MINERALOGICAL TRANSFORMATIONS IN CERAMIC PROCESSES AND THEIR APPLICATION IN QUALITY CONTROL

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SUMMARY

The resulting conclusions from the study of raw materials submitted to thermic processes are presented in this report, the results obtained being analysed using a mineralogical analysis; their application in the control of the ceramic transformations produced is also examined.

The study was carried out on two ceramic pastes used in industry, one for gres and the other for porous single firing; these are obtained through damp grinding of natural clays from various deposits being worked in Castellon at present. After grinding, the clays were subsequently atomised following the normal industrial process.

Samples were prepared by pressing, and were submitted to firing processes at temperatures ranging from 860°C to 1160°C, thus obtaining eight specimens of each ceramic paste, which were submitted to various temperatures in the study.

The analyses of the products obtained in the aforementioned firings were carried out, previous grinding, using X-Ray diffraction, with the aim of establishing their mineral dynamics at various temperatures. This is possible on account of the marked relationship that exists between the physical properties and the mineralogy of products, which is responsible to a great extent for their qualitative behaviour.

INTRODUCTION

As it is well known, minerals have regions of stability that are strongly linked to temperature. It is obvious, therefore, that an increase in temperature leads to a crossing of a mineral's energy threshold of reactivity. , producing a series of reactions in the materials present in a ceramic paste that lead to the apparition of new phases and the disapppearance of others; depending on the temperatures reached, there are few minerals that remain unchanged in the new material formed, i.e. in the ceramic piece. (Peña et al., 1980)

As a result of this, it is very important when determining ceramic quality to follow and be aware of the mineralogical transformations that take place during the ceramic process, since the physical and chemical properties that a ceramic material exhibits are determined and conditioned to a great extent by the properties that the integral minerals exhibit, which, in turn, arise from those pre-existent in the clay constituting the raw material, and also from the rhythm and intensity of the energetic programmed in the firing process.

In this analysis, the mineralogical transformations undergone in the ceramic process by various complex minerals integral in clay samples used as raw material in the Castellón ceramic industry were examined by means of X-Ray diffraction.

Using this, we tried to mineralogically follow the dynamics caused by an increase in temperature, which leads to the disappearance of existing phases in the raw material and the formation of new mineralizations that compose the new piece.

The prediction of new mineral formations after the ceramic process and the study of the dynamic process is carried out by means of the intepretation and evaluation of the corresponding X-Ray diffractograms, which is the most effective system for identifying mineralizations formed as a result of the ceramic process.

X-Ray diffraction, duly applied, constitutes a very powerful technique for exact determination and quality control; these processes are involved in the production of any ceramic piece and are carried out by means of determination of mineral dynamics.

As this study shows, X-ray diffraction as an evaluation technique and control of quality is very advantageous, since it is the most precise method for exact characterization of materials, this is because it provides structural data, as well as information on chemical compounds present, of enormous importance for the interpretation of the physical and chemical properties of a ceramic material.

On the other hand, the speed of the method and the almost instantaneous obtainment of informatized analytical results makes it a suitable technique for use in quality control on numerous samples, of a process or phases of same, usual case in the industry.

Another interesting and advantageous characteristic of X-ray diffraction is the small amount of sample that is needed to carry out a quantitative analysis.

THEORETICAL BASES

During the ceramic firing of silicated raw materials, a series of reactions occur between the clay minerals and accompanying minerals (feldspar, quartz, calcite, dolomite, etc.). To understand and possibly stablize the end properties of the ceramic product, it is necessary to examine all reactions that take place during the thermic process which the ceramic paste is submitted to, since the phases formed and texture obtained govern its properties to a great extent.

The dynamics of these reactions is intially determined by the proportion and characteristics of the different minerals intergral in the raw material; it is therefore interesting to know its composition and the reaction that occur during thermic treatment in the fring proocess.

As we have previously indicated, an accepted principle in the theory of firing of traditional ceramic materials is the criterion that ceramic reactions are incomplete, that is, the reactions, be they physical or chemical, move towards a theoretical equilibrium, but they never reach it, since the reaction can only continue until the product has developed the phases and texture. X-ray diffraction is especially useful in Ceramic since it allows one to follow the evolution of various stages of the processes of temperature-time-transformation to which the used raw material are submitted and so it is possible to determine the major or minor grade of the equilibrium achived. If we take in consideration that Ceramic is the science of incomplete reactions, X Ray diffraction reaffirms this theory and allows us to determine till what point the reactions that take place in the ceramic process are incomplete of great importance for technologists in this creation of a dynamic process due to the possibility of halting the process at an opportune moment. Kinetics are necessary to achieve the desired product; these stages can be conserved by cooling.

Only when we know how and when the reactions happen can we control the process of firing to achieve an optimum result.

It is already known (Brindley, 1958) that when a phyllosilicate is heated, it does not undergo a general decomposition from which new thermodynamically controlled mineral phases and variations in composition due to the addition of other compounds would apppear, instead the base material is transformed into a product that has a defined three dimensional orientation between the base material and itself and which is related to both. These types of transformations are known as topotactic.

A much studied topotactic transformation is that of kaolinite (Brindley, 1961), in which between 450°C and 650°C, a dehydroxylation of the mineral takes place. In the process, layers of SiO_4 tetraedrous remain unchanged, however, the composition of Al changes from octahedric to tetrahedric.

In this transformation the reticular parameters $\underline{a}$ and $\underline{b}$ are unchanged but parameter $\underline{c}$ does change due to the structural collapse that is produced in this direction. From this structure, known as metakaolinite, a spinel type strcture with a direction (111) perpendicular to plane (001) of the original Kaolinite is formed. Finaly, Mullite is formed with axis $\underline{c}$ parallel to direction (110) spinel. The structure of the mullite is composed of octahedric chains of Al-0 along his axis $\underline{C}$, these are laterally joined by tetrahedric chains of Al-0 and Si-0. Chains of this type are found in spinel-axial direction (110), and it is in this direction that the $\underline{c}$ axis of the resulting mullite is oriented.

We may thus see, from this mechanism, how the transformation of Kaolinite produces first a spinel type phase and finally results in mullite, without undergoing a total decomposition. We could thus affirm that, throughout the ceramic process, crystalline structures, once they exceed their limits of stability, are partially broken down in sucessive stages or phases of the process as other structures are formed, but this does not cause an instantatneous "destructive impact" to the pre-existing structures.

It is clear that the presence of determined mineralizations, and thus pre-existent structures, greatly governs the formation of new structures; so Brindley studied the reactions that result from various mixtures of Kaolinite, Moscovite, or Illite, and Quartz, observing the principal components present in samples subjected to temperatures of over 900°C that are quartz, a spinel type phase, and mullite. In Illite mixtures, hematites and a ferric type spinel phase are also present.

It has also been experimentally proved that, when the raw materials contain carbonates of Mg and Ca, their presence tends to totally change the direction of the reactions to the point of producing totally different phases. These carbonates decompose above 900°C releasing CO_2 and leaving very reactive oxides in the paste. At these temperatures the fine particles of quartz and the aluminium silicates of the clay are very reactive and facilitate reactions in solid state with these oxides. From this moment, at this temperature, if a particle of silica encounters another particle of calcium oxide.

The reaction is as follows:

$2CaO + SiO_2 \rightarrow 2CaO.SiO_2$	Belite
$3\,(2CaO.SiO_2) + SiO_2 \rightarrow 2(3CaO.2SiO_2)$	Rankinite
$3CaO.2SiO_2 + SiO_2 \rightarrow 3(CaO.SiO_2)$	Wollastonite

And a zonal distribution of the mineral phase mentioned is formed from the area rich in Cao to the area rich in SiO_2. This fully agrees with the sequence of stable phases at low temperature established between pure SiO_2 and pure CaO.

The calcium oxide also reacts with aluminosilicates to form Gehlenite ($2CaO.Al_2O_3.SiO_2$) and Anortite ($CaO.Al_2O_3.2SiO_2$). When the content of CaO is lower than 10%, Anortite is the stable phase; however, if the CaO content is higher than 20%, Gehlenite is immediately formed after the decomposition of the carbonates.

From this initial reaction, the concentration of Gehlenite increases until a maximum is above 1100°C. In cases where there is sufficiently big particles of CaO, the oxide will react with the aluminosilicates to give Gehlenite, since its setting, is very rich in CaO, although it is not a stable phase, on account of its overall composition; hence metastable Gehlenite will be formed, until, as the reaction progresses, the equilibrium phase is reached.

In the case of the additional presence of MgO, which is very reactive at these temperature ranges, especially when is present in Chlorite, pyroxenes are gradually formed, and the Gehlenite disappears. As a result of this transformation, the alumina and some of the calcium oxide from the Gehlenite, take part in the formation of calcic plagioclases (Ravaglioli, 1977).

MATERIALS AND METHODS

·In order to carry out the study, sixteen samples of ceramic pastes were chosen for analysis, these were submiitted to different firing temperatures for three and a half hours with a period of five minutes at maximum temperature, in a similar cycle to that used in manufacturing centres.

Of these samples, eight corresponded to ceramic paste for the production of porous materials, and the remaining were for the production of gres. Both are habitually used by the Castellon ceramic industry.

In order to determine the mineralogical content of the samples, conventional X-ray (DRX) diffraction techniques were applied to powder samples using a Siemens D500 automatic diffractometer from the Technical and Scientific Services Department of the University of Barcelona, this is equipped with a copper anode, registering corresponding spectrums in a four to seven degree interval of the 2theta angle, at intervals of 0.05 degrees, with an accumulation time of three seconds and applying a 40KV voltage and 30mA current.

RESULTS AND DISCUSSION

Because of the low Mg content in all the samples analysed, all the Mg reacted to form pyroxenes, so that the remaining phases are found within the compatibility triangle (An-W-Q).

The path of the reactions, when the temperature is varied, is totally different in the two types of paste. The diffractograms for the samples at low temperature give us an idea of their mineral composition. In the case of substances used for the manufacture of porous materials the compounds that appear are quartz, illite, calcite and feldspar. The paste for manufacture of gres is composed, for the most part, of quartz, with a lesser presence of illite, feldspar, and calcite, accompanied by hematites. This difference, which is above all quantitative, of the minerals present shows the changes undergone in the process and the characteristics of the final products.

In the paste for manufacture of porous materials, calcium carbonate decomposes at temperatures above 850°C, and the corresponding oxide appears. The increase in temperature causes the progressive break down of phyllosilicates (illite) and the apparition of spinel phases, as well as hematites. The calcium oxide reacts with the silica and aluminosilicates forming metastable Gehlenite and Wollastonite, along with calcic plagioclases. When 1100°C is exceeded, the two metastable phases break down, and the content of plagioclases increases, resulting in a final mineralogy of quartz, ortosa, plagioclases hematites and spinel.

In the case of the paste for gres, possessing a lesser quantity of calcite and illite in its initial composition, especially in the case of the carbonate, the reaction paths are simpler, and the decomposition of feldspar present over 1050°C, as well as the formation of mullite are added to a sequence similar to that mentioned for the first case.

CONCLUSIONS

In drawing conclusions from this investigative study that will satisfy the initial objectives, there is one conclusion that, although evident, is interesting nevertheless; in the study the indiscutible importance of X-ray diffraction, and its value as a powerful and efficient analytical technique in the quality control of ceramic pieces are once more made obvious.

The other conclusions of the study serve to reinforce this first conclusion even more.

In the study it was proved that, in the thermic process which a ceramic piece undergoes, there is a temperature range for firing, between 920°C and 950°C, within which we can say that it is undesirable to halt the thermic process. This applies to both paste for gres and porous material pastes.

This is because the X-ray diffractometries show that at these temperatures there is still calcite present, which, if it remains in the fired piece, must logically lower its resistance to chemical attack.

The diffractograms also reveal the existence of many unstable phases within the above temperature range, these are detrimental to the homogeneity of the piece and to the control of uniformity of properties.

It was also proved for both types of paste that, above 1150°C, the end composition is greatly simplified mineralogically, and the material acquires a greater homogeneity.

Also, the paste for gres has a simpler mineralogical composition and as a result the final composition is also simpler.

The diffractograms show too that the paste for gres has a higher quartz content and a lower content of illite, calcite, and feldspars. It also has a high content of more stable iron oxides. There are few feldspars in this paste and the predominant phases at the end of the process are quartz and spinel.

Having proved these facts we can say that, in order to guarantee a desirable homgemeity of a ceramic material, the optimum firing temperature should be situated above 1100°C, and in fact it would be advisable to exceed 1140°C, in order to simplify to a maximum the number of mineral phases present in the final product, and to ensure that these phases are the most stable possible.

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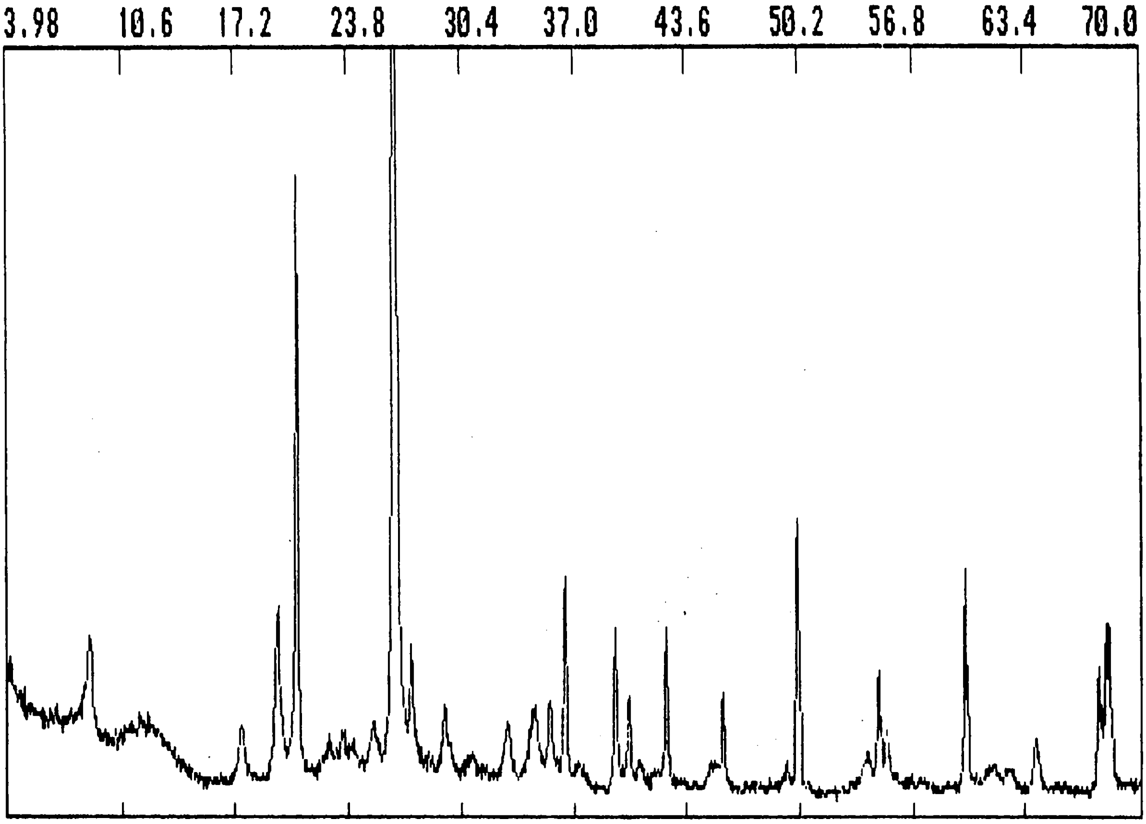


Fig. 1

GRES - 8

860º

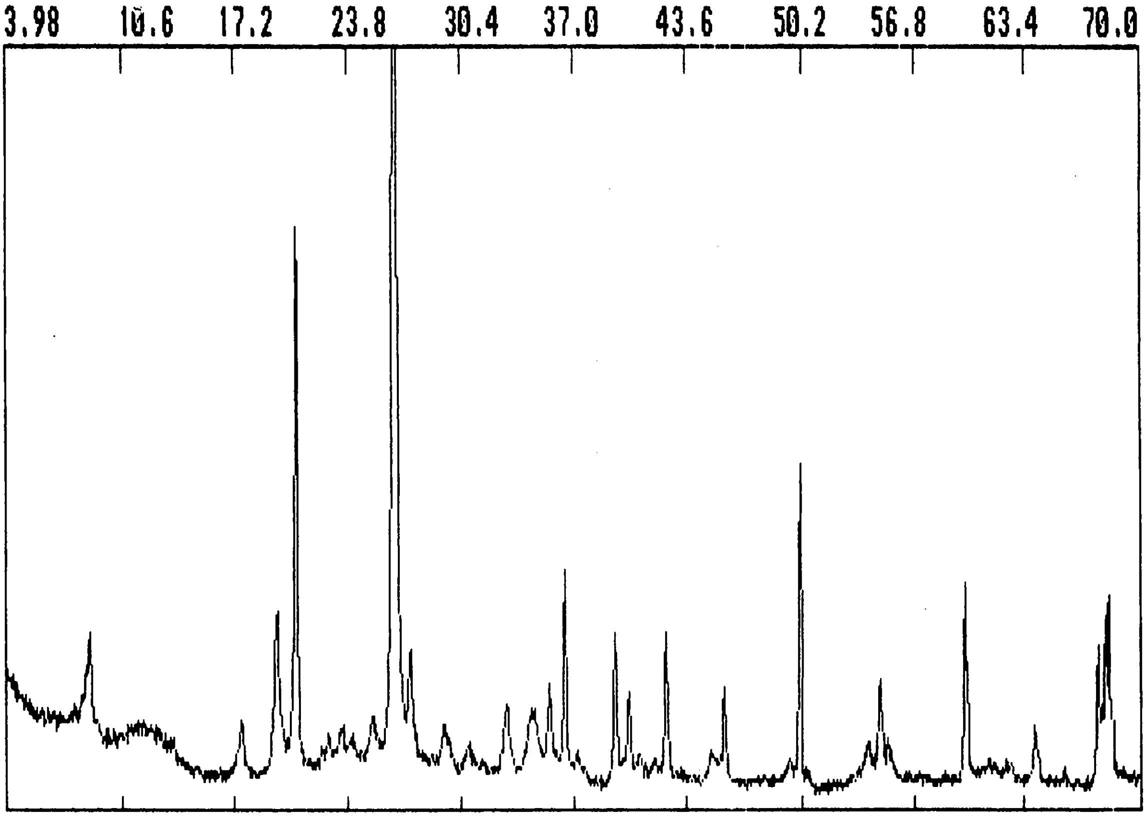


Fig. 2

GRES - 7

892º

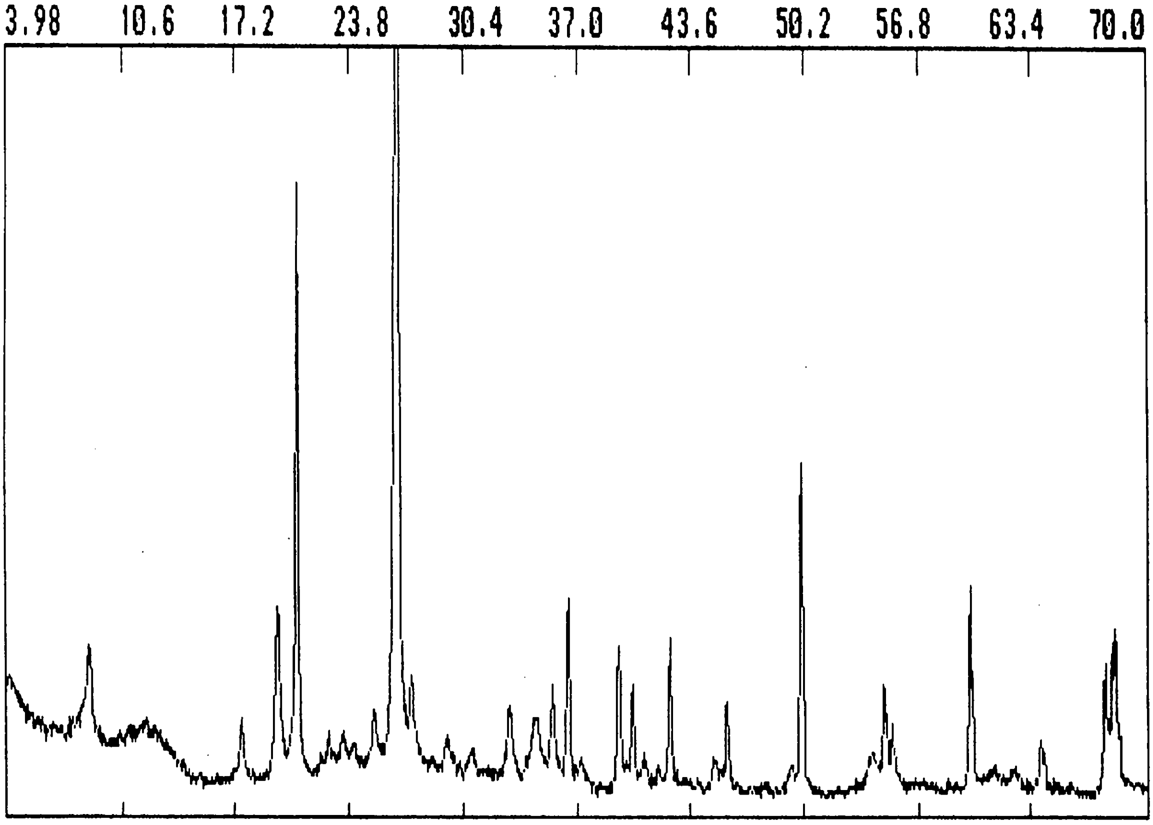


Fig. 3

GRES – 6

927º

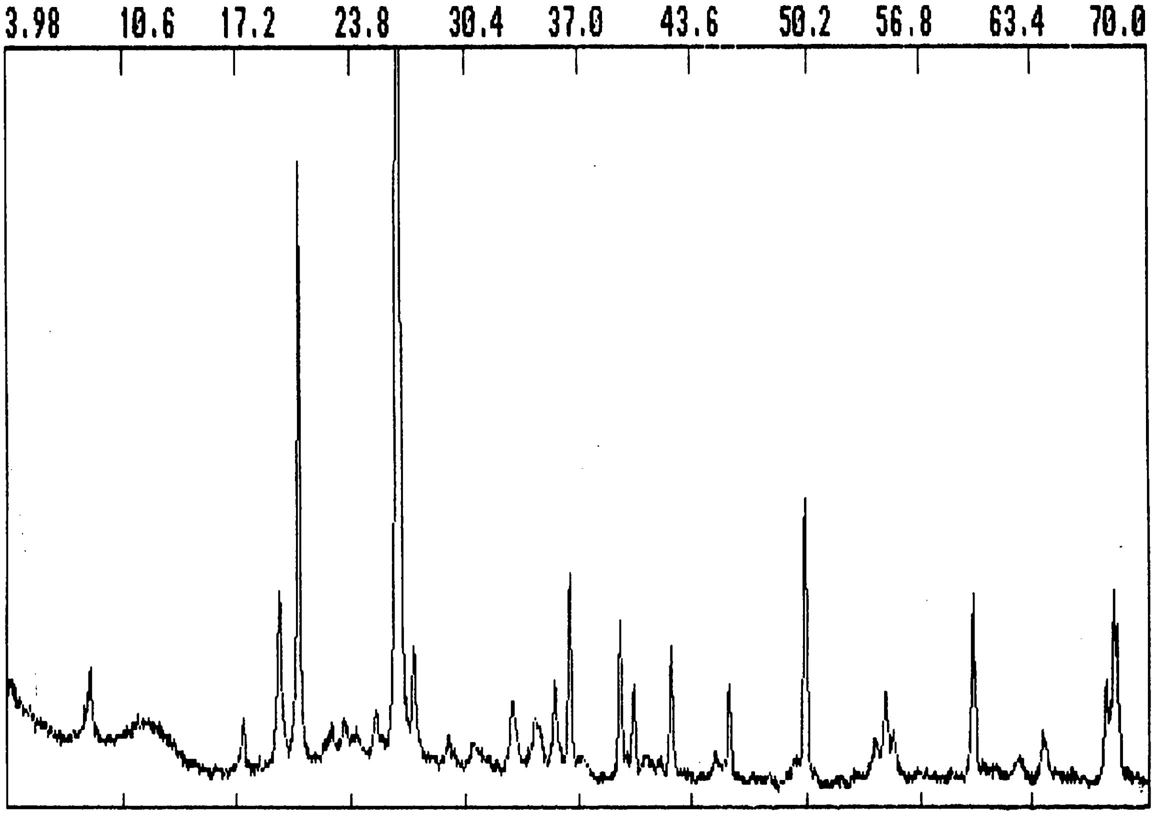


Fig. 4

GRES – 5

975º

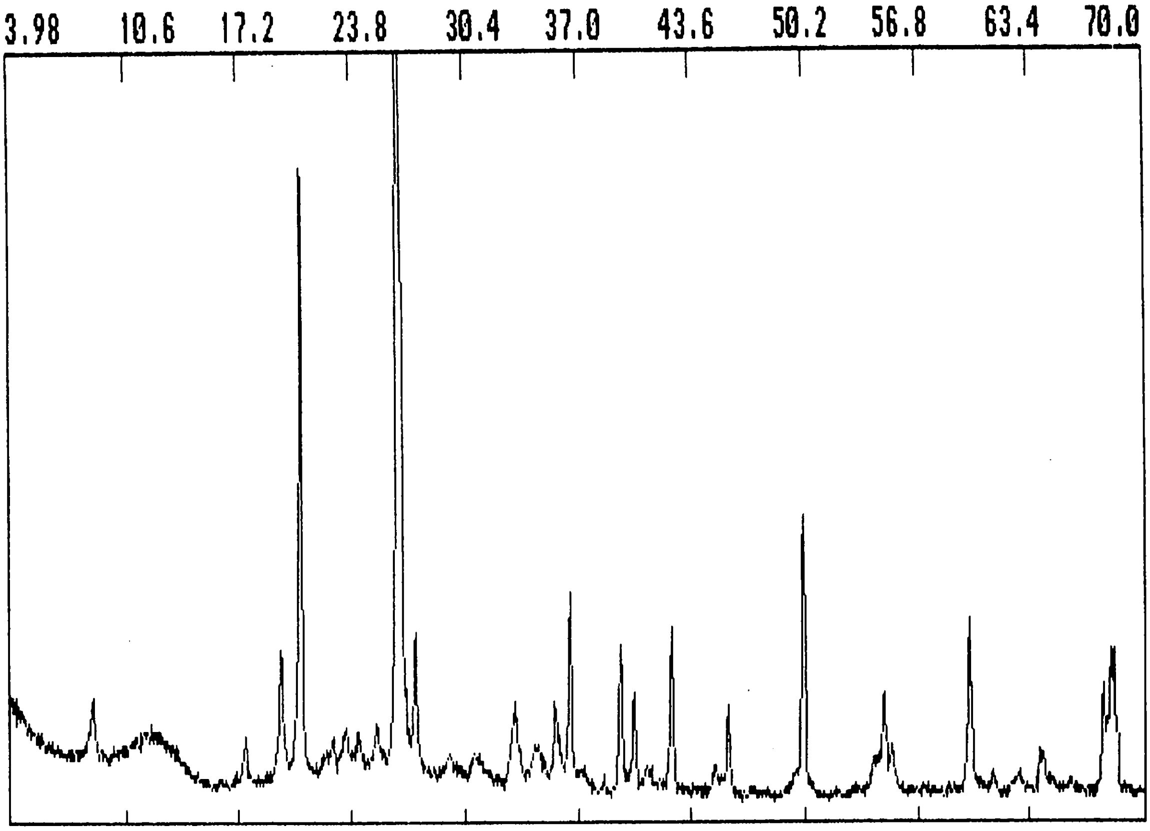


Fig. 5

GRES - 2

1.025º

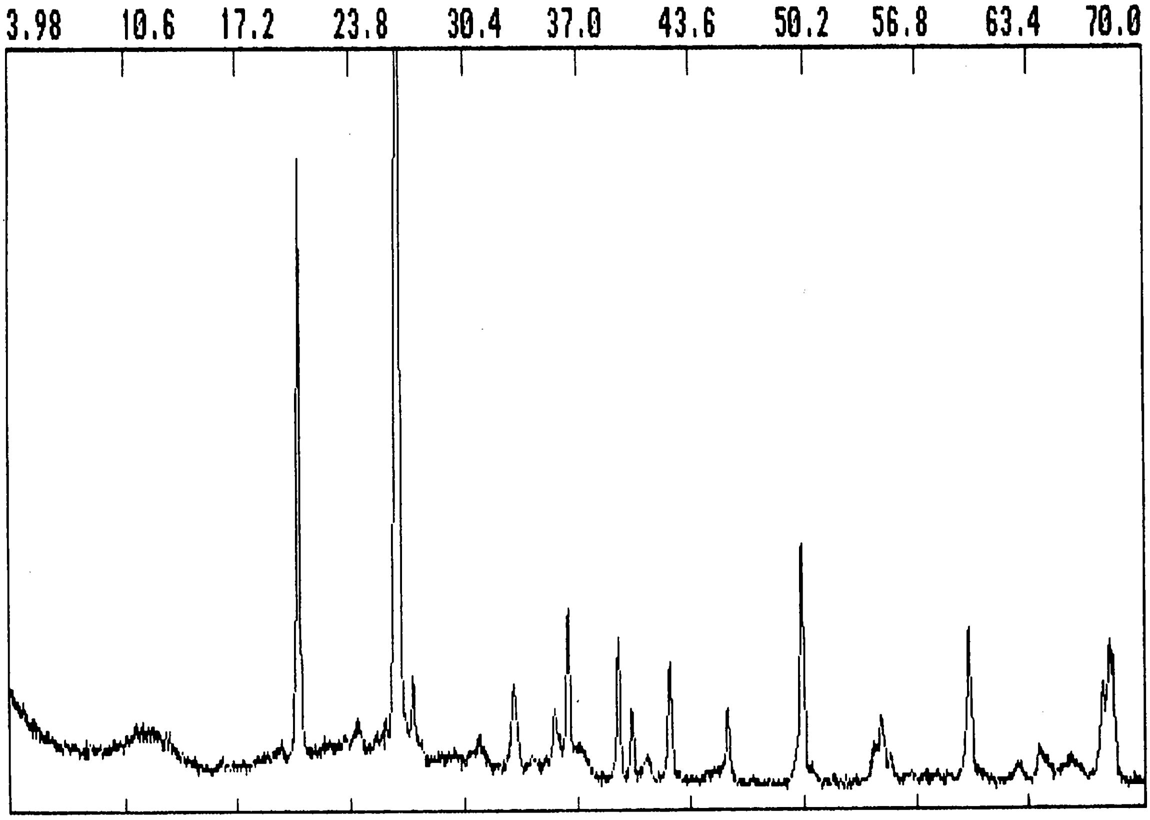


Fig. 6

GRES - 3

1.065º

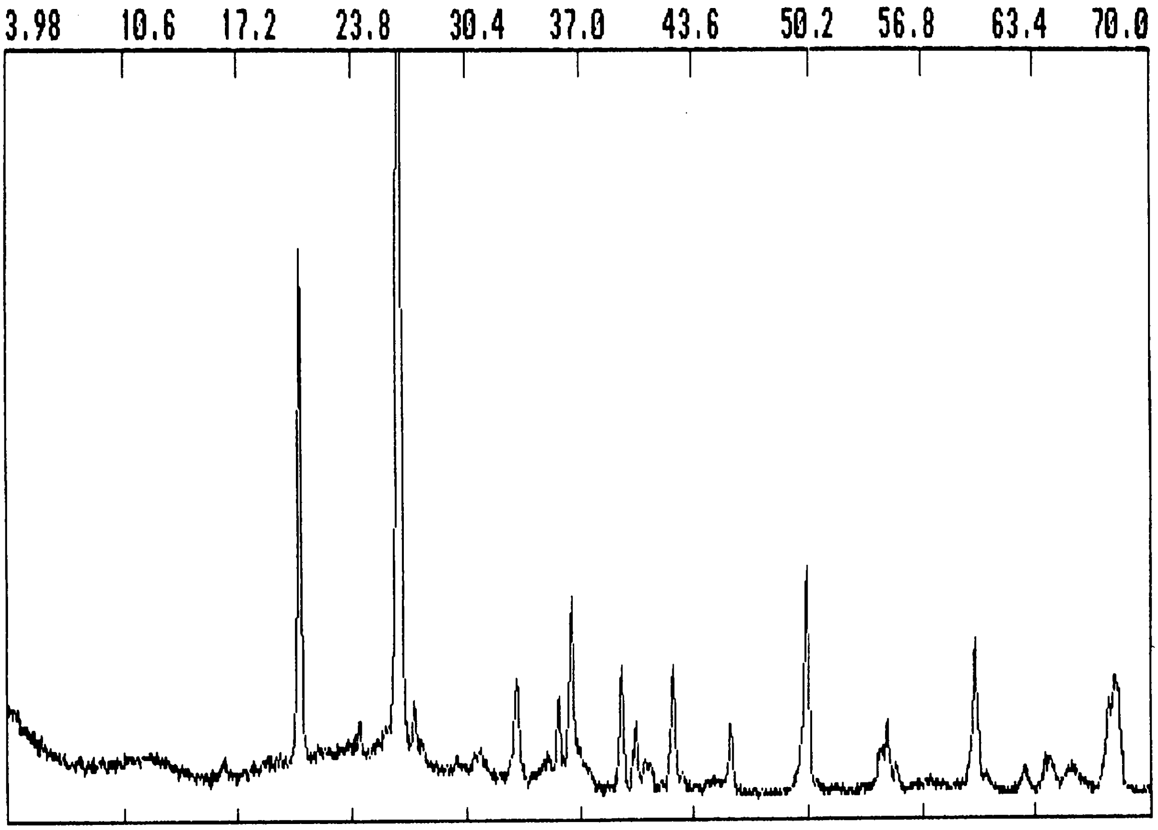


Fig. 7

GRES - 2

1.110º

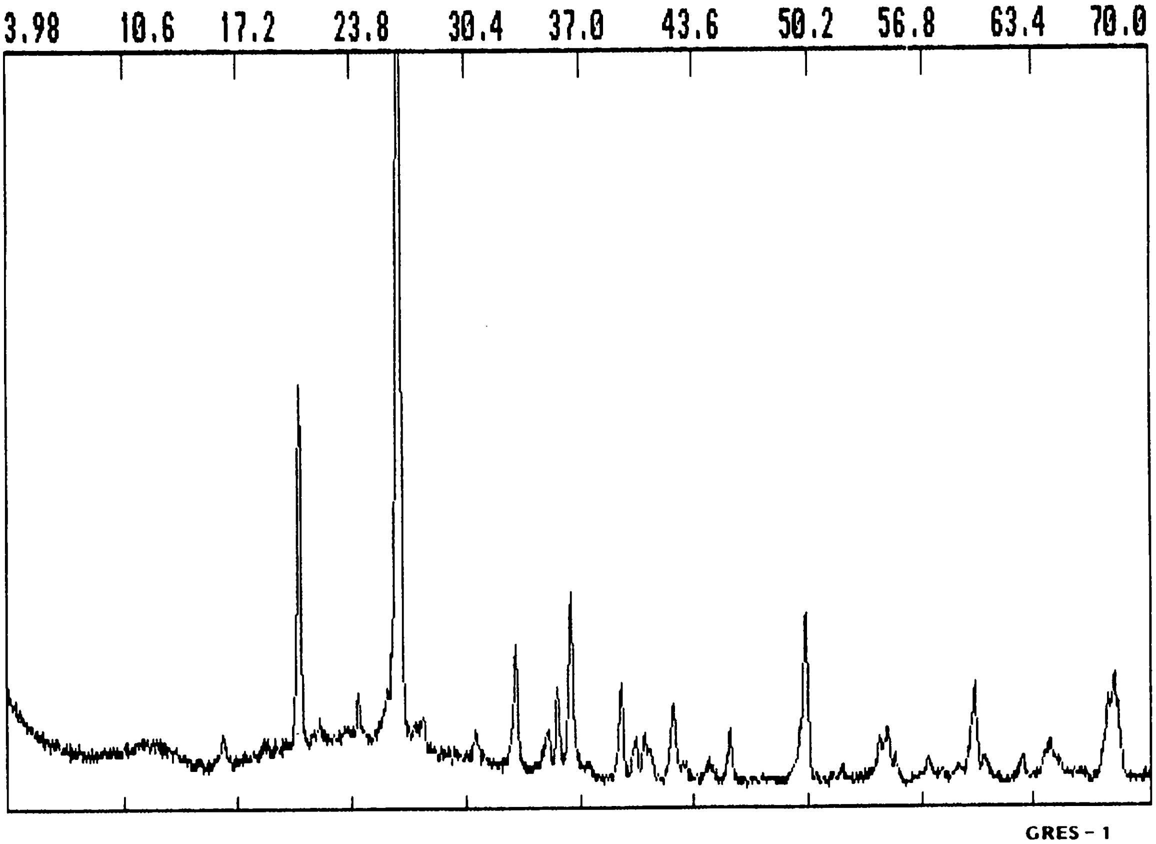


Fig. 8

GRES - 1

1.160º

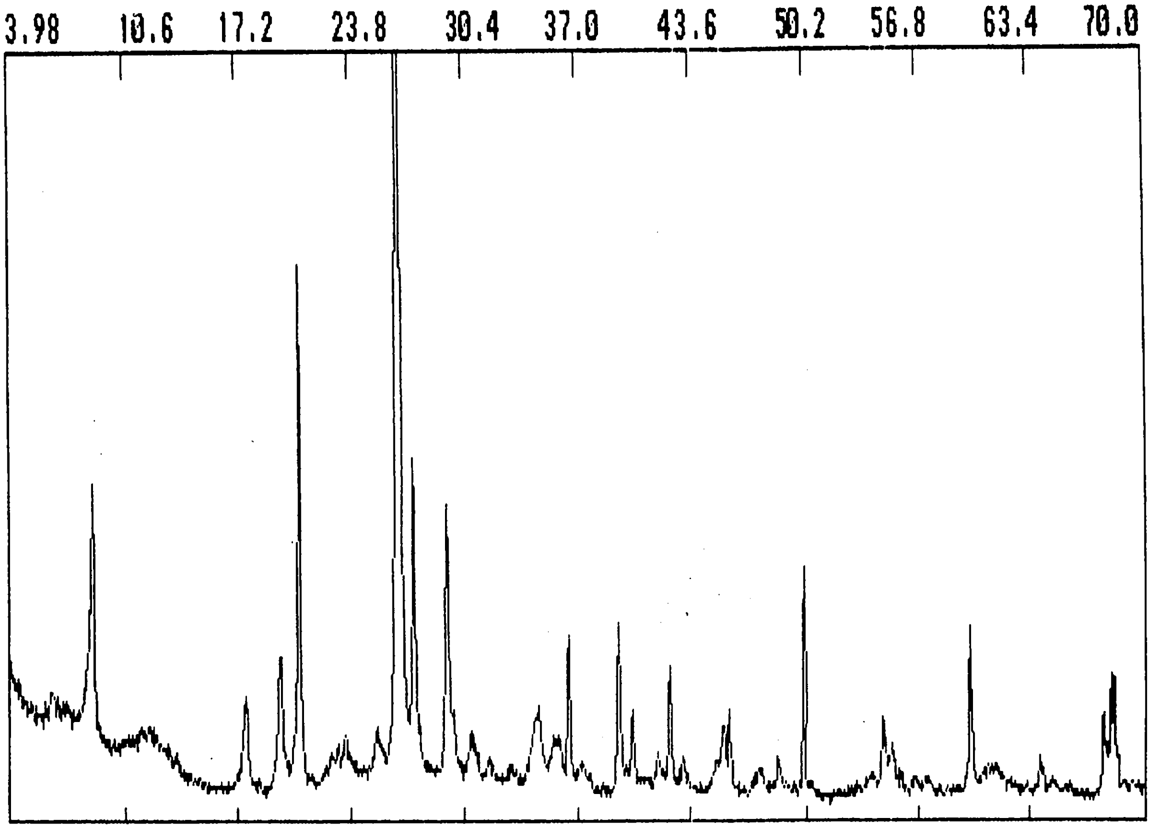


Fig. 9

POROSO - 8

860º

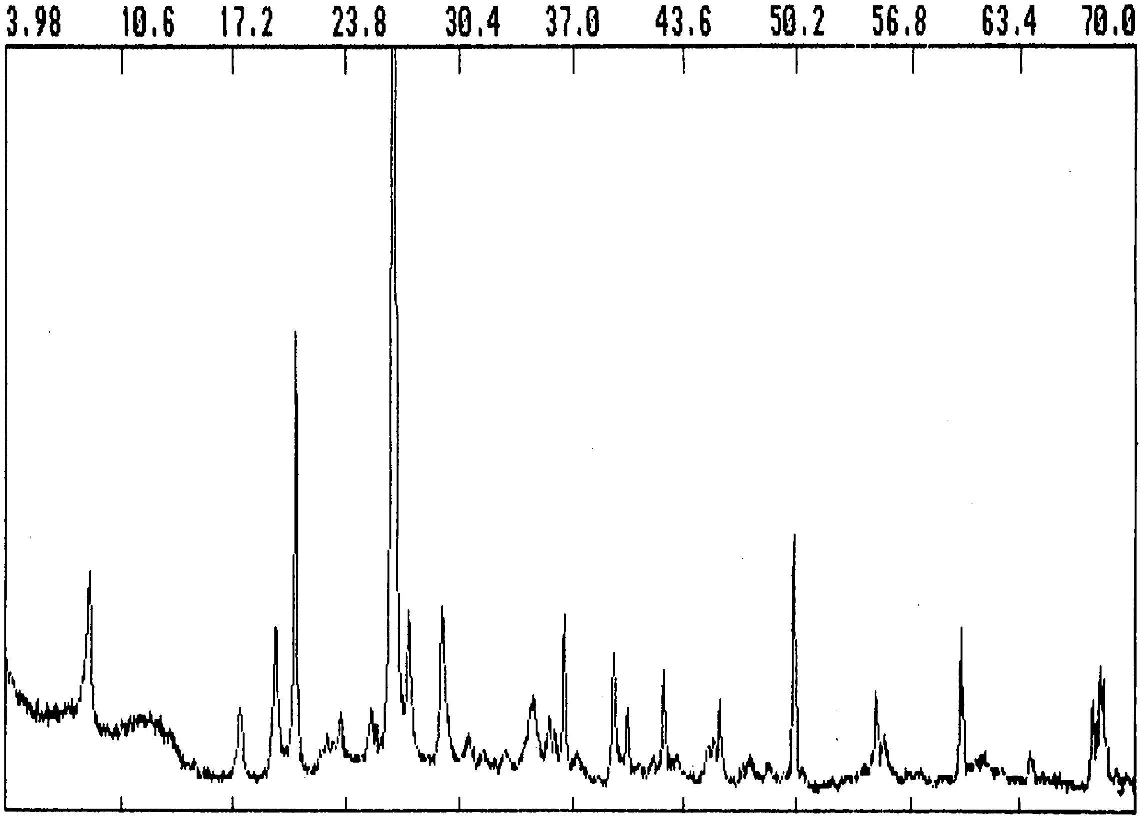


Fig. 10

POROSO - 7

892º

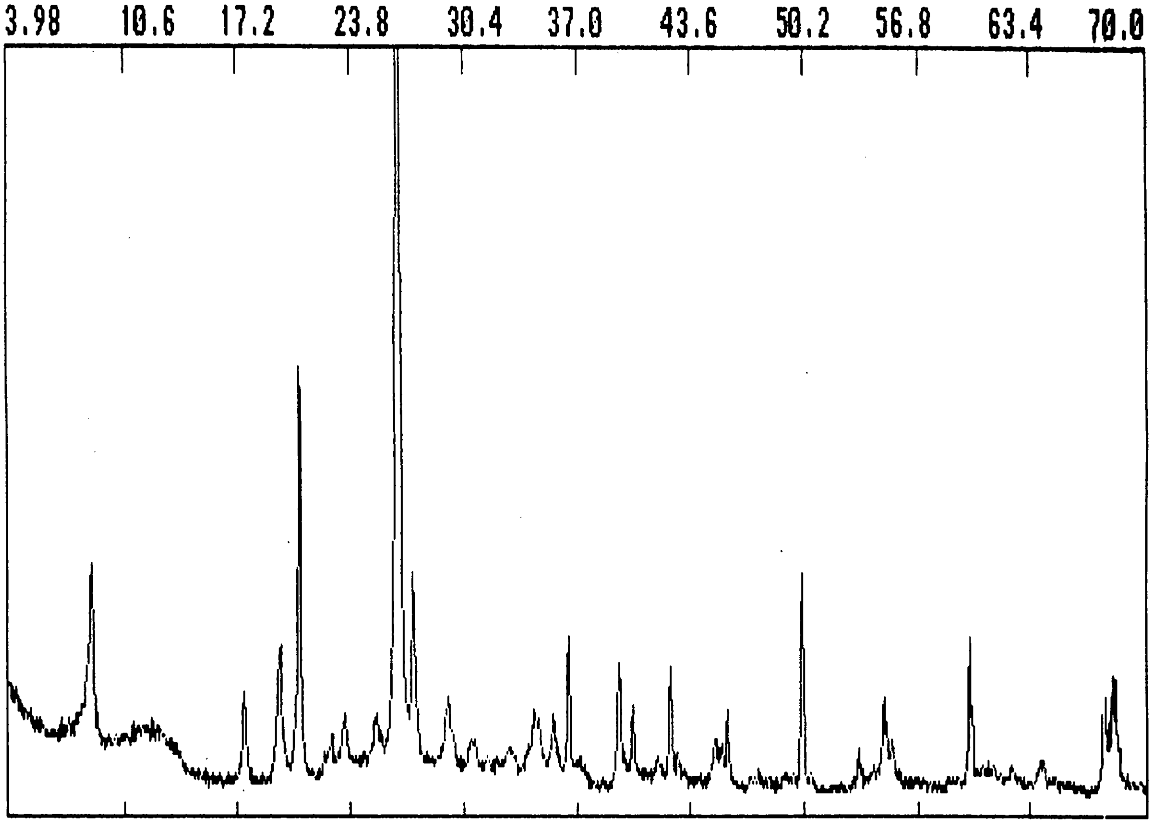


Fig. 11

POROSO - 6

927º

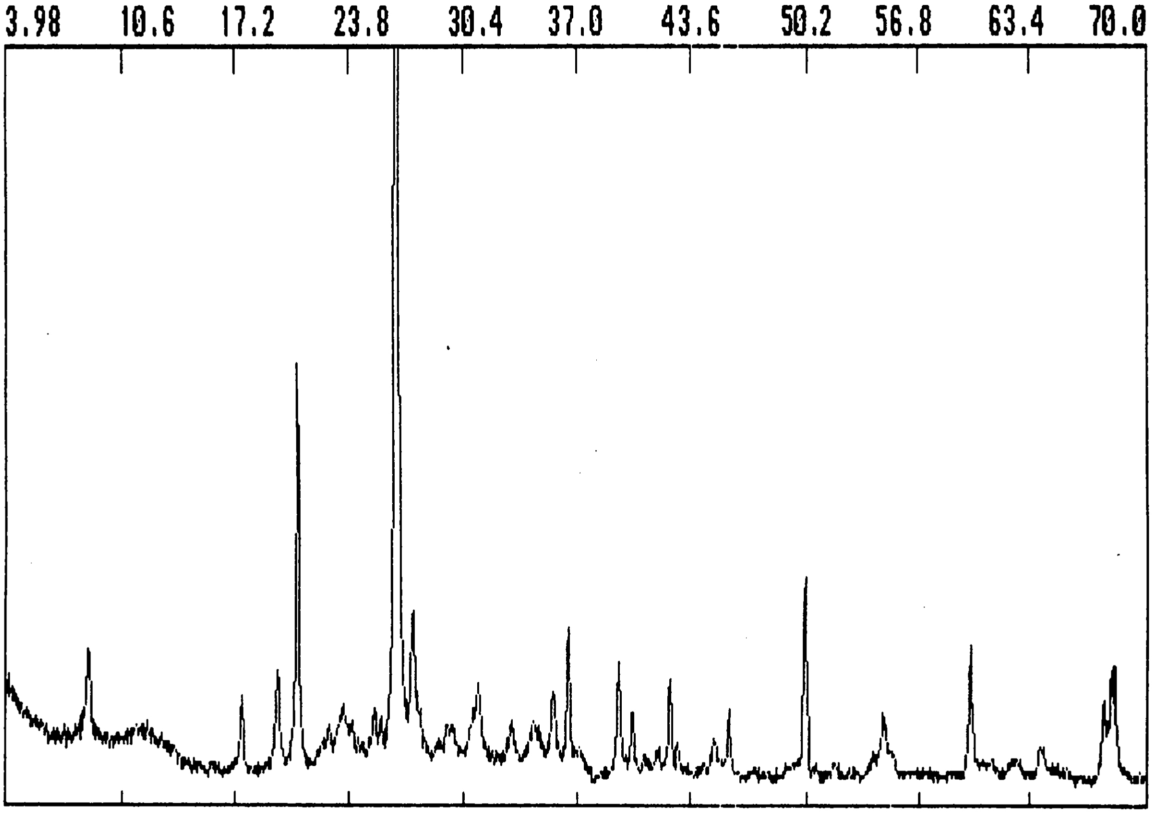


Fig. 12

POROSO - 5

975º

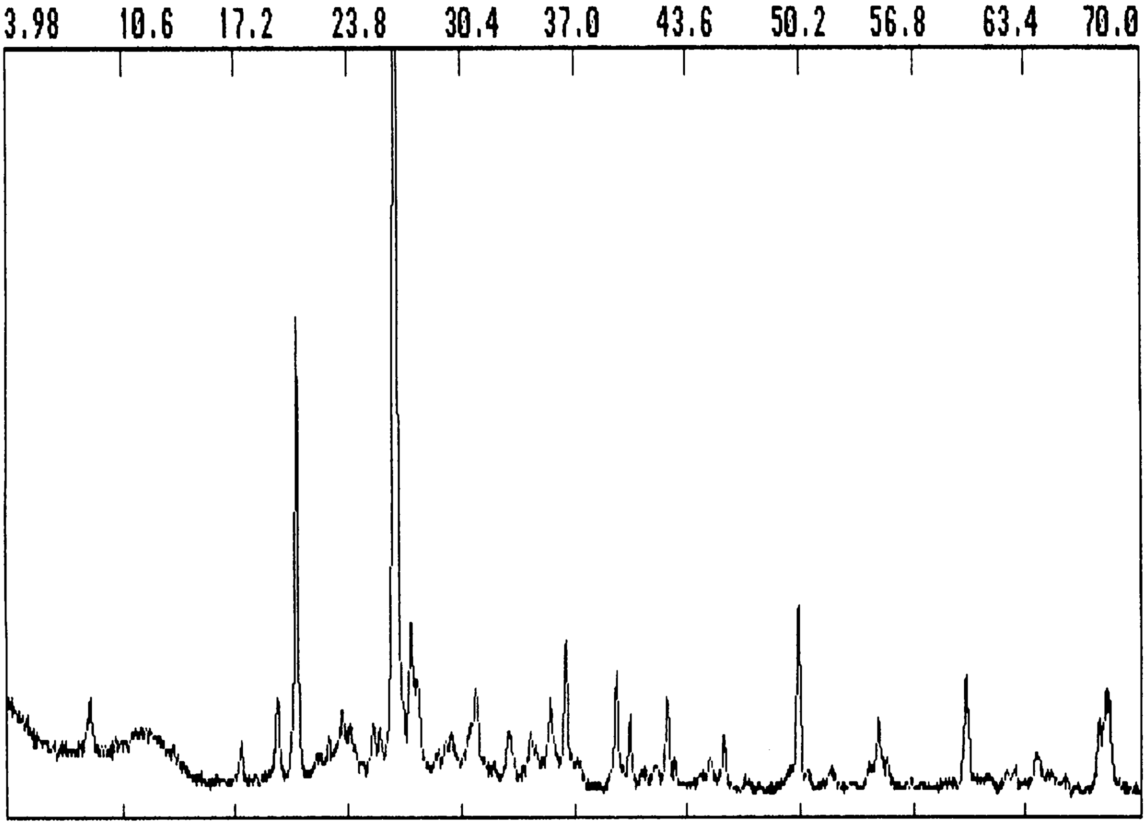


Fig. 13

POROSO - 4

1.025º

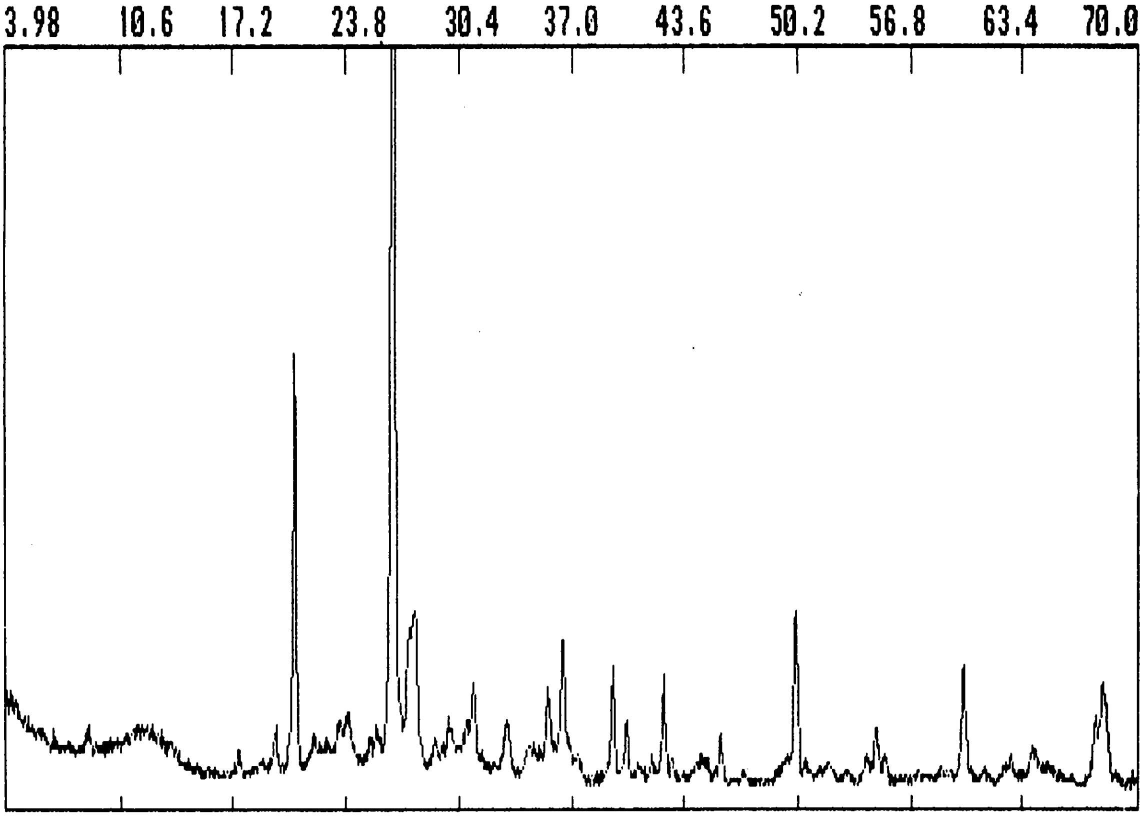


Fig. 14

POROSO - 3

1.065º

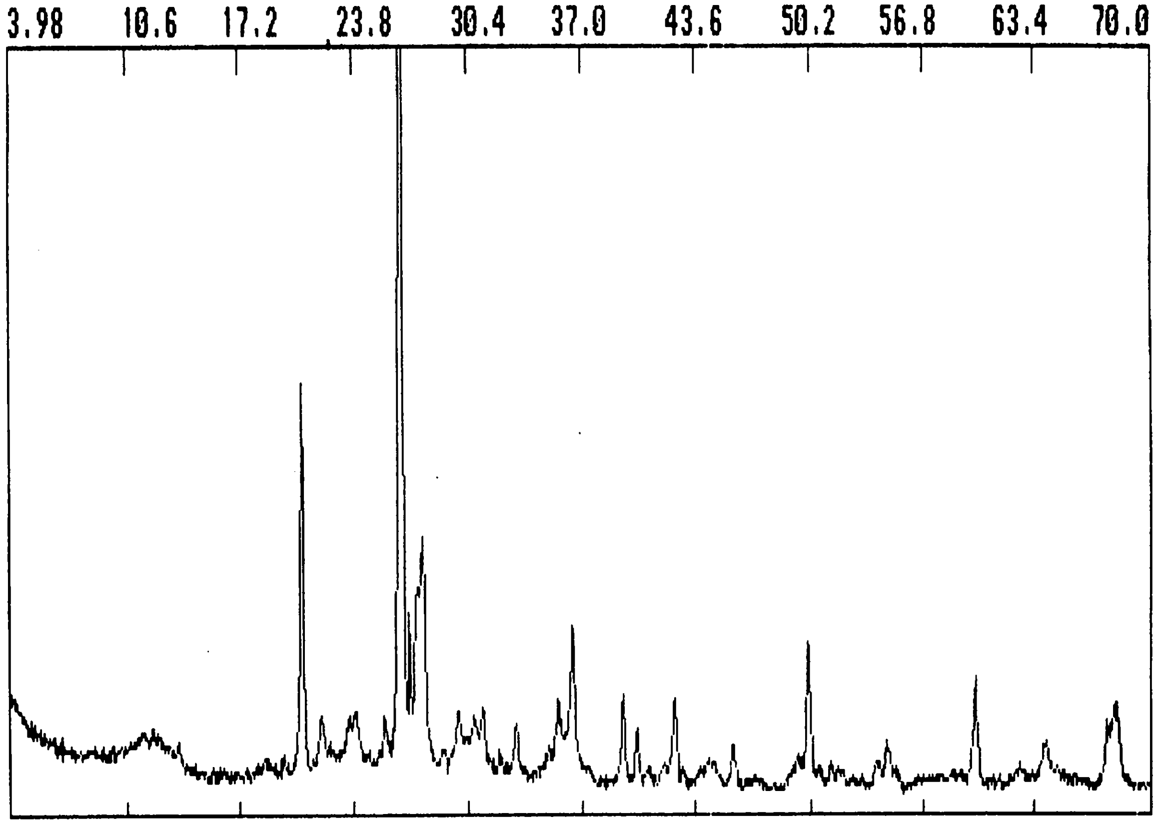


Fig. 15

POROSO - 2

1.110º

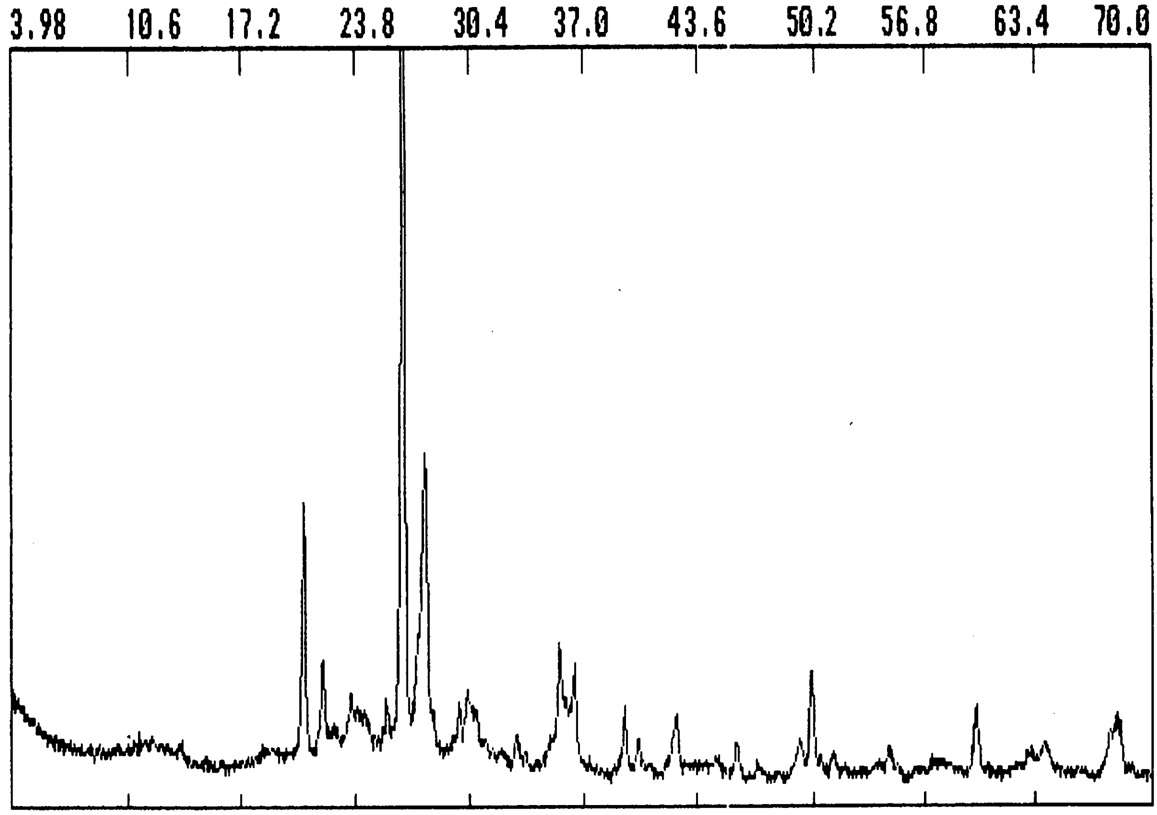


Fig. 16

POROSO - 1

1.160º

CLAY FOR GRES

CHEMICAL ANALYSIS - The results are expressed in percentages and refer to the dry weight of the samples, after having been heated at 110°C for 24 hours.

SiO2	64.09
TiO2	0.89
Al2O3	17.83
Fe2O3	4.90
MgO	1.28
CaO	1.40
Na2O	0.37
K2O	2.88
L.O.I.	6.06

PLASTICITY - Test carried out with TONNITEKNIC apparatus, following the nfefferkorn method, the result was: 18.31

CALCIUM CONTENT - (CO3Ca form): 2.43%

ORGANIC MATERIAL: 0.091%

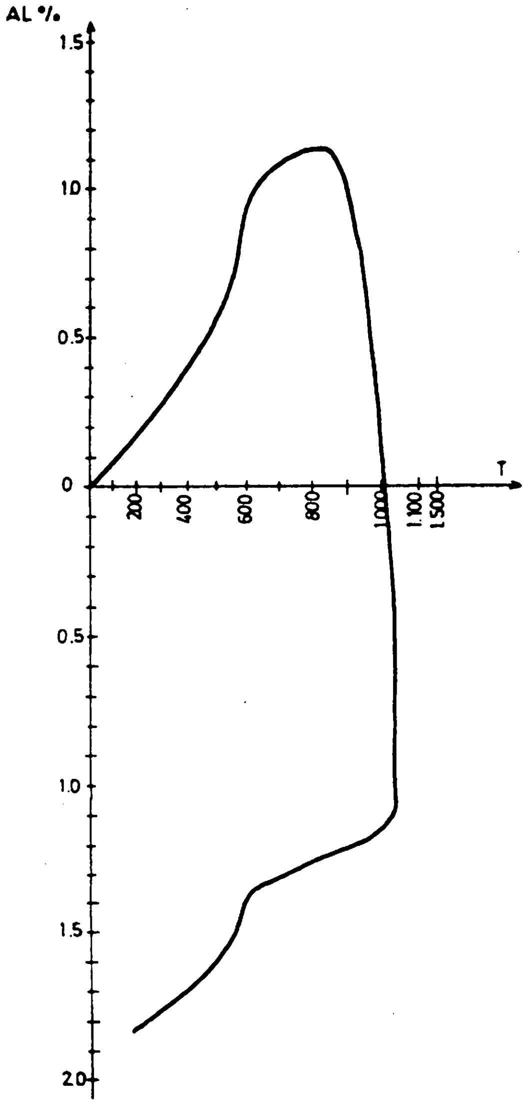
60 MICRONS SCREENING: 7.10 %

Mesh Aperture	%	CO3Ca
177	1.97	-
120-177	16.37	4.22
120	81.66	2.85

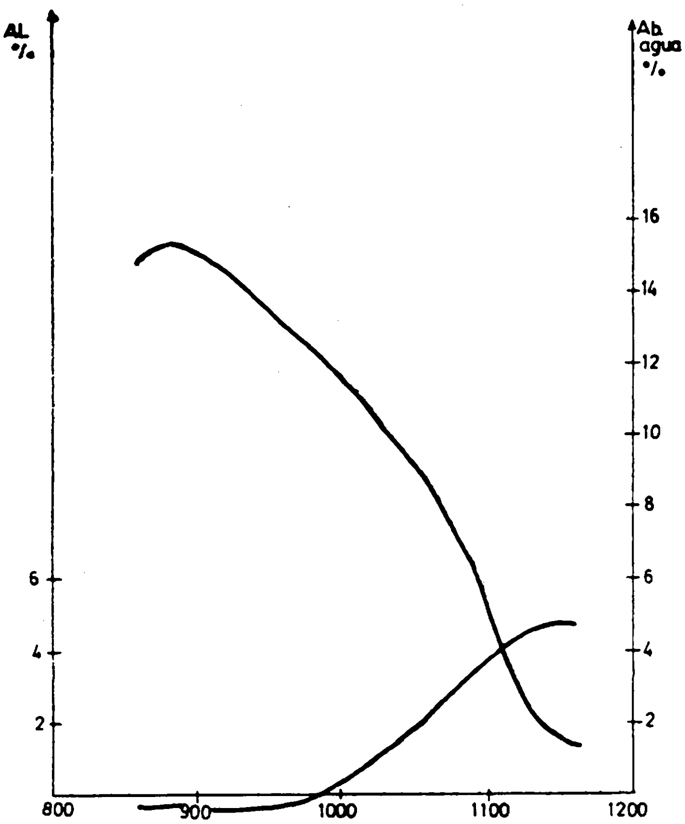
DILATION COEFFICIENT DETERMINATION:

Linear average (between 20 and 100°C):	6.5 x 10-6/°C
Linear expansion (at 300°C):	77.6 x 10-7/°C
Cubic expansion (at 300°C):	232.8 x 10-7/°C

CLAY FOR GRES

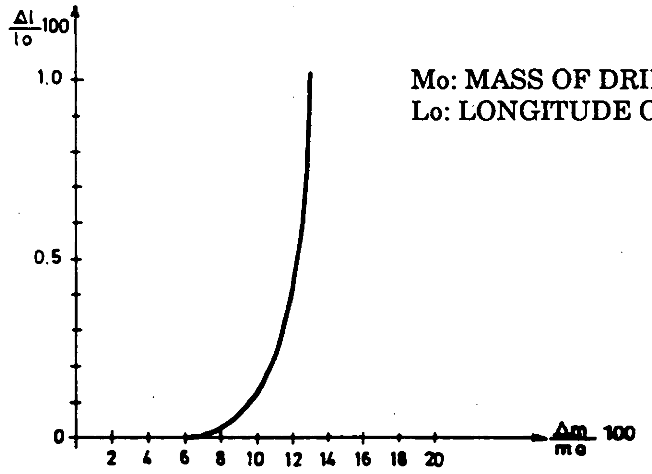


DILATOMETRY



Tª C	900	950	1000	1050	1075	1100	1125	1150
AL%	-0.38	-0.40	-0.32	-1.82	-2.75	-3.70	-4.48	-4.78
ab. agua %	15.15	13.58	11.65	9.22	7.45	5 20	2.65	1.50

GRESIFICATION



Mo: MASS OF DRIED SAMPLE
Lo: LONGITUDE OF DRIED SAMPLE

DRY SHRINKAGE RECORDING

Fig. 17

POROUS CLAY

CHEMICAL ANALYSIS - The results are expressed in percentages and refer to the dry weight of the samples, after having been heated at 110°C for 24 hours.

SiO2	55.95
TiO2	0.67
Al2O3	16.71
Fe2O3	4.25
MgO	2.79
CaO	5.72
Na2O	0.32
K2O	3.34
L.O.I.	9.73

PLASTICITY - Test carried out with TONNITEKNIC apparatus, following the nfefferkorn method, the result was: 20.59

CALCIUM CONTENT - (CO3Ca form): 9.64%

ORGANIC MATERIAL: 0.24%

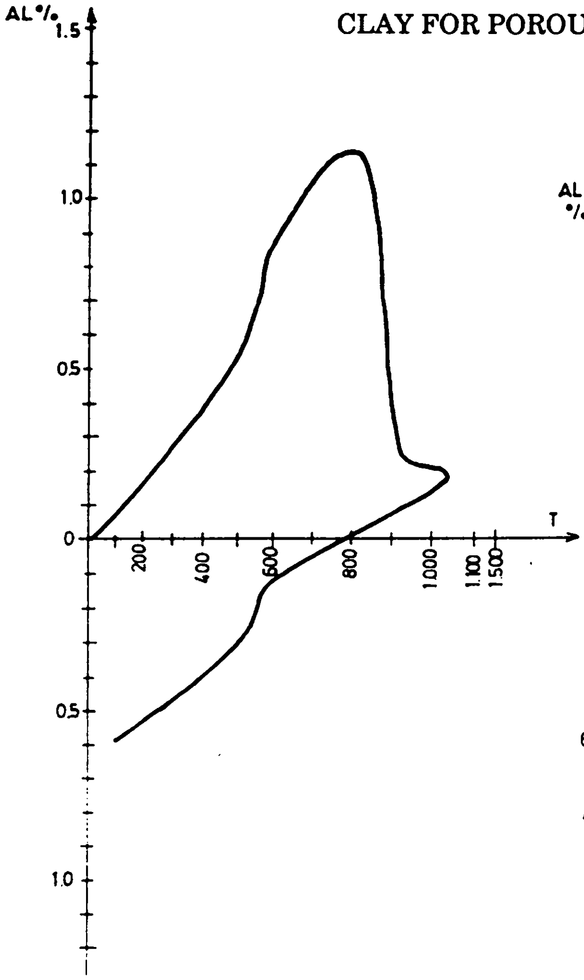
60 MICRONS SCREENING: 3.7%

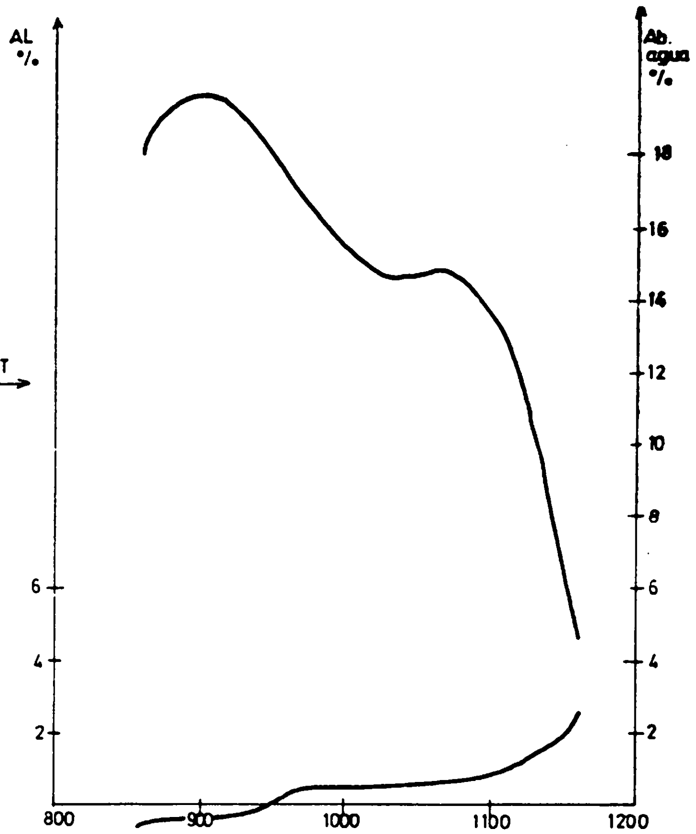
Mesh Aperture	%	CO3Ca
177	2.07	-
120-177	18.91	7.06
120	79.02	5.91

DILATION COEFFICIENT DETERMINATION:

Linear average (between 20 and 100°C):	6.6 x 10-6/°C
Real line (at 300°C):	79.3 x 10-7/°C
Cubic (at 300°C):	237.8 x 10-7/°C

CLAY FOR POROUS PASTE

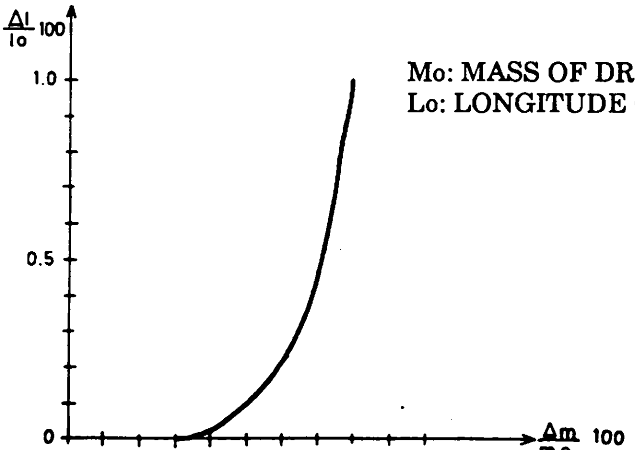




T° C	900	950	1000	1050	1075	1100	1125	1150
AL %	-0.43	-0.05	0.42	0.50	0.58	0.78	1.12	1.95
ab. agua %	19.69	17.90	15.48	14.71	14.71	15 55	10.90	6.60

DILATOMETRY

GRESIFICATION



Mo: MASS OF DRIED SAMPLE
Lo: LONGITUDE OF DRIED SAMPLE

DRY SHRINKAGE RECORDING

Fig. 18