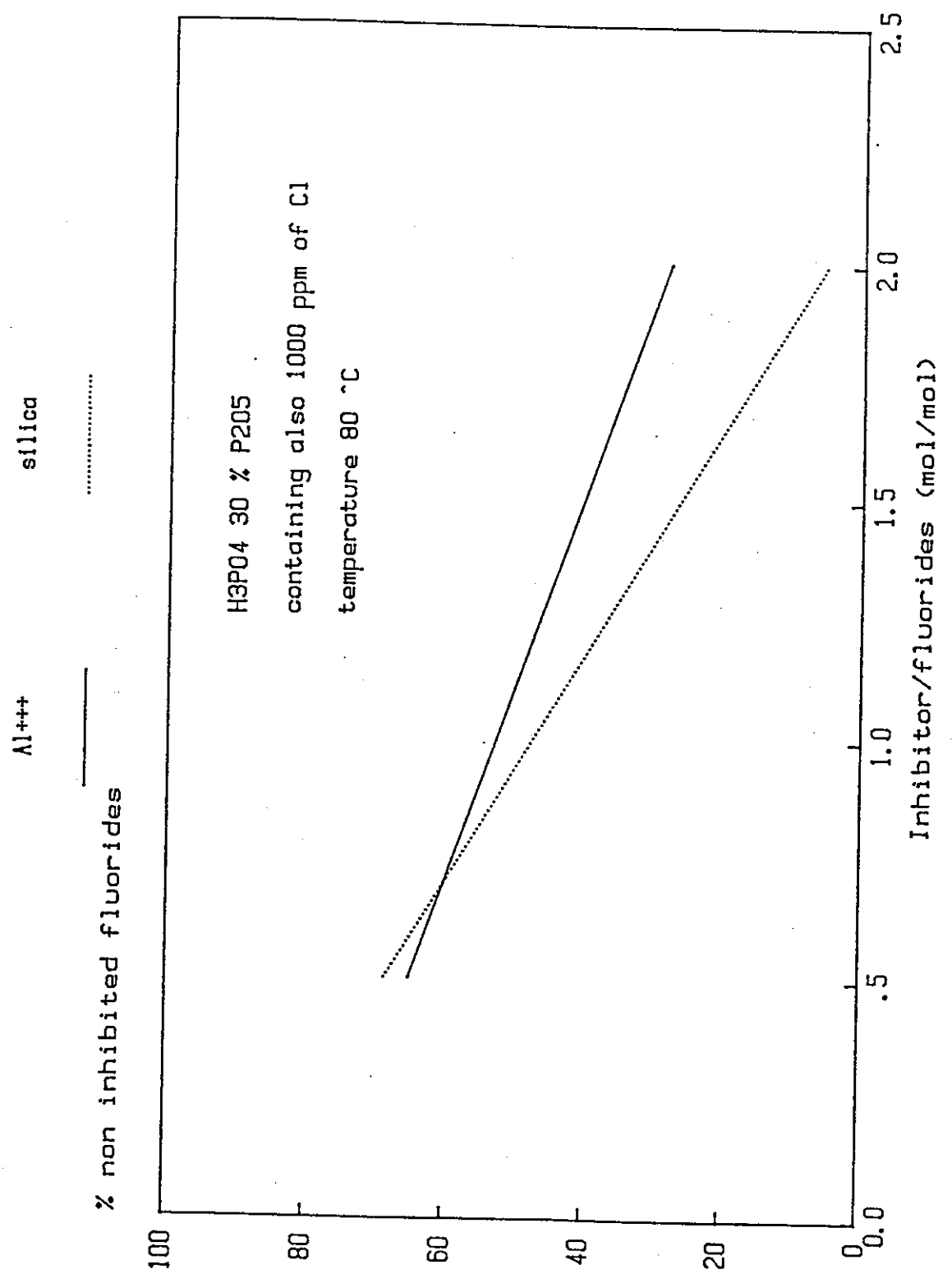


FIGURE 6

Type : KHOURIBGA 72/73 BPL

DATE : 1982

1	CHEMICAL ANALYSIS		2	PHYSICAL ANALYSIS																									
Umidity P ₂ O ₅ CaO SO ₄ CO ₂ F SiO ₂ reactive SiO ₂ total Al ₂ O ₃ Fe ₂ O ₃ MgO Na ₂ O K ₂ O Organics (C)	2.0 % 32.9 % 50.2 % 2.2 % 4.5 % 3.7 % 0.6 % 2.1 % 0.2 % 0.2 % 0.3 % 1.1 % 0.1 % 0.1 %	Zn 320 ppm Cr 160 ppm Pb 50 ppm Hg < 0.1 ppm As 17 ppm Cd 23 ppm Cu 34 ppm Ni 57 ppm V 336 ppm Be 2 ppm		<p><u>X rays</u></p> <p>cell parameters a : 9.3 Å c : 6.9 Å</p> <p><u>Crystallites dimensions :</u></p> <p>x axe 370 Å z axe 525 Å</p> <p><u>Specific surface</u></p> <p>total 24,600 cm²/g external 264 cm²/g</p> <p><u>Porosity (75,000/38 Å)</u> 0.10 cm³/g</p> <p><u>Real density</u> 3.03 Kg/dm³</p> <p><u>Bulk density</u> 1.37 Kg/dm³</p> <p><u>K reaction at 10°C</u> 0.017 cm/sec</p>																									
3	SCREEN ANALYSIS CUMULATIVE		4	GRINDING TEST																									
	<table border="0"> <tr><td>+ 2 mm</td><td>3.2 %</td></tr> <tr><td>1 "</td><td>6.4 %</td></tr> <tr><td>0.5 "</td><td>20.4 %</td></tr> <tr><td>0.425 "</td><td>22.9 %</td></tr> <tr><td>0.300 "</td><td>36.3 %</td></tr> <tr><td>0.212 "</td><td>55.5 %</td></tr> <tr><td>0.150 "</td><td>86.3 %</td></tr> <tr><td>0.100 "</td><td>96.7 %</td></tr> <tr><td>0.075 "</td><td>97.8 %</td></tr> <tr><td>0.063 "</td><td>98.1 %</td></tr> <tr><td>0.050 "</td><td>98.6 %</td></tr> <tr><td>0.033 "</td><td>99.0 %</td></tr> </table>		+ 2 mm	3.2 %	1 "	6.4 %	0.5 "	20.4 %	0.425 "	22.9 %	0.300 "	36.3 %	0.212 "	55.5 %	0.150 "	86.3 %	0.100 "	96.7 %	0.075 "	97.8 %	0.063 "	98.1 %	0.050 "	98.6 %	0.033 "	99.0 %		<p>Grinding rate + 20 % compared to Florida rock data sheet n° 1</p>	
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5 PHOSPHORIC ACID PRODUCTION																											
5.1	Operating conditions	5.2	Gypsum analysis and P ₂ O ₅ recovery																								
<u>Raw materials per ton P₂O₅</u> - Ground rock 316.6 Kg (35% on the 0.15 mm screen) - H ₂ SO ₄ 75% 271.7 Kg - Bentonite 6.9 Kg - Tensioactive Montaline SP-CV 0.04 Kg - Return acid 896 Kg " " 19.6% P ₂ O ₅ - Wash water 383 Kg - Slurry density 1.501 Kg/dm ³ - Solid/liquid (volume) 375/625 - Free H ₂ SO ₄ 2.4% Temperature 76°C		Humidity 24% P ₂ O ₅ water soluble 0.09% P ₂ O ₅ lattice 0.46% P ₂ O ₅ insoluble 0.10% P ₂ O ₅ recovery 96.0 %																									
		5.3	Rates and notes																								
		- Same production rate as Florida card n° 1 - Filtration rate 15 t P ₂ O ₅ /m ² day - Acid concentration 28% P ₂ O ₅ - Bentonite rate is lower than theoretical - Corrosion on the impellers 316 L 2.34 g/m ² day URANUS B6 0.33 " " HASTELLOY C 0.00 " "																									
6 SUPERPHOSPHATE PRODUCTION																											
6.1	Operating conditions	6.2	chemical analysis																								
<u>Feed per ton of product</u> - Ground rock 559 Kg + 0.150 mm 14% 0.15 - 0.075 mm 36% - 0.075 mm 50% - H ₂ SO ₄ 100% 351 Kg (concentration 75% temp. 60°C) - H ₂ SiF ₆ 100% 20 Kg (concentration 25%)		<u>After days</u> <table border="1"> <thead> <tr> <th></th> <th>1</th> <th>6</th> <th>12</th> </tr> </thead> <tbody> <tr> <td>H₂O</td> <td>12.9 %</td> <td>12.4</td> <td>12.0 %</td> </tr> <tr> <td>Free P₂O₅</td> <td>4.4 %</td> <td>4.2 %</td> <td>3.5 %</td> </tr> <tr> <td>W.S. P₂O₅</td> <td>17.2 %</td> <td>17.3 %</td> <td>17.5 %</td> </tr> <tr> <td>Available</td> <td>17.8 %</td> <td>18.0 %</td> <td>18.3 %</td> </tr> <tr> <td>Total P₂O₅</td> <td>18.2 %</td> <td>18.3 %</td> <td>18.4 %</td> </tr> </tbody> </table> Stickiness = absent Friability = good			1	6	12	H ₂ O	12.9 %	12.4	12.0 %	Free P ₂ O ₅	4.4 %	4.2 %	3.5 %	W.S. P ₂ O ₅	17.2 %	17.3 %	17.5 %	Available	17.8 %	18.0 %	18.3 %	Total P ₂ O ₅	18.2 %	18.3 %	18.4 %
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7		NPK PRODUCTION - GRADE 12.12.12	
7.1	Operating conditions	7.2	Chemical analysis
<p><u>Raw materials per ton of finished product</u></p> <ul style="list-style-type: none"> - Rock (not ground) 310 Kg - H₂SO₄ (100%) 102 Kg - HNO₃ (100%) 290 Kg - NH₃ 79 Kg - H₃PO₄ (as P₂O₅) 26 Kg - Kcl (60% K₂O) 206 Kg - Antifoaming ROL - SOL 4015 R 0.1 Kg - <u>Mole ratio of the slurry</u> = 0,98 - <u>Foam formation</u> : under control - <u>NO_x formation</u> : normal 		<ul style="list-style-type: none"> - H₂O 1.8 % P₂O₅ W.S. = 4.1% - N amm. 6.2 % P₂O₅ available = 12.1% - N nitric 6.1 % P₂O₅ total = 12.2% - N total 12.3 % K₂O = 12.2% 	
		7.3	Corrosion
		<p>On AISI 316 L 2.6 g/m² day (normal corrosion)</p>	
8	HANDLING	9	NOTES
<p>Non dusty during unloading</p>		<p>The sample has a CaO/P₂O₅ ratio lower than the normal Marocco rocks.</p>	
10	ECONOMICAL EVALUATION		
<ul style="list-style-type: none"> - For the H₃PO₄ production the rock can cost 0.91 times the reference rock - For the superphosphate production the rock can cost 1.04 times the reference rock - For the NPK production the rock can cost 1.01 times the reference rock 			