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STUDY OF THE F/SiO_2 RATIO IN ORDER TO MINIMIZE FLUORINE EMISSIONS

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RESUME

Le travail consiste en une approche sur les formes de silice qui entrent dans la composition des phosphates et leur participation lors de la fabrication d'acide phosphorique par voie humide. En fait, la silice se présente sous deux formes qui ont des comportements différents par rapport à l'acide HF formé.

- *Dans le premier cas une forme de silice dite "Active" qui provient des argiles et qui a la possibilité de réduire l'émission du fluor.*
- *Dans le deuxième cas il s'agit de la silice dite "Non active" ; cette forme ne réagit pas avec le milieu réactionnel, par conséquent elle ne réduit pas l'émission du fluor.*

L'étude de deux phosphates : un phosphate tunisien et un phosphate étranger a permis :
- *d'identifier toutes les formes de silice dans le minerai et dans le phosphogypse.*
- *de prévoir la réactivité de l'acide phosphorique produit par attaque sulfurique en fonction du rapport F/SiO_2 et l'influence de ce rapport sur la filtrabilité du phosphogypse.*
- *de dresser un bilan dans le but de quantifier les formes de silice ayant participé aux réactions dans la bouillie phosphorique.*

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1. INTRODUCTION

In phosphoric acid plants, fluorine emissions occur during the reaction of phosphate rock with sulphuric acid as HF and SiF_4 as well as other gases or vapours. Decomposition of phosphate rock follows the reaction:

$$Ca_{10}(PO_4)_6F_2 + 10H_2SO_4 + 20H_2O \dashrightarrow 6H_3PO_4 + 10CaSO_4.2H_2O + 2HF$$

At present, phosphoric acid producers try to purify polluting gas effluents before discharging them in order to comply with existing regulations.

2. THE ORIGIN OF FLUORINE EMISSION

The following presentation will be limited to secondary reactions of fluorine or siliceous compounds which may occur when phosphate rock is reacted with sulphuric acid. These specific reactions can be summarized as follows:

$$SiO_2 + 4HF \leftrightarrow SiF_4 + 2H_2O$$

$$SiO_2 + 6HF \leftrightarrow H_2SiF_6 + 2H_2O$$

$$3\ SiF_4 + 2H_2O \leftrightarrow 2H_2SiF_6 + SiO_2$$

HF and SiF_4 combine with silica to give H_2SiF_6 which is soluble in the reaction medium.

The distribution of fluorine and silica between the various dihydrate process streams depends mainly on the chemical composition of the phosphate and process water in particular (F, Si, Na, K, Al and Mg).

SiO_2 participating in the reaction is the so-called « Active » silica. It is present in the rock in the form of silicates of various origins. In this case, the theoretical ratio F/Active SiO_2 is close to 1.9. If the ratio exceeds this figure, one can anticipate that the excess fluorine in relation to active silica will be in the form of HF.

The main aim of this paper is to identify all the silicate forms in two phosphate rocks. We will expand on the distribution of active silicates in two phosphate rocks. We will emphasize the distribution of active silicate and its positive relationship with complex fluorine. We will mention fluorine distribution in the various process streams of the dihydrate process in relation to the mineralogical and chemical composition of the two rocks.

3. MINERAL IDENTIFICATION OF THE ROCKS

Rock 1:

The qualitative characterization of rocks (1) by X ray diffraction (Diagram 1) enabled the following minerals to be identified:

- A carbonate-fluorapatite
- Quartz
- Montmorillonite (a clay containing small amounts of magnesium and sodium)
- Cristobalite
- Zeolite (hydrated aluminium silicate)
- Calcite
- Dolomite (very little).

Chemical analyses of this rock are given in Table 1.

Table 1

P_2O_5	CaO	SiO_2	MgO	SO_3	Fe_2O_3	Al_2O_3	Na_2O	K_2O	F
30.18	48.98	3.41	0.65	3.21	0.26	0.50	1.38	0.07	3.25

Rock 2:

The qualitative characterization of rock (2) by X ray diffraction (Diagram 2) enabled the following minerals to be identified:

- A carbonate-fluorapatite
- Gypsum
- Palygorskite (clay containing magnesium)
- Smectites (a mixture of illite-ferrous montmorillonite)
- Quartz
- Dolomite

Chemical analyses of this rock are given in Table 2.

Table 2

P_2O_5	CaO	SiO_2	MgO	SO_3	Fe_2O_3	Al_2O_3	Na_2O	K_2O	F
30.51	45.94	3.25	0.62	5.14	4.11	0.27	0.080	0.06	2.59

4. DISTRIBUTION OF SILICATES IN THE ROCK

Both rocks have almost the same mineralogical characteristics as a whole. The main difference is the presence of cristobalite and zeolite in the rock (1). Both diagrams show this clearly.

In the rock (1), silica is produced by:

- Clay
- Cristobalite
- Zeolite
- Quartz

In the rock (2), silica is produced by:

- Clay
- Quartz

SiO_2 present in the rock can have two forms:

- A free form made up of quartz and cristobalite
- A combined form with aluminium and, secondarily, with sodium and magnesium in the zeolites and clays.

5. DISTRIBUTION OF SiO_2 IN DIFFERENT SILICATE MINERALS

In the first stage, a quantitative evaluation was made of the silicate minerals present in the composition of the raw materials. Results are given in Tables 3 and 4 for Rocks 1 and 2.

Table 3 - Rock 1

Carbonate-fluorapatite	86 %
Calcite	1 %
Dolomite	1 %
Quartz	3 %
Zeolite	2 %
Clay	3 %
Cristobalite	4 %

Table 4 - Rock 2

Carbonate-fluorapatite	87 %
Gypsum	4 %
Dolomite	2 %
Quartz	3 %
Clay	4 %

The results obtained make possible a fairly accurate calculation as regards the distribution of SiO_2 in the various silicate minerals (Tables 5 and 6).

Table 5 - Rock 1

		SiO_2 in the rock
	SiO_2 in quartz	1.22
Combined silica	SiO_2 in zeolites	0.50
	SiO_2 in clays	0.60
	SiO_2 in cristobalite	1.08

Table 6 - Rock 2

		SiO_2 in the rock
	SiO_2 in quartz	2.10
Combined silica	SiO_2 in clays	1.15

At this stage of identification, we can only discuss free silica and combined silica.

In the two identified rocks, the distribution was as follows:

<u>Rock 1</u>:

Combined silica = 1.10%
Free silica = 2.30%

<u>Rock 2</u>:

Combined silica = 1.15%
Free silica = 2.10%

6. IDENTIFICATION OF SILICATES IN PHOSPHOGYPSUM AFTER TREATMENT

As with the rocks, phosphogypsum obtained after filtration was identified by X ray diffraction (Diagrams 3 and 4).

The identified minerals are shown in Tables 7 and 8.

Table 7 - Rock 1 - Phosphogypsum

Gypsum dihydrate
Traces of clay
Quartz
Traces of phosphate

Table 8 - Rock 2 - Phosphogypsum

Gypsum dihydrate
Traces of clay
Quartz
Traces of phosphate

The interesting fact in this process is the complete disappearance of zeolites and cristobalite in the gypsum (1). Quartz is present in both residual products (gypsum), clays are present only as traces.

In our opinion, combined silica is not the only factor responsible for fluorine complexes. Cristobalite, which is a cryptocristalline silica, participates in the reactive medium for complexing fluorine; it is therefore active. An interesting comparison can be made between the diagram of the rock (1) and a diagram of a siliceous earth generally used as an additive in the reactive mediu m to increase the amount of active silica. (Diagram 5)

The active silica contents in Rocks (1) and (2) are shown in Tables 9 and 10.

Table 9 - Rock 1

Active silica	2.18
Inactive silica	1.22

Table 10 - Rock 2

Active silica	1.15
Inactive silica	2.10

These measures involved the combination of two identification methods: chemical and mineralogical, but the interesting fact in this case is the identification of the two silicate compounds (zeolites and cristobalite) which exist naturally in the raw material and which will fully play the role of active silica. These two minerals exist frequently in some rocks and their identification should allow the behaviour of the raw material during the reaction to be predicted.

As an indication, we give the chemical characteristics of the phosphogypsum and phosphoric acid obtained after reaction. The results appear in Tables 11 and 12.

Table 11 - Rock 1

	Filtered Phosphoric Acid	Phosphogypsum
P_2O_5	28.60	0.85
CaO	0.20	36.70
SiO_2	0.35	1.54
MgO	0.55	0.07
Fe_2O_3	0.21	0.06
Al_2O_3	0.34	0.12
K_2O	0.03	0.03
F	0.87	0.9
Na_2O	0.18	0.65

Table 12 - Rock 2

	Filtered Phosphoric Acid	Phosphogypsum
P_2O_5	25.49	1.53
CaO	0.28	33.24
SiO_2	0.21	1.65
MgO	0.56	0.03
Fe_2O_3	1.97	2.21
Al_2O_3	0.29	0.11
K_2O	0.03	0.01
F	0.62	0.29
Na_2O	0.09	0.26

The gypsum factor is roughly equal to 1.45 t/t of reacted rock for rock (1) and 1.36 for rock (2). For the acid produced, the factors are respectively 1.04 and 0.98.

Initially, the amounts of silica were:

- 3.41 for rock (1)
- 3.25 for rock (2)

The silica balance is as follows:

Rock (1)	SiO_2 in the gypsum	= 1.54 x 1.45 = 2.23
	SiO_2 in the acid	= 0.35
	Total SiO_2	= 2.58
Rock (2)	SiO_2 in the gypsum	= 1.65 x 1.36 = 2.24
	SiO_2 in the acid	= 0.21
	Total SiO_2	= 2.45

The amounts of silica missing in relation to the initial raw material are respectively:

* 3.41 - 2.58 = 0.83 Rock (1)
* 3.25 - 2.45 = 0.80 Rock (2)

Before washing, these siliceous fractions are probably to be found in the gases as SiF_4. We give below the fluorine and silica balances.

7. SILICA AND FLUORINE BALANCES

Rock 1

	Silica Balance 3.41% = 34.1 kg/t phos.	Fluorine Balance 3.25% = 32.5 kg/t phos.
Acid	0.35 x 1.04 = 3.6 kg/t phos.	0.87 x 1.04 = 9.0 kg/t phos.
Gypsum	1.54 x 1.45 = 22.3 kg/t phos.	0.9 x 1.45 = 13.0 kg/t phos.
Gas	34.1 - (3.6 + 22.3) = 8.2 kg/t phos. before washing	32.5 - (9 + 13) = 10.5 kg/t phos. before washing

Rock 2

	Silica Balance 3.25% = 32.5 kg/t phos.	Fluorine Balance 2.59% = 25.9 kg/t phos.
Acid	0.21 x 0.98 = 2.0 kg/t phos.	0.62 x 0.98 = 6.1 kg/t phos.
Gypsum	1.65 x 1.36 = 22.4 kg/t phos.	0.29 x 1.36 = 3.9 kg/t phos.
Gas	32.5 - (2 + 22.4) = 8.1 kg/t phos.	25.9 - (6.1 + 3.9) = 15.9 kg/t phos.

8. REMARKS AND INTERPRETATION

For Rock (1), gases contain 8.2 kg silica capable of complexing 10.37 kg fluorine into SiF_4 gas. The fluorine balance leaves in the gas an amount of 10.5 kg. Considering that the residual amount of fluorine is in the form of HF, this quantity is quite negligible. In any case, washing only concerned SiF_4 gas

For Rock (2), things would not evolve in the same way since the excess fluorine in the gases would be 15.9 kg. The amount of silica present could only complex about 10.1 kg. The amount of fluorine in the form of HF is 5.8 kg. This amount represents 22% of the initial quantity. For this rock, a very intensive washing would be needed to minimize gas emissions.

We give the significant complexation ratios of fluorine to explain the importance of the active silica supply for complexing fluorine in the form of H_2SiF_6 on the one hand and non-corrosive precipitates on the other. Moreover, during the plant maintenance periods, we have identified in the reactor and in the pipes the following products:

- Na_2SiF_6
- Na_3AlF_6

These products can be present in phosphogypsum and in the slimes.

9. COMPLEX RATIOS OF FLUORINE

The significant ratios are the following:

* Active F/SiO_2 (a)
* $\frac{F}{\text{Active } SiO_2 + Al_2O_3 + MgO}$ (b)

In the first ratio, we only illustrate the value of active silica in comparison with the theoretical value announced initially (1.9).

The second ratio indicates the evaluation of the corrosion of phosphate rock and of the filtrability of the acid produced. In that case, the rock may contain enough active silica, aluminium and magnesium to form non corrosive fluorine complexes.

The following tables give the values of complexation ratios for both rocks:

Rock 1:

$$\text{Active } SiO_2/F = \frac{3.25}{2.18} = \boxed{1.49}$$

$$\frac{F}{\text{Active } SiO_2 + Al_2O_3 + MgO} = \frac{3.25}{2.18 + 0.50 + 0.65} = \boxed{0.97}$$

Rock 2:

$$\text{Active } SiO_2/F = \frac{2.59}{1.15} = \boxed{2.25}$$

$$\frac{F}{SiO_2 \text{ active} + Al_2O_3 + MgO} = \frac{2.59}{1.15 + 0.27 + 0.62} = \boxed{1.27}$$

The values are significant and demonstrate the corrosive nature of the rock (2).

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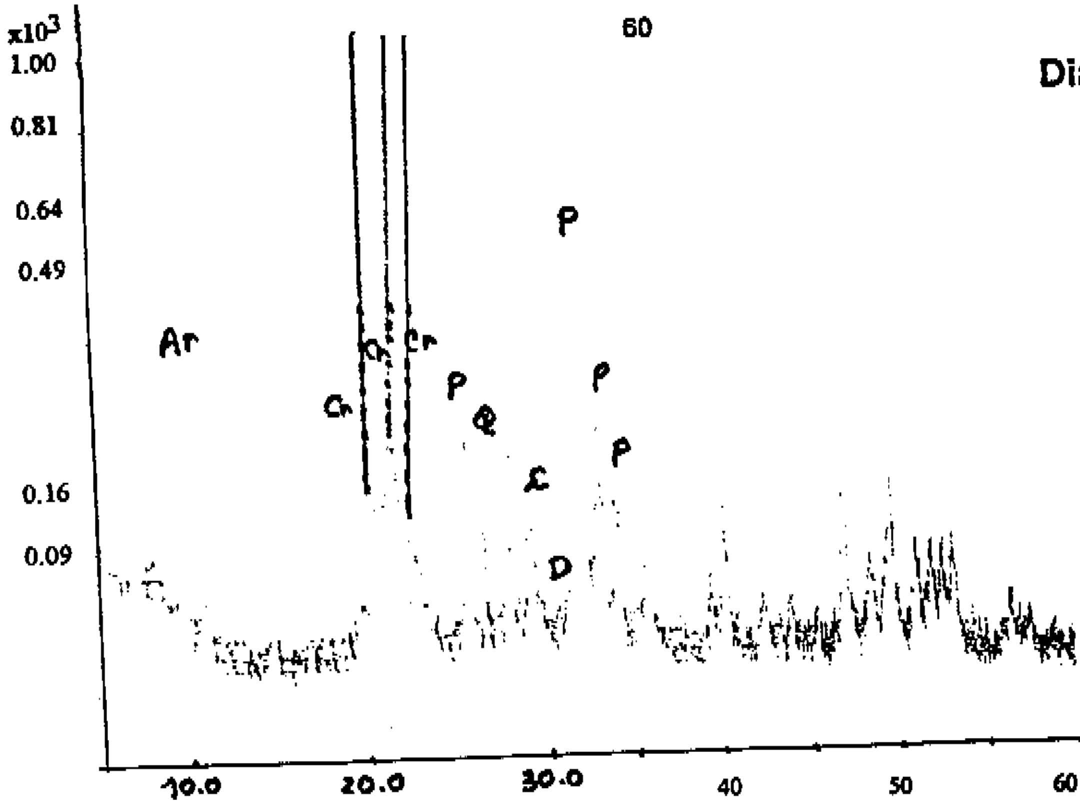
Diagramme 1



Peak no	Angle (deg)	Tip width (deg)	Peak (cts)	Backg (cts)	D-spac (Ang)	I/Imax (%)
1	6.3350	0.10	10.	88.	13.9404	2.32
2	9.8875	0.10	207.	66.	8.9383	47.02
3	11.1725	0.07	37.	36.	7.9130	8.44
4	14.7450	0.15	26.	19.	6.0028	5.90
5	16.9200	0.07	22.	20.	5.2358	5.01
6	19.0350	0.25	10.	22.	4.6585	2.32
7	20.5225	0.40	104.	26.	4.3241	23.59
8	21.6725	0.45	159.	49.	4.0972	36.00
9	22.4425	0.15	31.	81.	3.9583	7.11
10	22.9825	0.30	12.	81.	3.8665	2.62
11	23.7800	0.07	10.	85.	3.7386	2.32
12	25.8600	0.17	213.	27.	3.4424	48.34
13	26.6900	0.12	146.	26.	3.3372	33.20
14	28.1625	0.10	74.	25.	3.1660	16.77
15	29.4900	0.12	81.	35.	3.0264	18.37
16	30.8800	0.15	10.	48.	2.8933	2.32
17	32.0525	0.17	441.	29.	2.7901	100.00
18	32.3450	0.07	306.	29.	2.7655	69.44
19	33.3725	0.17	190.	41.	2.6827	43.18
20	34.2475	0.17	83.	53.	2.6161	18.78
21	35.9525	0.45	41.	37.	2.4959	9.29
22	39.4625	0.20	37.	22.	2.2816	8.44
23	40.3075	0.12	94.	22.	2.2357	21.34
24	42.5000	0.15	31.	22.	2.1253	7.11
25	43.9450	0.25	24.	24.	2.0587	5.44
26	45.4675	0.20	13.	27.	1.9932	2.94
27	47.0875	0.25	102.	20.	1.9284	23.13
28	48.4875	0.30	50.	20.	1.8759	11.43
29	49.6400	0.17	125.	26.	1.8350	28.44
30	51.0700	0.30	55.	28.	1.7869	12.42
31	51.9200	0.20	48.	28.	1.7597	10.80
32	52.5075	0.20	41.	32.	1.7413	9.29
33	53.1525	0.25	45.	36.	1.7217	10.18
34	56.3350	0.30	23.	18.	1.6318	5.22
35	57.4525	0.25	16.	20.	1.6027	3.63
36	58.7275	0.30	10.	25.	1.5709	2.32

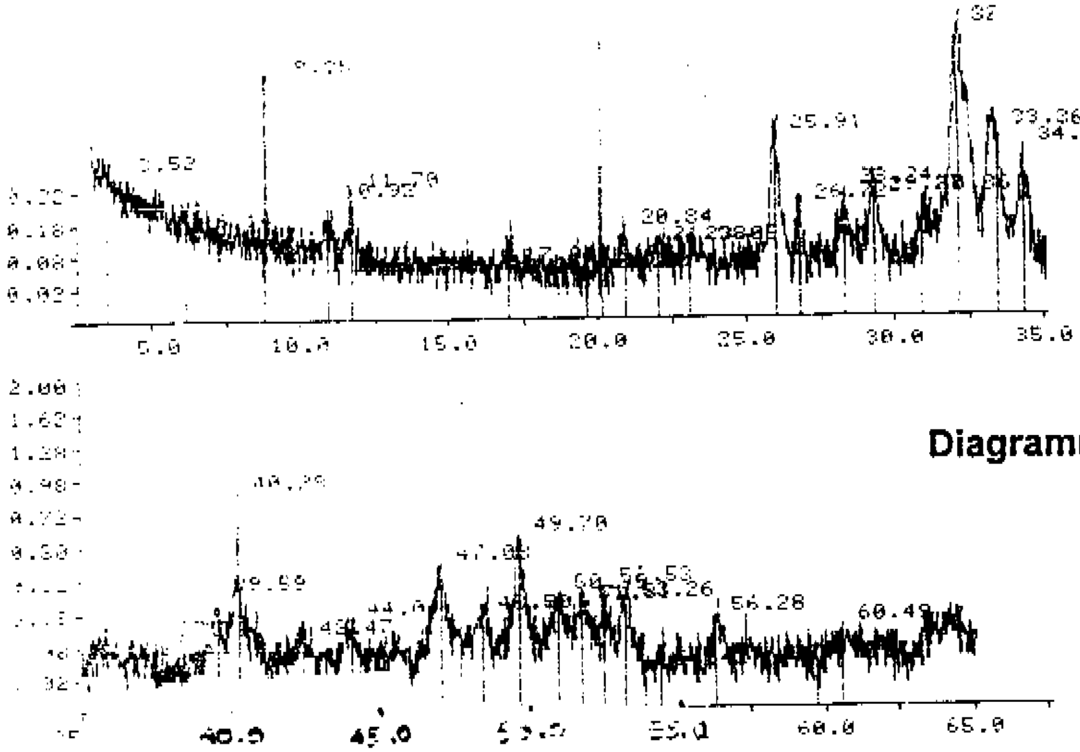


Diagramme 2

Peak no	Angle (deg)	Tip width (deg)	Peak (cts)	Backg (cts)	D-spac (Ang)	I/Imax (%)
1	3.5175	0.25	10.	53.	25.0978	6.77
2	6.1450	0.30	10.	21.	14.3710	6.77
3	8.8450	0.07	14.	12.	9.9893	9.54
4	10.9200	0.30	10.	8.	8.0954	6.77
5	11.7025	0.07	21.	9.	7.5558	13.99
6	17.0075	0.30	10.	6.	5.2090	6.77
7	19.5925	0.12	10.	3.	4.5272	6.77
8	20.0775	0.07	23.	3.	4.4189	15.23
9	20.8450	0.25	12.	3.	4.2579	8.10
10	21.9800	0.50	10.	3.	4.0406	6.77
11	23.0500	0.30	10.	4.	3.8553	6.77
12	25.9100	0.30	64.	4.	3.4359	42.30
13	26.7225	0.20	21.	6.	3.3333	13.99
14	28.2400	0.25	18.	4.	3.1575	12.22
15	29.2700	0.25	28.	6.	3.0487	18.57
16	30.8650	0.20	14.	7.	2.8947	9.05
17	32.0950	0.17	151.	7.	2.7865	100.00
18	33.3600	0.12	59.	12.	2.6837	39.19
19	34.2325	0.25	21.	20.	2.6172	13.99
20	37.1100	0.30	10.	5.	2.4206	6.77
21	37.7000	0.07	10.	4.	2.3841	6.77
22	39.5900	0.12	23.	3.	2.2745	15.23
23	40.2825	0.10	49.	4.	2.2370	32.39
24	42.4700	0.40	10.	9.	2.1267	6.77
25	44.0400	0.35	10.	5.	2.0545	6.77
26	47.0775	0.20	30.	6.	1.9287	19.99
27	48.5000	0.40	11.	8.	1.8754	7.20
28	49.6975	0.12	45.	7.	1.8330	29.67
29	50.9875	0.15	16.	7.	1.7896	10.58
30	51.8075	0.30	10.	12.	1.7632	6.77
31	52.5275	0.15	10.	12.	1.7407	6.77
32	53.2575	0.30	14.	10.	1.7186	9.54
33	54.4225	0.30	10.	10.	1.6845	6.77
34	56.2850	0.15	11.	4.	1.6331	7.20
35	60.4950	0.80	10.	4.	1.5291	6.77

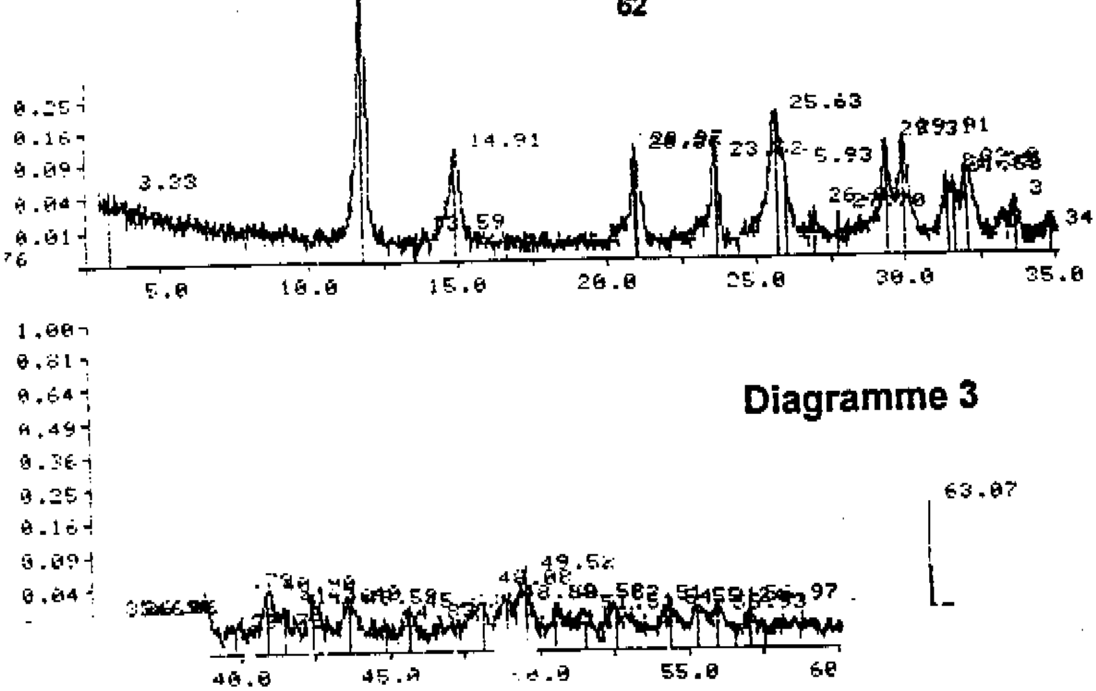
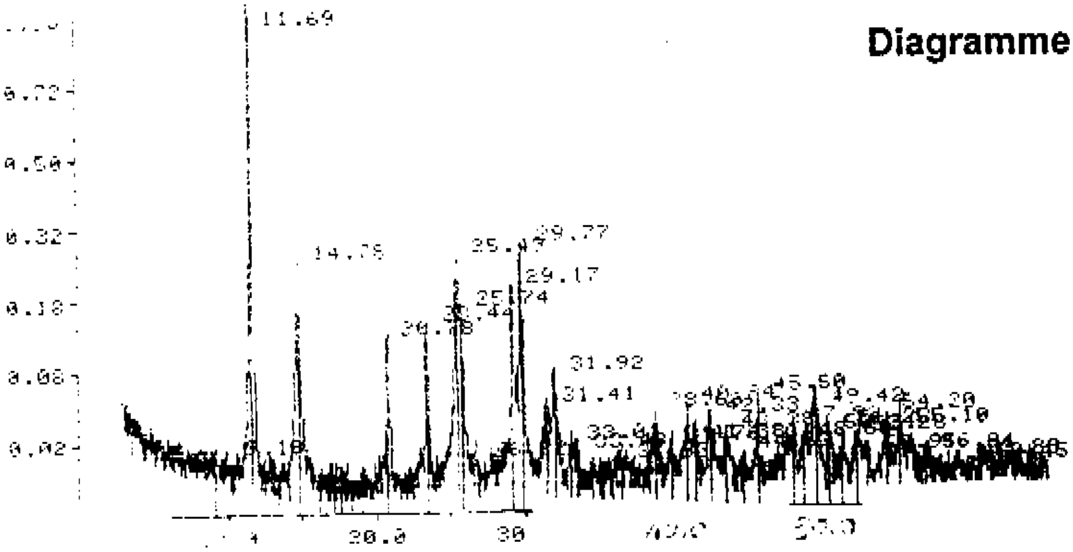


Diagramme 3

Peak no	Angle (deg)	Tip width (deg)	Peak (cts)	Backg (cts)	D-spac (Ang)	I/Imax (%)
1	3.3275	0.07	10.	37.	26.5305	1.56
2	11.8150	0.22	655.	4.	7.4841	100.00
3	13.5875	0.05	10.	4.	6.5115	1.56
4	14.9150	0.17	110.	3.	5.9348	16.82
5	20.8650	0.10	102.	3.	4.2539	15.57
6	20.9625	0.10	106.	3.	4.2447	16.19
7	23.6175	0.17	121.	3.	3.7640	18.46
8	25.6300	0.20	199.	2.	3.4728	30.34
9	25.9350	0.15	76.	2.	3.4327	11.55
10	26.8775	0.15	12.	2.	3.3144	1.87
11	27.7050	0.07	10.	4.	3.2172	1.56
12	29.3125	0.12	123.	4.	3.0444	18.80
13	29.9100	0.17	128.	5.	2.9849	19.48
14	31.3200	0.07	49.	6.	2.8537	7.48
15	31.5825	0.15	41.	4.	2.8305	6.25
16	32.0050	0.12	74.	4.	2.7941	11.29
17	33.6200	0.20	20.	6.	2.6635	3.09
18	34.7600	0.30	10.	4.	2.5787	1.56
19	35.6350	0.15	10.	4.	2.5174	1.56
20	36.1500	0.20	10.	4.	2.4827	1.56
21	36.2625	0.20	10.	4.	2.4813	1.56
22	38.7900	0.40	24.	3.	2.3196	3.66
23	39.7800	0.40	10.	3.	2.2641	1.56
24	40.9025	0.25	34.	3.	2.2045	5.13
25	41.4575	0.25	14.	3.	2.1763	2.09
26	42.4000	0.15	18.	8.	2.1301	2.82
27	43.5950	0.50	17.	4.	2.0744	2.57
28	44.8350	0.25	10.	4.	2.0199	1.56
29	45.6250	0.40	11.	4.	1.9867	1.66
30	48.0775	0.10	29.	4.	1.8909	4.45
31	48.8800	0.25	21.	5.	1.8618	3.23
32	49.5200	0.12	50.	8.	1.8392	7.69
33	50.5250	0.25	10.	13.	1.8049	1.56
34	51.5100	0.35	10.	5.	1.7727	1.56
35	52.5075	0.12	10.	7.	1.7413	1.56
36	54.3150	0.25	15.	5.	1.6876	2.32
37	55.2450	0.30	13.	5.	1.6614	1.98
38	55.9300	0.25	11.	6.	1.6426	1.66
39	56.9750	0.10	10.	7.	1.6150	1.56
40	60.8700	0.80	10.	3.	1.5206	1.56
41	[illegible]	0.07	31.	3.	1.4727	4.79

Diagramme 4



Peak no	Angle (deg)	Tip width (deg)	Peak (cts)	Backg (cts)	D-spac (Ang)	I/Imax (%)
1	9.1850	0.40	10.	10.	9.6203	1.02
2	11.6925	0.17	1005.	6.	7.5622	100.00
3	14.7800	0.20	250.	4.	5.9887	24.84
4	20.7850	0.17	114.	3.	4.2701	11.39
5	23.4450	0.20	139.	3.	3.7913	13.86
6	25.4875	0.20	256.	4.	3.4919	25.48
7	25.7425	0.07	166.	5.	3.4579	16.56
8	26.7225	0.20	10.	4.	3.3333	1.02
9	29.1750	0.17	196.	6.	3.0584	19.50
10	29.7700	0.28	262.	6.	2.9986	26.12
11	31.4075	0.20	36.	6.	2.8459	3.58
12	31.9225	0.12	69.	7.	2.8012	6.86
13	33.0100	0.30	10.	12.	2.7113	1.02
14	33.4350	0.15	10.	12.	2.6778	1.02
15	34.5150	0.30	10.	3.	2.5965	1.02
16	36.3200	0.25	10.	3.	2.4715	1.02
17	38.6250	0.25	24.	4.	2.3291	2.39
18	39.7625	0.20	12.	5.	2.2651	1.22
19	40.8375	0.25	27.	7.	2.2079	2.69
20	41.3775	0.25	18.	5.	2.1803	1.76
21	42.3350	0.30	19.	14.	2.1332	1.93
22	43.3750	0.15	16.	5.	2.0844	1.59
23	44.6200	0.07	10.	4.	2.0291	1.02
24	45.5050	0.07	21.	3.	1.9917	2.11
25	47.9250	0.12	21.	4.	1.8966	2.11
26	48.6050	0.30	10.	7.	1.8716	1.02
27	49.4250	0.40	44.	7.	1.8425	4.33
28	50.3100	0.12	16.	6.	1.8121	1.59
29	51.2250	0.25	12.	5.	1.7819	1.22
30	52.2850	0.20	18.	4.	1.7482	1.84
31	52.9150	0.30	10.	4.	1.7289	1.02
32	54.2050	0.40	14.	10.	1.6908	1.44
33	55.0975	0.20	21.	6.	1.6655	2.11
34	56.8400	0.25	10.	9.	1.6185	1.02
35	59.8300	0.12	10.	4.	1.5445	1.02
36	60.4475	0.30	10.	3.	1.5302	1.02

Diagramme 5

Peak no	Angle (deg)	Tip width (deg)	Peak (cts)	Backg (cts)	D-spac (Ang)	I/Imax (%)
1	8.3500	1.20	10.	11.	10.5803	4.49
2	11.7150	0.30	10.	7.	7.5477	4.49
3	20.9725	0.35	31.	11.	4.2323	13.75
4	21.9275	0.15	228.	17.	4.0501	100.00
5	22.8475	0.07	10.	21.	3.8891	4.49
6	23.2200	0.12	12.	21.	3.8275	5.07
7	23.4700	0.12	12.	21.	3.7873	5.37
8	25.4650	0.20	10.	18.	3.4949	4.49
9	26.8400	0.07	45.	14.	3.3189	19.69
10	27.1875	0.15	19.	14.	3.2773	8.49
11	28.4325	0.30	10.	18.	3.1365	4.49
12	29.0825	0.20	11.	19.	3.0679	4.78