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THE RETENTION OF ORGANIC AND INORGANIC COMPOUNDS ON CLAY MINERALS

Part I : Basic Studies on Attapulgus Clay

by

H. NORDMEYER

1966

ORGEL Program

Joint Nuclear Research Center
Ispra Establishment - Italy

Chemistry Department
Organic Chemistry Service

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With regard to organic reactor coolant purification a fundamental characterization of Attapulgus clay is given, summing up literature data as well as completing these data with an intensive study on the behaviour of natural and technically activated Attapulgus clay samples at elevated temperatures.

Chemical analysis, granulometry, mineralogical composition and crystal structure of the clay and clay components are reported. Thermal dehydration and phase changements with rising temperature have been followed by D.T.A., T.G.A., X-rays and electron micrographs. The influence of thermal activation on the dehydration process, on cation adsorption and specific surface areas is demonstrated. Observations on terphenyl - clay contacts and Attapulgus grain stability are given.

General Introduction

Polyphenylic mixtures are used as coolants in the organic cooled OMRE- and ORGEL-type reactors. In order to maintain the desired high purity of the coolant, continuous purification is necessary to remove the impurities which have been formed by pyrolytic and radiolytic processes from the coolant itself (heavy polymeric species, radioactive matter), by gas contacts (oxygen) and by corrosion of the loop materials (inorganic matter in dissolved and particulate form). Especially the removal of organic and inorganic fouling constituents or promoters is of extreme importance for the success of the organic cooled reactor concept. Particulate matter can be taken out by filtration. But dissolved molecular species, such as organic oxygen compounds, unsaturated organic compounds, soluble iron or other metals, must be removed by sorption and/or chemical reaction mechanisms.

This series of reports treats the possibilities of the use of clay minerals and related species for the removal of the above mentioned compounds. In order to obtain a reliable and economic performance, such clay materials should have a sufficiently high sorption capacity (especially in the desired temperature range between 250-350°C), good qualities for column employment as depends on granulometry, porosity and swelling properties, a good mechanical, chemical and thermal resistance, a low cost-price and easy and inexpensive regeneration and disposal possibilities.

A material combining all these properties is difficult to find, the more as the mechanism of retention in polyphenylic medium is not completely understood. Some experience with a natural clay, Attapulgus clay, had already been gained at OMRE and AECL (e.g. DUERKSEN and CHARLESWORTH, 1963). It was decided to start own investigations with this material in order to understand the mechanism of removal.

Since understanding of the problem is impossible without thorough knowledge of the material used, a basic study of Attapulgus clay is of great importance. The first report in this series tries to give a fundamental characterization of the clay, including literature data as well as recent research work. Other reports will treat the retention capacity of Attapulgus clay for iron, polar organic substances and high boilers.

R. Lopes Cardozo H. Nordmeyer

H. Nordmeyer :

BASIC STUDIES ON ATTAPULGUS CLAY

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The author likes to express his thanks to Mr. S. Paracchini for many sample preparations and for his skilful painting of the diagrams included in this report, and to all people in the EURATOM Ispra laboratories, who have given their useful help to this study.

1. USE AND ORIGIN OF ATTAPULGUS CLAY

Attapulgus clay is well known under the name "Fuller's earth" for numerous industrial applications, mainly for decolorizing, dehydrating, deodorizing, neutralizing of oils, gases and liquids, cracking of hydrocarbons, as catalyst and catalyst support in the petroleum industries, as drilling mud component in oil wells, chromatographic adsorbent, diluent for insectizide dust, etc..

The main component of Attapulgus clay is a hydrous magnesium aluminium silicate, the clay mineral "attapulgite". Its name is derived from the deposit at Attapulgus/Georgia/USA by deLAPPARENT (1935). It belongs to the palygorskite group of minerals whose members seem to be more or less identical in their properties, so that CAILLÈRE and HÉNIN (1961) proposed to consider the names "palygorskite" (SSAFTCHENKOV 1862, FERSMANN 1913), "pilolite" (HEDDLE 1879), "lassalite" (FRIEDEL 1907) and "attapulgite" as synonyms.

Other palygorskite deposits (but mainly in form of mineral accessory) are reported from Gadsden County/Florida/USA (McCARTER et al. 1949), Bakkasetter/Shetland Isles (STEPHEN 1954), Dornboom/South Africa (HEYSTEK and SCHMIDT 1954), Mormoiron (deLAPPARENT 1935) and Meyssonial en Mercoeur/Upper Loire/France (LACROIX 1910), Can Pey/Eastern Pyrenees/France (LACROIX 1910), Taodeni/Algeria (CAILLÈRE 1934), Tafraout/Marocco (CAILLÈRE 1951), Permsk and Dogniaska/USSR (FERSMANN 1913) and Nizhnii-Novgorod/USSR (CAILLÈRE 1936). GRIM (1963) reports almost pure attapulgite deposits from West Central India.

Attapulgite may have formed in nature by sedimentary (Attapulgus/Ga., KERR 1937) or hydrothermal processes (Tafraout/Alg., CAILLÈRE 1951), sometimes derived from pyroxenes and amphiboles (LONGCHAMBON 1935).

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2. CRYSTAL STRUCTURE AND FORMULA

Several authors tried to give a description of the attapulgite structure (CAILLÈRE 1934, KERR 1937, deLAPPARENT 1936, LONGCHAMBON 1938, NAGELSCHMIDT 1938). Attapulgite was first regarded as a kind of mica mineral, but under the electron microscope the fibrous form of the small individual crystallites can be seen very well (MARSHALL et al. 1942, DAVIS et al. 1950, see also the electron micrographs in this report). At present, the structural scheme of attapulgite as predicted by NAGELSCHMIDT (1938) and proposed by BRADLEY (1940) is generally accepted (see figure 1).

The attapulgite unit cell consists of two silicate chains - like in amphiboles - running parallel to the crystallographic c-axis and linked together on either side of the oxygen sheets by Al-, Mg- and Fe-atoms in octahedral coordination. These octahedral parts are similar to the octahedral layers in the layer clay minerals, but continue in one direction only. Open sites are completed with OH groups, giving the bound water, OH_2, on edge positions. Between silicate chains and octahedral parts channel-like interstices are running parallel to the c-axis, filled up with water molecules. The fixed diameter of these zeolitic cavities is given by CAILLÈRE and HÊNIN (1961) with 4 x 6,5 Å and by JASMUND (1955) with 3,7 x 6 Å. There is no swelling property as with the montmorines. A certain cleavage is observed parallel (110). The cell dimensions by BRADLEY are $a.\sin\beta = 12{,}9$ Å, $b = 18$ Å, $c = 5{,}3$ Å, space group probably C^3_{2h} - C 2/m. X-ray powder data with observed and calculated intensities see table 1. The ideal formula for the half unit cell is

$$Si_8\ Mg_5\ O_{20}\ (OH)_2\ (OH_2)_4 \cdot 4\ H_2O$$

where hydroxyl (OH), bound water (OH_2) and zeolitic water are distinguished. The structure is balanced. Only a small substitution rate of Al^{3+} for tetrahedral Si^{4+} is expected. CAILLÈRE and HÉNIN calculated from chemical analysis the following formula for attapulgite from Attapulgus/Ga.:

$$(Si_8)(Al_{1,68}Fe^{3+}_{0,40}Fe^{2+}_{0,03}Ti_{0,08}Mg_{2,15})O_{19,58}(OH)_{4,49}(OH_2)_{1,93}Ca_{0,35}$$

3. NOMENCLATURE OF PRODUCTS USED

For scientific purpose natural attapulgite from Attapulgus/Ga. is available as Clay Mineral Standard no.44 from Ward's Natural Science Establishment Inc., Rochester 3, N.J./USA, P.O.Box 1712. In our research work this material - under the designation "ATTAPULGITE" - has been taken as a true natural reference sample in contrast to the technical pretreated material and for comparison with the results from other authors reported in literature.

Because of its very low medium grain size and hence colloidal behaviour, natural attapulgite can be employed in columns only if brought into an aggregated and granulated form. Granular Attapulgus clay for technical application is normally produced by crushing the natural raw clay in roll crushers, drying it in oil-fired rotary dryers (thus inducing a certain thermal activation) and milling it to the desired mesh sizes. It is furnished by several firms. We took it from the Minerals and Chemicals Philipp Corporation, 20 Essex Turnpike, Menlo Park, N.J./USA. Among different qualities available under designations as "Attasorb", "Attaclay","Attagel", "Attacote", etc., we chose a granular 24-48 mesh (Taylor screens) Attaclay, in this report under the name "ATTAPULGUS", and for comparison in special cases "Attagel 20", a very fine grained product, in the following reported under "ATTAGEL". (The term "attapulgite" will be used for the mineral, which forms the main component of Attapulgus clay.).

4. CHEMICAL ANALYSIS

Chemical analyses of ATTAPULGITE, ATTAPULGUS and ATTAGEL have been done in our Ispra laboratories by Mr. J. COLLIN and co-workers*), using wet chemistry, spectral and flame photometric methods. The results are given in table 2a and on volatile-free basis in table 2b. Additional analysis taken from literature and from the Minerals and Chemicals Philipp Corp. are presented. Table 2c gives the trace element content of the clay, detected with X-ray fluorescence and emission spectrography by Mr. G. VOS and Mr. Z. HAINSKI*).

5. GRANULOMETRY

5.1. Methods

Fractionation of aggregated attapulgite and grain size distribution measurements of the accessory minerals have been done above 63 µ ø by wet sieving (DIN 4188, standard logarithmic scale) and below 63 µ ø by sedimentation analysis (Atterberg method).

The electron microscope (Siemens equipment) has been employed**) for the detection of shape and size of attapulgite single crystals in the <2 µ ø fractions, using sedimentation preparates on collodium films.

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*) Analytical Chemistry Section

**) in collaboration with Mr. E. RUEDL, Physico-Chemistry Section

5.2. Aggregation and dispersion

For every Attapulgus clay sample it was found, that all attapulgite particles which can be seen, even those under the polarization microscope, that means down till dimensions of 2 μ Ø, are not single crystals but aggregates, of more or less uniform habit and nearly isometric shape (see plate 1-6). Fibrous single crystals occur in the <2 μ Ø fractions, but besides one also finds a lot of aggregates in the finest fractions. Two kinds of aggregation can be distinguished on electron micrographs (see plate 8). Aggregates showing strong parallel orientation of fibres seem to be primary and originally present in the sediment, while those resulting from the quick flocculation in prepared suspensions have a more unoriented texture. The fibrous shape of the attapulgite crystallites favours the collision and tangling of primary particles. But the main influence on coagulation results from the exchangeable cations present on the clay, their ionic hydration, valency and concentration, varying the zeta potential (MARSHALL 1949). Divalent ions, for instance, are less hydrated and coagulate at much lower concentrations than the monovalent do. From solubility tests (see chapter 10) we know, that mainly Ca^{++} and some Mg^{++} and K^{+} are exchangeable from Attapulgus clay. For the coherence of the larger ATTAPULGUS grains, however, silice seems to be responsible, as discussed in chapter 10.3.2.

In order to recognize the dimensions of single crystallites from all samples, it was necessary to bring aggregates into suspension. This was only possible employing Na^{+} as exchangeable cation and working in very diluted suspensions. The best dispersion was reached after shaking a sample with 0,1 n NaCl for 16-20 hours in a rotary shaking machine, followed by ultrafiltration and washing with distilled water on the membran filter. Other suspending agents well known in clay research have also been tried: 0,01 n NH_4OH led to flocculation especially in the <2 µ Ø region; 0,002 m $Na_4P_2O_7 \cdot 10\ H_2O$ was successful, but not identifiable impurities remained in the dried suspensions, which could not be used for electron microscope preparations afterwards.

5.3. Grain size distribution

ATTAPULGUS 24-48 mesh as furnished consists of aggregated particles only (plate 1). Aggregation is favoured by the technical procedure described above (chapter 3). The granulometry is fixed by the producer. 24-48 mesh of the Taylor sieve system correspond to 701-295 µ Ø. But by handling, shipping and transportation a certain breakdown of grains can be observed. Therefore, for all estimations and research operations a well-defined sieve fraction was taken from the material by wet sieving technics. The fraction 630-200 µ Ø has been chosen as a usual member of the logarithmic scale from DIN 4188, well suited for column work. Further fractions <63, <6,3 and <2 µ Ø have been prepared for T.G.A. and electron microscope work.

The dimensions of attapulgite single crystallites have been measured on electron micrographs (except the third dimension, which could not be measured without shadowing). Table 3a presents a rough size distribution for length and width of attapulgite fibres in ATTAPULGITE and ATTAPULGUS samples. For comparison literature data are added, demonstrating the size distribution in a < 2 µ Ø centrifuge fraction by MARSHALL (1947). The medium fibre length in the technical pretreated ATTAPULGUS as well as in the centrifuge sample is much shorter than in not pretreated ATTAPULGITE. Probably, centrifugation and other mechanical treatment cause a certain breakdown of the attapulgite needles.

The granulometry of ATTAGEL is in the range of 2-0,02 µ Ø, with its maximum at 0,1 µ Ø grain size, obtained after centrifugation by the Minerals and Chemicals Philipp Corporation.

6. MINERALOGICAL COMPOSITION

6.1. Methods

The mineralogical composition of the Attapulgus clay samples has been estimated with the polarization and phase contrast microscope and by X-ray diffraction methods. Microscope work was possible with the fractions above 2 µ Ø, using buthylcarbitol, o-nitro-toluol, anethol and o-toluidin as immersion liquids with a refractive index of n = 1,430, n = 1,544, n = 1,562 and n = 1,572 respectively. For quantitative analysis 3-4 preparations have been done for every grainsize fraction, counting as a minimum 400 particles per preparate.

For the X-ray performances of the fine clay fractions powder preparations have been preferred, as the needle-like attapulgite structure gives no favourable textural effect. Ethylene glycol and glycerol preparates were useful for the swelling clay minerals detection.

Semiquantitative estimations of the main components - attapulgite, montmorillonite, quartz - have been done by X-ray diffraction using the inner standard method and, especially for montmorillonite, by calculating the results of the ethylene glycol specific surface measurements (chapter 8.3.).

6.2. Clay minerals

All Attapulgus clay samples, the standard as well as the technical material, are heterogeneously composed mineral mixtures although their chemical analysis are looking rather uniform. The semiquantitative mineral composition of ATTAPULGITE, ATTAPULGUS and ATTAGEL is given in table 3.

The main mineral, of course, is attapulgite with about 50%. X-ray powder data for attapulgite obtained from all three Attapulgus clay samples under investigation are in good agreement with each other and with the data presented by BRADLEY (see table 1).

The second clay mineral present in a remarkable amount between 10 and 20% is a montmorillonite, which was discovered by its swelling properties with ethylene glycol and glycerol and could clearly be distinguished from attapulgite and other minerals on the X-ray diffraction powder patterns (figure 4). Its (001)-reflexion for the ATTAPULGITE sample lies on 15,7 Å, with ethylene glycol on 17,5 Å, with glycerol on 17,8 Å and after heating to 400°C on 9,5 Å. On ATTAPULGUS powder patterns the first montmorillonite reflexion coincides with the very strong attapulgite (110) at 10,5 Å. This behaviour is due to the thermal activation given to the material by the producer. The swelling mechanism is still intact. The presence of this montmorillonite in all samples is of great importance for the adsorption process, because it is the only important accessory mineral with remarkable adsorption properties but with a much more different adsorption behaviour than attapulgite.

The grain size of the montmorillonite single particles is between 0,25 and 0,05 µ Ø. These are the dimensions of all the more or less well crystallized hexagonal platelets occuring among the attapulgite needles on the electron micrographs. However, by X-ray and D.T.A. also a minor amount of kaolinite has been detected, which crystallizes with the same habitus as montmorillonite. Montmorillonite, normally, occurs less well crystallized than kaolinite. But it is difficult in the present case to distinguish between the two clay minerals on the electron micrographs. The accessory kaolinite content in ATTAPULGUS is about 3% only.

6.3. Accessory minerals

Figure 2 and table 4 show the grain size distribution of the accessory non clay minerals. Among them the detritic quartz has the highest quantity in all samples and fractions. The ATTAPULGITE sample shows a strong quartz maximum in the 63-20 µ Ø fraction, but there are two maxima for ATTAPULGUS, certainly due to the raw materials dressing process. Feldspar is present as ortoclase and microcline with about 10% and has its maximum also between 63 and 20 µ Ø. Calcite is restricted to <1% and was found in the 200-63 µ Ø fraction only. The quantities estimated optically are in good agreement with the CO_2-content from the chemical analysis (table 2). Further accessory minerals gathered under "others" are a few mica platelets (muscovite), some heavy minerals and not identified particles.

6.4. Iron

Only a small part of the iron content in Attapulgus clay products is bound within the crystal lattice in the form of an isomorphous replacement of ions such as Mg^{++} and Al^{+++} in the octahedral layers of the silicate clay minerals or on other lattice positions. Most of the iron occurs free as amorphous ferric hydroxide films and crystallized α-ferric oxide monohydrate clouds (goethite) on the surface of alterating feldspars and clay aggregates, or sometimes concentrated into special iron concretions (counted as "iron minerals" under the microscope). In the course of time, but more quickly by heat treatment, beginning at 250-300°C, the yellow-brown goethite is changing to red hematite, α-Fe_2O_3. From this behaviour results the much higher hematite content of the preheated ATTAPULGUS. The presence of lepidocrocite, γ-FeO(OH), was thought possible but is without proof.

7. THERMAL DEHYDRATION AND PHASE CHANGEMENTS

As already mentioned above, the working temperature for terphenyl used as reactor coolant is in the 350-410°C range and the coolant purification has to take place also at about 250-350°C. For this reason, but also in respect to activation and regeneration procedures, it is necessary to know very well the behaviour of the purification clay at rising temperature, whether and to what extent there are reversible and/or irreversible dehydration reactions, what changes and modifications the crystal structure undergoes and where its stability limits are.

Differential thermal analysis seems to be the best way to follow and to register endothermic and exothermic reactions of a clay heated continuously at a certain constant heating rate to a desired end temperature. Qualitative D.T.A. has, therefore, been done till 1150°C for the Attapulgus clay samples, giving temperature position and character of each registered reaction. The second step was to discover by X-ray investigations the phase changes which are connected to the D.T.A. reactions. Finally, it was tried to detect visible modifications of the clay crystal habitus on electron micrographs. Quantitative estimations of the dehydration reactions have been effected by thermogravimetric analysis and are described in chapter 8 together with the problems of thermal activation.

7.1. Differential Thermal Analysis

7.1.1. Method

D.T.A. performances have been carried out by a Deltatherm modell D-2000 equipment with electronic heating rate controle and Inconel sample holders under normal lab conditions (1 atm. air). According to the international standard procedure recommended by the D.T.A. Sub - Committee of C.I.P.E.A. in 1948, a heating rate of 10°/min has been chosen and the samples have been kept in an exsiccator over a saturated $Ca(NO_3)_2 . 4 H_2O$ solution (= 51% relative humidity at 24,5°C) four days in advance. A <2 μ Ø caolinite fraction from Hirschau/Bavaria precalcined to 1200°C served as inert material.

7.1.2. Interpretation of D.T.A. reactions

Figure 3 shows the D.T.A. curves ($\Delta T/T$) obtained from ATTAPULGITE, ATTAPULGUS and ATTAGEL at 25 and 50% recorder sensitivity. The main endothermic and exothermic reactions are marked with capital letters (A - F) on the diagram. The medium values for reaction extents and maximum peak temperatures are enlisted in table 5.

Differential thermal and thermogravimetric analysis of palygorskite minerals are presented by several authors, summarized and commentated especially by MACKENZIE (1957). In general, the own results concerning the presence of the typical attapulgite reactions are in good agreement with literature data. Certain deviations have been observed for the reaction extents and maximum peak temperatures, which are probably due to differences in the quantitative mineral composition, but also to variations in size and shape of single crystals and aggregates. The presence of montmorillonite in a remarkable but variable amount must not be overlooked. An interpretation of the main D.T.A. reactions, to be seen on figure 3 and table 5, can be given as follows:

As proved by T.G.A. (chapter 8) the principal endotherm D.T.A. reactions are water loss reactions. The first endotherm reaction A (100-235, max. 151±9°C) is caused by the escape of sorbed water molecules which are held

a) on the outside surface of all components,

b) on the internal aggregate surface of clay granules,

c) as free "zeolitic" water in the interstices of the attapulgite lattice,

and d) in the easy expandable interlayer space of the montmorillonite structure.

The strongest first peak system is observed with ATTAGEL (50% sens.).

This sample has the lowest medium grain size (<2 μ Ø) and the highest montmorillonite content (20%). Some of the curves presented in figure 3 show a splitting up of the first peak, so that there occur two maxima. This behaviour is well known from montmorillonites. It depends from the hydration state of the exchangeable ions. After HENDRICKS (et al. 1940) splitting of the first peak is due to the presence of divalent ions on the sorption complex, while for monovalent ions this was not observed. We found divalent ions on attapulgite exchangeable. But in the present case splitting may also result from a partial overlapping of two reactions from two different clay minerals.

The endotherm reaction B (235-400, max. 280±8°C) contains the second strongly separated dehydration step of attapulgite, certainly due to the loss of the so-called "bound" water, which is held within the zeolitic channels by excess charges of lattice atoms (marked as OH_2 in figure 1 and in the formula by BRADLEY). As far as this reaction peak still shows a general connection to the first reaction A, it may also be influenced by the montmorillonite content. The dehydration of the montmorillonite interlayer space is going on continuously till about 300°C.

The endotherm reaction C (400-600, max. 485±10, 562°C) results from the dehydroxylation of attapulgite, loosing the hydroxyl groups associated with the octahedral layers. The second small maximum which occurs at 562°C on some of the curves should be due to a small kaolinite content.

The last endotherm reaction D (680-750, max. 730±5°C) represents the dehydroxylation of the montmorillonite component. This peak can well be recognized with ATTAGEL only. It is very weak for the other samples containing smaller amounts of the swelling clay mineral.

The exotherm reaction E (810-1000, max. 853/875°C) and the second exotherm reaction F (1000-1150, max. 1073±9°C), which one could be detected after prolonging the normal D.T.A. performance till 1150°C, can be explained from X-ray investigations (described in the next chapter) as belonging to the new formation of enstatite and cristobalite respectively.

7.2. X-ray investigations

7.2.1. Method

X-ray investigations have been done by x-ray diffraction (Philips equipment) using an ATTAPULGITE sample which had been preheated according to the D.T.A. reaction end temperatures at 400, 600, 800, 1000 and 1150°C, for one hour. The resulting diffraction patterns are given in figure 4. An exact measurable quantitative comparison of the patterns does not seem possible owing to a certain variable textural effect in the powder preparates. However, a good impression of the course of the heating process is given. To obtain further information, additional ATTAPULGITE samples have been preheated up to 300, 350, 450, 500, 550, 700 and 900°C.

7.2.2. Lattice modifications and phase changes

The first two low ~~temperatures~~ temperature dehydration reactions (D.T.A. : A and B) have no influence on the attapulgite lattice. No shrinkage occurs. The x-ray peak positions and intensities remain unaffected also at preheating temperatures of

300 and 350°C. But after heating up for one hour to 400°C a slight change begins with the diminuition of the relative intensity of the (110)-reflexion. This diminuition goes on continuously - as could be seen with other samples preheated at 450, 500 and 550°C - till 600°C, where the reflexion practically disappears. The intensity loss of the (110)-reflexion begins at the end of the second dehydration reaction when all zeolitic and nearly all bound water is driven out from the structural channels, and it continues as long as the dehydroxylation of the octahedral (and tetrahedral) layers takes place. At the end of the dehydroxylation, at about 600°C, the first attapulgite x-ray reflexion has completely disappeared.

The disappearance of the (110) plane during dehydroxylation can be explained by a continuous contraction of the attapulgite single fibres perpendicular to the fibre axis. As suggested by CAILLÈRE and HÉNIN (1961), the rotation of the amphibolic chains around the lines of oxigen atoms which connect neighbouring chains is probably acting as a mechanism for the contraction. The 600°C x-ray diffraction pattern on figure 4 shows a very strong attapulgite (400)-reflexion and the (390)-reflexion appears also remarkably stressed. Although this may be due to a certain texture in the preparates, it could be a hint that there is not an allside contraction of the fibres but a more preferred direction of shrinkage during the dehydroxylation process. This was, however, not supported by PREISINGERs (1963) research of the palygorskite "anhydride" structure. He found shortened unit cell dimensions in the a - as well as in the b - direction.

Above 650°C all attapulgite reflexions are weaker and; finally, disappear at about 800°C (see figure 4). The clay is becoming amorphous for x-rays.

The montmorillonite component shows a somewhat different behaviour. The first dehydration step till about 300°C is accompanied by a continuous contraction of the interlayer space. The (001) basis reflexion is shifted from about 15,7 Å to 9,5 Å. The interlayer collapse is partially reversible, also at 400°C. Above this temperature the swelling mechanism is gradually disappearing. The final dehydroxylation is registered by D.T.A. between 680 and 750°C. At 800°C the montmorillonite x-ray reflexions are disappearing.

The formation of new high temperature phases from Attapulgus clay begins above 800°C. Two separated exotherm reactions have been registered by D.T.A.. At the end of the first reaction, at 1000°C, enstatite could be detected, whereas the second reaction till 1150°C was due to the formation of cristobalite.

The dehydrated attapulgite structure above 400°C is called "attapulgite II" by LONGCHAMBON (1936). PREISINGER (1963) speaks of a palygorskite "anhydride" structure which should be stable from about 350 to 680°C. But it must be stressed that there is no phase modification stable for the whole temperature range mentioned. As demonstrated above, dehydration, dehydroxylation and lattice shrinkage are continuously progressing with rising temperature. Modification names, therefore, should be given to shorter or better defined temperature ranges. Otherwise it must be taken into account that attapulgite "anhydride" may have some different properties, depending on the degree of the heat treatment it has undergone.

7.3. Electron micrographs

It can be seen from the electron micrographs (plates 7-13) that there is no principal modification of the attapulgite and montmorillonite crystal shape during heat treatment till 800°C. The needle-like habitus of attapulgite and the original form of montmorillonite and kaolinite platelets are still existing at this temperature, although X-ray patterns demonstrate the change into the amorphous state. At 400°C pretreated samples show no difference from the not pretreated. Measurements of the attapulgite fibre length and width, as given in table 3a, show a diminuishing of the medium fibre length and width with rising pretreatment temperature. It is possible that mechanical handling during the pretreatment causes a certain breakdown and shortening of fibres, but the modification of fibre width seems to be due to the pure heat treatment. A fibre contraction is obvious, especially at 600°C, while between the 600°C and 800°C sample there is no remarkable difference. By heating an ATTAPULGITE sample already preheated at 800°C a second time under the electron microscope, an escape of gas bubbles (water, which was adsorbed during preparation for the electron microscope) and a broadening of the (amorphous) needles was caused. The bubbles are to be seen as black points on plate 13.

8. THERMAL ACTIVATION

Thermal pretreatment of clays in order to obtain a granular form and/or to improve the adsorptive properties is well known for all fields of its technical application. With Attapulgus clay useful thermal activation effects have also been observed. The producers of technical Attapulgus clay take a certain heat pretreatment into account and several authors are still trying to find the correlations between activation temperatures and physical properties of the clay (BARRER and MACKENZIE, McCARTER et al., NEDERBRAGT, ROBERTSON, a.o.m.). Terphenyl purification has to take place at much more elevated temperatures than normally used in clay application, and for regeneration necessities still higher temperatures would be required. It was, therefore, necessary to prove whether activated clays could be employed in this case and which activation temperature would provide an optimum of adsorption capacity and structural stability.

Certain information can be taken from chapter 7, but the results reported there have to be completed with quantitative estimations of the thermal dehydration reactions, gained from thermogravimetric analysis. The adsorptive properties depending on activation temperature have been tested by estimations of the cation adsorption capacity in aqueous medium. Finally, the influence of the thermal pretreatment on the specific surface of the clay samples has been investigated.

8.1. Thermogravimetric Analysis

8.1.1. Method

Thermogravimetric analysis (T.G.A.) have been executed under normal lab conditions (1 atm. air) by means of a thermobalance type ADAMEL, recording continuously both, weight loss and temperature against time till 1000°C at a constant heating rate of 10°C/min. Sample preparation has been done in the same way as for D.T.A. (see chapter 7.1.1.), in order to obtain comparable results from the two methods. Al_2O_3-containers and initial sample weights of E = 0,5 g have been employed. The detection limit was about 0,3 mg weight loss corresponding to 0,05% of the initial weight.

8.1.2. Interpretation of T.G.A. reactions

Figure 5 shows the thermobalance curve (weight loss in % of initial weight against temperature) of an ATTAPULGITE sample, on which four different S-shaped reaction zones (A-D) can be distinguished at 50-280, 280-400, 400-650 and 650-1000°C. These reactions have been observed for all Attapulgus clay samples, but with differences in quantity (see also table 6). With T.G.A. only weight change reactions are recorded, which in the present case correspond to the main endotherm D.T.A. reactions. (The two exotherm D.T.A. reactions are not connected to weight changes.).

Reaction extents	A	B	C	D
from D.T.A.	50 - 235°C	235 - 400	400 - 600	680 - 750
from T.G.A.	50 - 280	280 - 400	400 - 650	650 - 800+)

+) = end of reaction; end of performance = 1000°C

In comparison to D.T.A. the reaction extents on thermobalance curves are shifted slightly to higher temperatures. This is due to the fact that equilibration requires a finite time period. The faster the heating rate, the greater the shift. On the other hand faster heating facilitates the distinction of the single reactions.

The interpretation of the T.G.A. reactions in general is the same as described in chapter 7.1.2. for D.T.A. : reaction A includes all adsorbed and zeolitic water, reaction B the bound water from attapulgite, reaction C the hydroxyl water from attapulgite and reaction D the hydroxyls from montmorillonite. A comparison of the observed weight losses with those from ideal palygorskite shows some remarkable differences especially as regards bound water (B) and hydroxyl content (C), even under consideration of the fact that the ATTAPULGITE sample is in reality a mineral mixture containing only about 50% of attapulgite mineral:

Reaction	ideal palygorskite+)	ATTAPULGITE++)
A	8,60	11,51±0,60% weight loss
B	8,60	3,13±0,33
C	2,15	4,50±0,10
	19,35	19,14

+) $Si_8(Mg_5)O_{20}(OH)_2(OH_2)_4 \cdot 4H_2O$ (CAILLÈRE and HÉNIN)

++) containing 51% attapulgite mineral

The survey makes it evident, that the attapulgite mineral component of the ATTAPULGITE sample has a content of about 25% lower bound water and about four times higher hydroxyl water than can be derived from the ideal formula. The less bound water content can very well be explained by the hydratized exchangeable cations, such as Ca^{++} and Mg^{++}, occupying part of the bound water sites at the edges of the octahedral layers inside of the structural interstices (see figure 1). The higher hydroxyl content seems to be due to the cation substitution occuring mainly in the octahedral (Al^{3+},Fe^{3+},$Fe^{2+}$and $Ti^{4+}$for Mg^{2+}) layers, where remaining free charges are balanced by OH^-. A small amount of the C-reaction may also belong to the montmorillonite dehydroxylation. The quantity of the D-reaction is normally insufficient to explain the montmorillonite content detected. According to GRIM (1953) montmorillonites with moderate to low substitution rates of iron and magnesium for aluminium are beginning to loose their hydroxyl water already above 500°C.

8.1.3. Pretreated and not pretreated samples

Figure 6 shows the thermobalance curves for the three Attapulgus clay samples investigated and gives an impression of the reproducibility of the performances for two of the samples. The shape of the curves is more or less the same, but the quantities of the weight loss reactions differ remarkably, especially between ATTAGEL and ATTAPULGITE on one side and ATTAPULGUS on the other. There is also a much better reproducibility for ATTAPULGUS in contrast to ATTAPULGITE.

The following survey gives a numerical comparison of the total water losses till 1000°C, obtained from the three samples by chemical analysis (see chapter 4) and thermobalance performances:

	chemical analysis	thermobalance
ATTAGEL	19,2	19,3±1,2% weight loss
ATTAPULGITE	19,5	20,0±0,7
ATTAPULGUS	10,7	12,9±0,2

The two methods are in good agreement. The differences between the three samples could be due to differences in clay mineral content, granulometry and kind of pretreatment. From these three factors an important influence on the dehydration curves is expected.

But the differences in clay mineral contents given in table 3 are not big enough for a valid explanation. As second factor, therefore, the granulometric effect has been tested. An ATTAPULGUS sample has been ground in an agate mortar, and two fractions of smaller grain size have been gained by sieving and sedimentation. The results of the thermobalance performances of all fractions are to be seen on figure 7. Although the granulometry was now comparable to that of ATTAPULGITE and ATTAGEL, the big difference was still remaining. Thus it became evident that pretreatment must have the main influence on dehydration. As described in chapter 3, only ATTAPULGUS had undergone a certain heat pretreatment during its technical preparation.

Figure 8 presents T.G.A. curves from ATTAPULGITE and the same ATTAPULGUS fractions as before, but obtained after preheating all the samples for one hour at 400°C (allowing rehydration for 16 hours). Thus eliminating the pretreatment influence, one finds all traces closely together and it is obvious, that the still perceptible differences are connected to granulometry and - in the relation between ATTAPULGITE <63 and ATTAPULGUS <63 - also to the clay minerals content.

8.1.4. Activation temperature

Figure 9 demonstrates the influence of activation temperatures on the T.G.A. curves of natural Attapulgus clay. Several ATTAPULGITE samples have been preheated in a Heraeus-VZ-100 furnace, each for one hour at the desired temperature, then cooled down and rehydrated for 16 hours in an exsiccator over $Ca(NO_3)_2 \cdot 4H_2O$ and, finally, treated in the thermobalance till 1000°C. In respect to coolant purification necessities the temperature range from 300 to 500°C has been considered for activation. The higher the activation temperature, the slower is rehydration and the lower is the water content still remaining on the clay, as detected by T.G.A.. The proportion of irreversible to reversible water loss is augmenting with activation temperature, especially above 390°C.

The introduction of the T.G.A. curve of ATTAPULGUS <63 μ ∅ (which has a grain size distribution comparable to ATTAPULGITE) into figure 9, permits the detection of the temperature range at which the sample should have been pretreated during its technical preparation. One can state, that the ATTAPULGUS sample shows the same dehydration behaviour as if it had been preheated at 390-400°C for one hour. The time of pretreatment does not seem to be of great influence, however. Figure 10 gives T.G.A. curves obtained from ATTAPULGITE samples which had been preheated at 350°C for one and seven hours. The deviations are within the limits of reproducibility.

Figure 11 shows the influence of activation temperatures on the different kinds of water present in Attapulgus clay, as represented by the T.G.A. single reactions A - D (see chapter 8.1.2.). In general, there is only a slight decrease of the water content (expressed as T.G.A. weight loss) till about 390°C activation temperature. Above this temperature, however, a remarkable decrease is noticed. Below 390°C mainly adsorbed (A) and only some of the bound water (B) is "irreversibly" lost, which means that this water is not completely rehydrated after 16 hours of rehydration time (under the conditions of the essay). Above 390°C not only adsorbed and bound water but also the hydroxyl water from attapulgite (C) is strongly affected. Here, true irreversibility is occuring in connection with lattice modifications, as already reported above. Pretreatment temperatures till 500°C have no influence on the montmorillonite hydroxyl water (D).

The aim of thermal activation should be to drive off all adsorbed, zeolitic and bound water from the outside surface and from the structural cavities of the clay in order to replace it by a maximum quantity of desired ions or molecules, but not to destroy or change the crystal lattice by the activation procedure. Therefore, activation temperatures at about 400°C have the main interest for Attapulgus clay, if its technical application is possible below or at this temperature. In this case the technical pretreated ATTAPULGUS could well be employed.

8.1.5. Rehydration

For the handling of ATTAPULGUS columns, for estimations of organic residues on the clay and for other practical purposes, the rehydration behaviour of the activated clay is of great importance. It has shortly been tested with an ATTAPULGUS $< 6{,}3\,\mu$ Ø fraction preheated for one hour at 400°C. T.G.A. has been done before the thermal treatment, directly afterwards and after 16 hours, 40 hours and 10 days rehydration in an exsiccator over aqueous calcium nitrate under normal lab conditions (= 1 atm., 23°C, 45% rel.hum.). The resulting T.G.A. curves are given in figure 12. Directly after the heat treatment the adsorbed, zeolitic and bound water is lost completely. Rehydration begins as soon as the sample is cooling down to room temperature, depending on the relative humidity of the surrounding air. Under the conditions employed, 21% of the water loss has been regained during the first hour after the heat treatment, 68% after 16 hours and 77% after 10 days, moving to an equilibrium.

Figure 13 demonstrates very well the rehydration rates of the adsorbed and zeolitic water (reaction A) and of the bound water (reaction B) after the heat pretreatment.

8.2. Cation adsorption

8.2.1. Literature data

Values for the cation adsorption capacity of palygorskites obtained in aqueous medium are presented in literature by several authors: BRADLEY (1940) reports 21 mequ./100 g for attapulgite from Attapulgus/Ga., GRIM (1953) 20-30 mequ./100 g for palygorskites in general, HEYSTEK and SCHMIDT (1954) 20 mequ./100 g for palygorskite from Dornboom/South Africa, STEPHEN (1954) 27,4 mequ./100 g for a sample from Cabrach/Aberdeenshire and 35,9 mequ./100 g for a montmorillonite containing sample from Bakkasetter/Shetland. MARSHALL and CALDWELL (1947) give the following more detailed table for some attapulgite grain size fractions, which had been changed to an H-form before the treatment:

fraction μ Ø	NH_4^+ pH = 7,0	Ca^{++} pH = 5,0	Ca^{++} pH = 7,0	Ca^{++} pH = 9,0	
2,0 - 0,5	18,0	21,4	22,8	24,2	mequ./100 g
0,5 - 0,2	19,0	19,2	21,2	21,2	dried clay
0,2 - 0,05	22,2	22,7	23,5	25,3	

The values for the cation adsorption capacity of ATTAPULGITE and ATTAPULGUS 24-48 mesh, serving as basis for the following interpretations, have been estimated by Mr. G. GIGLI and are presented in table 7. The method employed - the multistage batch procedure - is described in detail in the report of GIGLI. As connection to literature data a value of 19,5 mequ./100 g for Ba^{++} uptake by ATTAPULGITE at pH = 7,0 may well be given.

8.2.2. Influence of thermal activation on cation adsorption

Figure 14 presents the cation adsorption on ATTAPULGITE and ATTAPULGUS depending from thermal activation. The four curves have been obtained for the uptake of Fe^{++}, Ba^{++}, Cs^{+} and K^{+} on preheated ATTAPULGITE samples. While adsorption capacities for Ba^{++}, Cs^{+} and K^{+} have been estimated at pH = 7 with Cl^{-} anion, Fe^{++} has been detected as phenolate under quite different conditions and is presented here only for a rough comparison. (The question of iron uptake is treated separately by GIGLI). Ba^{++} had been chosen for the measurements as divalent cation which is not present on the sorption complex of the clay, K^{+} and Cs^{+} as monovalent cations with different ion diameter and hydratation.

The uptake intensity on ATTAPULGITE is given with $Ba^{++} > Cs^{+} \gg K^{+}$, as had been observed with Ca - montmorillonites in accord to the "lyotrope series", depending from valency, ion diameter and hydratation numbers (GRIM, MARSHALL, SCHACHTSCHABEL, et al.). The main complementary ions on Attapulgus clay are Ca^{++} and some Mg^{++} and K^{+}. The montmorillonite content detected in the Attapulgus clay samples could be responsible for about 50% of the cation adsorption capacity of the untreated material and seems to govern the uptake also after preheating the clay till 390°C. From specific surface measurements (figure 15, chapter 8.3.) it is obvious, that under heating the montmorillonite undergoes an interlayer collapse, which above 300°C is becoming more and more irreversible. The beginning interlayer collapse makes the replaceability of the exchangeable ions between the layers more difficult, so that Ba^{++} may still enter for Ca^{++}, but Cs^{+} and K^{+} only in smaller portions. This would explain the minima of the Cs^{+}- and K^{+}-curves in figure 14 in the 300-390°C region. The drop of exchange capacity of Ca - montmorillonite after heat treatment is reported among others by HOFMANN and KLEMENS (1950).

This behaviour is variable with the origin and chemical composition of the clay and with the kind and valency of the exchangeable ions present. The influence of the irreversible interlayer collapse on cation exchange capacity is so strong, because on montmorillonites over 80% of the exchangeable ions are held in the interlayer space as a consequence of lattice substitutions and only about 20% are held at "broken bonds", around the edges of flakes, etc.

Above 390°C pretreatment temperature the curves on figure 14 are suddenly rising up and reach nearly the double of the original adsorption capacity. Maxima for Cs^{+} and K^{+} are at 500°C, followed by the final dropping down of the curves. Ba^{++} shows its very maximum at 600°C, but it may be too high and too late and the end point of the curve may be reached as well at 850°C instead of 1000°C. The phenomenon of the sudden rise of the adsorption capacity must be due to the attapulgite mineral, which till this point has lost all zeolitic and bound water from the structural channels. The dehydration effect makes the internal exchange sites available. The following lattice shrinkage and deformation, however, again causes a continuous diminuition of the uptake rate with higher temperatures.

The availability of all attapulgite bound water positions for cation adsorption would be sufficient to explain the maximum adsorption capacities reached after dehydration at 500°C. But deviations from the ideal structure, distortions and blocking of interstices may decrease the quantity of available sites. This could have been proved, if not only the total uptake capacity but also the exchange capacity and the absorption capacity would have been measured.

The cation adsorption on ATTAPULGUS 24-48 mesh is demonstrated on <u>figure 14</u> by a vertical line applied to the preheating temperature of 395°C which had been detected by thermogravimetric analysis (chapter 8.1.4.). The uptake intensity follows the serie $Ba^{++} > Ca^{++} > Cs^{+} > K^{+} > Na^{+}$. The values obtained for Ba^{++}, Cs^{+} and K^{+} on the vertical line are at the same time perfectly situated on the curves of the preheated ATTAPULGITE. It is evident from the diagram that for ATTAPULGUS a much better activation effect for cation adsorption would have been reached by applying a 10°C higher pretreatment temperature.

8.3. Specific surface measurements

8.3.1. Method

Specific surface measurements have been done by using the ethylene glycol retention method after DYAL and HENDRICKS (1950), thus completing the information given by some authors about the B.E.T. measurements executed with Attapulgus clay (BARRER and MACKENZIE, 1954, McCARTER et al., 1950). Whereas B.E.T. gas adsorption supplies with data for external crystal surfaces only, it is possible to detect the total surface of swelling clay minerals by ethylene glycol adsorption, including the external as well as the interlayer surface areas. The formation of ethylene glycol double sheets in the interlayer space of not preheated montmorillonites can well be controlled by the position of the x-ray (001) reflexion, being at 17 Å in this case (MAC EWAN, 1948). The difference between the total and the external surface is equal to the available interlayer surface, which can be used very well for quantitative estimations of the montmorillonite content in mixtures with not swelling clay minerals. However, the question was whether the attapulgite intracrystalline channels would also be available for ethylene glycol adsorption.

Experimental : Exactly 1 g of every clay sample has been dried to constant weight over P_2O_5 in a vacuum desiccator at 0,1 Torr. About 1 ml of redistilled ethylene glycol has then been added to the dried sample, the weighing dish placed in the vacuum desiccator over anhydrous $CaCl_2$ and the system evacuated for about 24 hours to a pressure of less than 0,1 Torr in order to evaporate the excess glycol. The weight has been controlled every 6 hours till final constance ($\pm$0,000 2 g). The formation of single surface layers requires 0,25 g glycol on 810 m^2 of surface or 3,10 x 10^{-4}g glycol per m^2, corresponding 33 x $10^{-16}$$cm^2$ per glycol molecule (DYAL and HENDRICKS, see also for more discussion).

8.3.2. Ethylene glycol and B.E.T. surfaces

Table 8 contains the values obtained for ATTAPULGITE, ATTAPULGUS and ATTAGEL and figure 15 shows the influence of pretreatment temperatures on ethylene glycol and B.E.T. specific surface areas.

The ethylene glycol surface above 300°C preheating temperature is reduced continuously from 286 m^2/g at 20°C to 24 m^2/g at 800°C, where the clay is changing to the amorphous state. This behaviour demonstrates very clearly that the polar ethylene glycol molecules are not taken up into the attapulgite intracrystalline channels. These channels are available for cations and it can be seen from figure 14 that there is a maximum of cation adsorption after dehydration at 400-500°C. In contrast here to the ethylene glycol surface shows a considerable reduction at the same temperatures. The complex formation of ethylene glycol with montmorillonite is mentioned above, and this effect governs the curve in figure 15. The proportion between external and internal surface of montmorillonite is about 1 : 20 (table 9).

The external surface of Attapulgus clay is marked on figure 15 by the line of B.E.T. values, taken from McCARTER et al.. These data show only a slight decrease at rising temperature, certainly due to the shrinkage of the attapulgite needles. No entering in innercrystal positions can be deduced from the curve. Above 700°C the B.E.T. surface comes to minimum.

The difference between the ethylene glycol and the B.E.T. surface areas, as demonstrated in figure 15, is equal to the interlayer surface of the montmorillonite component in Attapulgus clay. From this difference the semiquantitative montmorillonite content of ATTAPULGITE and ATTAPULGUS could be calculated, taking literature values of montmorillonite surfaces as basis (table 9). For comparison surface areas of other clay minerals have been added to table 9. The montmorillonite percentages given in table 3 include the variations of B.E.T. and basis values within their limits. There is a good agreement between the X-ray and the ethylene glycol retention methods.

The kinds of surface and the surface areas obtained for ATTAPULGUS 200-630 μ Ø in this study are summarized in the following survey:

kind of surface	surface area in m^2/g obtained by		
	grain size distribution	B.E.T. (N_2)	ethylene glycol retention
a) external aggregates	0,03		
b) internal aggregates and external single crystals		125	175
c) montmorillonite interlayers			
d) attapulgite interchannels	not detectable with these methods!		

The attapulgite interchannel surface could not be measured by the methods employed. BARRER and MACKENZIE (1954) in their study of the kinetics and equilibria of sorption of N_2, O_2, CO_2, H_2O, NH_3, CH_3OH and C_2H_5OH on Attapulgus clay found that some lattice penetration and surface sorption was possible by H_2O, NH_3 and to a lesser extent by the alcohols. Sorption of the other species was restricted to the external surfaces and possibly to some extra sites at the entrances to the intracrystalline channels. But the possible presence of montmorillonite had not been taken into account in that study. Further more intensive studies on this subject are requested.

9. TERPHENYL CONTACTS

The behaviour of attapulgite - terphenyl mixtures has been tested by D.T.A., T.G.A., X-ray diffraction and some preliminary experiments which can give a hint on the kind of reactions taking place when coolant and clay are coming in contact with each other.

9.1. D.T.A. and T.G.A. performances

Figure 16 shows D.T.A. performances of "juvenile" terphenyl (OM-2) and of some ATTAPULGITE - terphenyl mixtures, executed under normal lab conditions. The mixtures have been prepared at 200°C and then cooled down to room temperature. Two endotherm reactions are recorded with pure terphenyl : melting above 50°C with maximum at 75°C (a) and vaporization above 350°C, maximum at 372°C (c). The main influence of terphenyl on the original clay curve results from the appearance of these two endotherm terphenyl reactions besides or coinciding with the ATTAPULGITE dehydration reactions.

Figure 17 presents the thermobalance performance of pure terphenyl (OM-2), effected under the same conditions as above. The only weight change reaction recorded is caused by terphenyl vaporization, which has its maximum between 230 and 450°C with a loss of 97,7% of the initial weight (E). The remainder of 2,3% is lost completely above 450 till 850°C. This remainder may be due to some higher boiling material contained already in OM-2 (for analysis see FRIZ et al., 1964), or to pyrolysis during the performance.

Figure 18 shows the same kind of thermobalance performance but with a 2 : 1 ATTAPULGITE - terphenyl mixture. The characteristic terphenyl vaporization reaction between 230 and 450°C can well be seen. But in two of the three reaction steps (II and III) some overlapping of terphenyl escape and ATTAPULGITE dehydration occurs. A separation was possible by calculating the data from pure ATTAPULGITE performances (chapter 8.1.). The result shows that the terphenyl is lost completely during the run, but only 85% between 230 and 450°C and 15% above this temperature. The higher percentage of higher boiling material cannot well be explained by stronger pyrolysis or variations of the high-boiler content originally present in the terphenyl sample. It must be due to a certain adsorption effect and/or surface reactions with the clay.

9.2. Adsorption

Terphenyl adsorption certainly takes place on the external surface and in the holes and capillars of clay aggregates. Terphenyl molecule dimensions do not fit into the attapulgite intracrystalline channels. Some penetration into the montmorillonite interlayer space has been proved to be true by X-rays. The following shift of the first basis reflexion has been observed:

Terphenyl : ATTAPULGUS		Montmorillonite (001) at
0 : 1	-	9,5 A
2 : 1	-	14,3 A
5 : 1	-	14,5 A

9.3. Surface reactions

During terphenyl adsorption on the clay certain surface reactions are taking place. A cracking activity of Attapulgus clay has already been reported by the petroleum industries (GRUSE and STEVENS, 1942). In fact, all Attapulgus clay grains in contact with terphenyl are changing their colour very soon from yellow-brown to grey and, finally, to black (see picture 2). This change of colour has been observed not only after treatment with highboiler containing, but also with extremely pure terphenyl samples and at temperatures between 100 and 150°C, far below pyrolysis. The black colour, due to carbon or carbonaceous residues, vanishes after heating the clay up to 500-600°C in an oxidizing atmosphere, whereas under high vacuum ($10^{-2,5}$ Torr) the clay retained its black colour till 1000°C. The cracking activity increases with temperature and high boiler content. The production rate of carbonaceous residues adsorbed on the clay surface may become a time limiting factor in the technical application of Attapulgus clay for terphenyl purification.

Not only cracking but also isomerisation reactions take place with terphenyl on the Attapulgus clay surfaces. Table 10 gives a survey on the results of some preliminary experiments to this question. Pure samples of ortho-, meta-, para-terphenyl (p.a. Merck) and OM-2 (PROGIL) have been boiled for five hours each together with activated ATTAPULGUS in the proportion clay : terphenyl = 1 : 4, using a backflow condenser. It can be seen from the table, that in contact with Attapulgus clay especially the pure ortho-terphenyl is changing to the more stable isomers, meta- and some para-terphenyl. Meta-terphenyl in clay contact produces some ortho- and para-terphenyl, pure para-terphenyl (not in the table) remains unchanged, whereas OM-2 in general shows the same tendency as pure ortho-terphenyl.

10. STABILITY TESTS

In order to prevent an introduction of impurities into the coolant circuit from the side of the adsorbent itself, clay granules and primary particles should have a good mechanical, chemical and thermal resistance or at least very low decomposition rates under working conditions. A decomposition of the adsorbent during column operation would produce particulate and dissolved matter. Whereas the removal of particulate matter is a question of backup filtration pore sizes, the dissolved material in the ionic or molecular state cannot be caught by filtration and its production rate may limitate the application of the adsorbent.

As mentioned above, the 24-48 mesh ATTAPULGUS granules, well-suited for column employment, are heterogeneously composed mineral aggregates and a certain breakdown of these granules to smaller sizes had been observed already after transportation and handling. Some tests on the stability of ATTAPULGUS granules in aqueous and organic medium, therefore, have been executed by Mr. S. PARACCHINI.

10.1. Sample preparation

The starting material for all test series was an ATTAPULGUS 200-630 μ Ø fraction. The required exactness of the granulometry had been gained by wet sieving, employing distilled water as dispersing agent and using two wetting - drying cycles at drying temperatures between 300 and 400°C.

Dry sieving was not possible in this case, because a lot of the finest grains still remained attached on the surface of the larger ones. But also after wet sieving and drying at 100°C a small percentage of material <200 μ Ø could be detected by repeated wet sieving. It was stated that repeated wetting and drying causes a certain decomposition of the ATTAPULGUS grains. Figure 19 shows the quantities of material <200 μ Ø estimated after each of five wetting - drying cycles executed with one sample of the 200-630 μ Ø fraction. The first two treatments caused the breakdown of the most instable grains originally present. The minimum decomposition was reached after the second treatment. This point was recommended for sample preparation. Owing to the following successive wetting - drying cycles more grains became instable, as a consequence of repeated handling, dispersing and heat influence.

10.2. Thermal resistance

Figure 20 demonstrates that thermal activation at 300-400°C has positive influence on the stability of the ATTAPULGUS grains. Wet sieved samples of the 200-630 μ Ø fraction have been dried at different temperatures and then wet sieved again with the 200 μ-sieve. Drying at 300 and 400°C caused decomposition rates (= material 200 μ Ø) which are about ten times smaller than those obtained at room temperature (25°C). It seems that the temperature-depending swelling state of the montmorillonite component is responsible for this behaviour.

10.3. Stability in aqueous medium

10.3.1. Method

The stability of ATTAPULGUS grains in aqueous medium has been studied by means of batch methods at pH end values from 1-13, employing solvents like HCl, NaCl, H_2O, NH_4OH, $Na_4P_2O_7 \cdot 10\ H_2O$ and NaOH of different concentrations, varying the contact time from 1-30 days and taking into account also the mechanical type of treatment. 5 g samples of the ATTAPULGUS 200-630 μ Ø grain size fraction, prepared as described above, have been used for the batch procedures (V/m = 40). At the end of each run the resulting material with smaller grain size than 200 μ has been sieved off. A separation of the particulate matter from the dissolved material in the ionic state was possible by ultrafiltration. Kind and quantity of the dissolved ions have been analysed in the ultrafiltrate.

10.3.2. Particulate and dissolved fractions

Figure 21 shows the influence of pH values and different solvents on the ATTAPULGUS grains after 11 days of static treatment. The resulting amounts of dissolved ions and particulate matter <200 μ Ø are given in percent of the initial sample weight. The total breakdown rates are between 2,5 and >13%, the dissolved fractions contain 0,1-12%. It can be seen from the diagram that there is much more particulate matter produced on the alcaline side than in the neutral and acid regions. Acid solutions (HCl) show much higher ionic dissolution rates than alcaline ones (NaOH) of comparable concentrations. Even in distilled water and neutral salt solutions some of the material is soluble (>0,1%). 30 days treatments do not bring about higher breakdown rates. The breakdown/time curve is moving to an equilibrium. But mechanical treatment (stirring) resulted in three times higher decomposition rates.

The dissolved fractions mainly contain Si^{4+}, Al^{3+}, Fe^{3+}, Ca^{2+}, Mg^{2+} and K^{+}. Figure 22 demonstrates the influence of pH values on the solubility of each of these ions from ATTAPULGUS (oxides in % of initial sample weight after 11 days of static treatment). Most of the ions investigated have their maximum solubility below pH 4, except Si^{4+} and K^{+}, which are more soluble in alcaline solutions. The important solubility rate of silice above pH 7,5 and the fact of the higher breakdown rate of ATTAPULGUS grains to particulate matter of smaller grain sizes in the same pH region lead to the conclusion that silice, possibly as free SiO_2, is responsible for the coherence of the larger ATTAPULGUS aggregates.

10.3.3. Soluble ions and crystal structure

If the ions solubility rates obtained are compared to the chemical analysis of ATTAPULGUS (table 2b), it can be deduced which maximum quantities of the elements originally present in Attapulgus clay have come into solution under the experimental conditions employed. Taking the analytical values for every element as 100%, one can say that till

about 10% of the SiO_2 (by 1,0 n NaOH),
30% " " Al_2O_3(by 1,0 n HCl),
25% " " Fe_2O_3(by 1,0 n HCl),
100% " " CaO (by 1,0 n HCl),
30% " " MgO (by 1,0 n HCl),
and 70% " " K_2O (by 1,0 n NaOH) have been soluble.

Generally this can be written in the following way:

$$Ca^{2+} > K^{+} > Mg^{2+} = Al^{3+} > Fe^{3+} > Si^{4+},$$

where Ca^{2+} shows the highest, Si^{4+} the lowest solubility rates (neglecting pH and other conditions). The ions with the highest solubility rates should occupy lattice positions where they can be replaced very easily. This is the case on exchange sites. Ca^{2+} and K^{+} are the main components of the exchange complex on Attapulgus clay. K^{+} is exchanged especially in contact with Na^{+}(NaCl,NaOH), Ca^{2+} against H^{+} till 100%. Less soluble are Mg^{2+} and Al^{3+} which are mainly situated within the octahedral units. Some Mg^{2+} on open edge positions may be exchangeable. Al^{3+} is moving to exchange sites under acid conditions. Most strongly bound are the Si^{4+} within the silicon-oxigen tetrahedral units. SiO_2 is present also as quartz and probably some free SiO_2.Few $Fe^{3+(2+)}$ occur on octahedral positions, but most of the iron belongs to iron minerals (chapter 6.4.), which are responsible for the iron's solubility behaviour.

10.4. Stability in benzene

Static batch experiments in benzene demonstrated that under comparable conditions, there is a much smaller production of particulate matter $< 200\,\mu$ ∅ than with aqueous solutions. The dissolved fraction, containing some Si^{4+}, Fe^{3+} and Ca^{2+}, is also small and comparable to that obtained with NH_4OH at neutral pH. The results from a three days static treatment are as follows:

solvent	% < 200 µ Ø		
	total	particles	dissolved
a) aqua dist., pH 6,45	1,41	1,20	0,21
b) 0,01 n NH_4OH, pH 7,78	1,16	1,03	0,13
c) benzene	0,31	0,15	0,16

The maximum values obtained during 30 days of benzene treatment are not exceeding 0,15% of particulate matter and about 1% of soluble ions.

10.5. Stability in terphenyl

The results of two lab scale column experiments show the stability behaviour of ATTAPULGUS granules in terphenylic medium under working conditions. For both runs ATTAPULGUS 200-630 µ Ø samples (prepared as described in chapter 10.1.) and juvenile OM-2 (PROGIL) have been used. The experimental conditions are summed up in table 11.

After run A was over, it was possible to break the glass column and to take undisturbed ATTAPULGUS samples from the top and bottom parts of the column at room temperature. The samples have been heated to 400°C in order to eliminate the terphenyl contained and then fractionated by sieving and sedimentation. The grain size distribution of the particles <200 µ Ø produced by the run is given in table 12. The breakdown rate of ATTAPULGUS grains during the 30 hours run by using upflow was 2,11% in the bottom and 3,56% in the top sample. The values contain about 0,3-0,4% higher boiling polymerisation products and carbonaceous residues adsorbed on the clay.

The analysis of the dissolved fraction are to be seen on table 13a. The initial impurities actually contained in OM-2 are taken up by the clay. With the beginning breakdown of some of the ATTAPULGUS granules the impurities are exceeding the initial values. The "dissolved fraction", in this case, is limited by the backup filter pore sizes, being 25 x 40 µ. This means that not only soluble ions or molecules but also particulate matter up to about 15 µ Ø (or even larger not spherical particles), which went through the filter, may be contained in this fraction. Column experiment B, therefore, has been installed, working with metal column and tubes under quite different semitechnical conditions (see table 11). Very pure OM-2 and 3 µ - backup filter candle have been used for the run. The analytical results in table 13b show that practically no impurities from the side of the adsorbent clay have been introduced into the circuit terphenyl, although a certain quantity of ATTAPULGUS granules have decomposed to smaller grain sizes during the run. Such breakdown material has been found on the filter candle.

11. CONCLUSIONS

a) The main result of the present study in regard to material research is the fact that Attapulgus clay, the standard as well as the technical material, is a clay mineral mixture and that this fact, although known before, should be stressed much more in all types of research on this clay and especially when deducing formulae from chemical analysis.

b) For technical purposes the admixed montmorillonite component has positive influence, augmenting the adsorption capacity considerably, while granulation and column employment are still possible.

c) The optimum activation effect is gained after dehydrating Attapulgus clay at about 400°C. At this temperature the adsorbed, zeolitic and bound water is lost from attapulgite and the cation adsorption capacity reaches nearly the double of its original value.

d) The rehydration behaviour of the clay makes it useful to heat the material directly before the column employment to the desired activation temperature, not allowing to cool down below 100°C before application.

e) The technical application of Attapulgus clay may well be done at or below 400°C. With rising temperature dehydroxylation begins, the attapulgite crystals show a certain continuous shrinkage perpendicular to their fibre axis and the montmorillonite interlayer spaces are collapsing more and more irreversibly. At about 800°C the dehydroxylated clay structures are changing to the amorphous state.

f) A non destructive thermal regeneration of spent Attapulgus clay is possible till about 550°C.

g) In contact with terphenyl not only physical adsorption occurs, but additional cracking and isomerization reactions take place on the clay surface.

h) The stability of Attapulgus clay granules employed in columns is fairly good, especially after activating the clay at 300-400°C. An introduction of fine clay particles into the terphenyl circuit could be prevented by the use of a 3 μ - backup filter candle.

i) Future more intensive studies on the availability of the attapulgite intracrystalline channels and on terphenyl - attapulgite surface reactions are needed.

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Tables

Table 1 : X-ray data

hkl	BRADLEY (1940)$^{x)}$				ATTAPULGITE		ATTAPULGUS	ATTAGEL
	d(Å) calc.	I calc.	d(Å) obs.	I obs.	d(Å) obs.	I obs.	d(Å) obs.	d(Å) obs.
110	10,48	330	10,50	10	10,52	100	10,52	10,52
200	6,45	17	6,44	6	6,46	12	6,41	6,41
130	5,44	12	5,42	5	5,40	9	5,37	5,34
220	5,24	1	-	-	-	-	-	-
040	4,50	66	4,49	8	4,46	26	4,46	4,48
310	4,18	13	4,18	3	4,15	9	4,13	4,15
240	3,69	18	3,69	5	3,67	12	3,67	3,67
330	3,49	12	3,50	3	3,47	5	3,52	3,49
150	3,47	2						
400	3,23	120	3,23	10	3,24	30	3,24	3,24
420	3,04	3	3,03	1	3,04	7	3,03	3,03
350	2,76	2	-	-	2,77	5	2,77	2,79
440	2,62	43	2,61	8	2,60	19	2,60	2,60
510	2,56	8	2,55	3	2,54	19	2,55	2,55
530	2,38	5	2,38	3	2,39	5	-	2,38
080	2,25	1	-	-	-	-	-	-
600	2,15	15	2,15	5	2,16	10	2,16	2,16
550	2,10	1	-	-	-	-	-	-
480	1,845	1	-	-	-	-	1,84	-
390	1,815	3	1,82	1	1,82	5	1,82	1,82
660	1,75	1	-	-	-	-	-	-
800	1,615	3	1,62	1	1,61	7	-	1,61
680	1,555	17	1,56	3	1,54	6	1,54	1,54
0,12,0	1,50	40	1,50	5	1,51	4	1,51	1,51

x) data taken from BROWN

Table 2a) : Chemical Analysis

Element	ATTAPULGITE Standard N° 44	ATTAPULGUS 24-48 mesh	ATTAGEL " 20 "	de Lapparent[x)] Attapulgus/ Ga.	Bradley[x)] Attapulgus/ Ga.	Caillère[x)] Palygorskite from Taodeni
SiO_2	53,23 %	59,41	54,29	53,64	55,03	54,71
TiO_2	0,45	0,48	0,39	0,60		
Al_2O_3	10,06	12,11	9,94	8,76	10,24	13,48
Fe_2O_3	3,20	3,72	3,42	3,36	3,53	2,10
FeO	0,12	0,18	0,12	0,23		
MnO	0,04	0,05	0,03	0,03		
MgO	8,46	8,98	9,99	9,05	10,49	5,44
CaO	2,76	2,37	1,19	2,02		2,79
Na_2O	0,08	0,07	0,06	0,83		
K_2O	1,83	1,72	1,46	0,75	0,47	
CO_2	< 0,20	0,40	1,40			
SO_4	< 0,05	<0,05	<0,05			
P_2O_5				0,79		
H_2O^+	10,59	7,11	11,28	10,89	10,13	12,63
H_2O^-	8,93	3,62	7,97	9,12	9,73	8,65
Sum	100,02	100,27	101,59	100,07	99,62	99,80

x) : literature values

Table 2b) : Chemical analysis, volatile-free basis

Element	ATTAPULGITE Standard N° 44	ATTAPULGUS 24-48 mesh	ATTAGEL " 20 "	Minerals Philipp Corp. "Typical Analysis"	de Lapparent$^{x)}$ Attapulgus/ Ga.	Bradley$^{x)}$ Attapulgus/ Ga.
SiO_2	66,20 %	66,0	67,0	68,0	67,0	68,9
TiO_2	0,56	0,53	0,48	0,7	0,75	
Al_2O_3	12,52	13,46	12,26	12,0	10,94	12,80
Fe_2O_3	3,98	4,14	4,22	5,0	4,20	4,42
FeO	0,15	0,20	0,15		0,29	
MnO	0,05	0,06	0,04		0,04	
MgO	10,52	10,00	12,32	10,5	11,30	13,12
CaO	3,43	2,64	1,47	1,7	2,52	
Na_2O	0,10	0,08	0,07		1,04	
K_2O	2,27	1,91	1,80	1,0	0,94	0,59
CO_2	< 0,20	0,45	1,73			
SO_4	< 0,05	< 0,05	< 0,05			
P_2O_5				1,0	0,79	
others				0,1		
Sum	100,03	99,52	101,59	100,0	100,0	99,83

x) : literature values

Table 2c) : **Semiquantitative trace element content of ATTAPULGITE and ATTAPULGUS**

ppm	elements
2000 - 500	V
500 - 100	Y, Zr, Ba
100 - 50	Cr, Zn, Ga, Sr, Nb, Tl
50 - 20	Be, B, Ni, Cu, Ag, Pb
<50[x)]	Sb, Cs, Th, U
<20[x)]	Co, Ge, As, Mo, Cd, In, Sn, Bi

[x)] detection limits

Table 3a) : Dimensions of attapulgite single fibres

A)

Fibre length µ	ATTAPULGITE not pretreated	 600°C	 800°C	ATTAPULGUS
>2,0	4 %	-	-	-
2,0 - 1,1	40	10	5	5
1,1 - 0,63	50	50	30	15
0,63 - 0,35	6	30	35	35
0,35 - 0,20	+	10	20	
0,20 - 0,11	+	+	10	45
<0,11	+	+	+	

	C.E. MARSHALL
2,0 - 0,5	19 %
0,5 - 0,2	51
0,2 - 0,05	26
<0,05	3

B)

Fibre width µ	ATTAPULGITE not pretreated	 600°C	 800°C
0,05 - 0,03	6 %	2	-
0,03 - 0,02	62	50	48
0,02 - 0,01	30	36	40
<0,01	2	12	12

Table 3b) : Semiquantitative mineral composition

Sample	mineral	Estimated by			medium content calculated
		X-ray diffraction	ethylene glycol retention	polarization microscope	
ATTAPULGITE	attapulgite	-	-	70	51 %
	montmorines	18	19 ± 2		19
	quartz	20	-	18	18
	accessories	10x)	-	12	12
ATTAPULGUS	attapulgite	-	-	61	47
	montmorines	13	15 ± 2		14
	quartz	20	-	20	20
	accessories	15x)	-	19	19
ATTAGEL	attapulgite	-	-	-	55x)
	montmorines	20	-	-	20
	quartz	20	-	-	20
	accessories	5x)	-	-	5x)

x) less exact values

Table 4 : Grain size distribution of accessory minerals

Sample	fraction	%	quartz	feldspar	calcite	Fe-minerals + opaque	heavy minerals + others
ATTAPULGITE	630 - 200 µø	-	-	-	-	-	-
	200 - 63	3,82	3,24	0,25	0,21	0,04	0,08
	63 - 20	15,22	9,45	2,89	-	1,37	1,51
	20 - 6,3	6,50	3,16	2,58	-	0,36	0,40
	< 6,3	4,16	2,07	1,59	-	0,30	0,20
		29,70	17,92	7,31	0,21	2,07	2,19
ATTAPULGUS	630 - 200 µø	3,00	2,00	-	-	1,00	-
	200 - 63	8,30	5,10	0,64	0,64	1,28	0,64
	63 - 20	10,40	4,15	3,75	-	1,25	1,25
	20 - 6,3	10,00	5,40	2,30	-	1,54	0,76
	< 6,3	7,30	3,32	2,00	-	1,32	0,66
		39,00	19,97	8,69	0,64	6,39	3,31

Table 5 : D. T. A. reactions
(medium values from all ATTAPULGITE, ATTAPULGUS and ATTAGEL samples investigated)

reaction	character	extent from - to °C	maximum at °C
A	endotherm	50 (100) - 235	151 ± 9, resp. 130 + 162
B	"	235 - - 400	280 ± 8
C	"	400 - 600	485 ±10, 562
D	"	680 - 750	730 ± 5
E	exotherm	810 - 1000	853x), 875
F	"	1000 - 1150	1073 ± 9

x) for ATTAPULGITE only

Table 6 : Results of the thermogravimetric analysis

Sample	grain size µ ø	pretreatment		rehydration time	weight loss in %				
		temp. °C	time		complete	0 - 280°C	280 - 400	400 - 650	650 - 1000
ATTAPULGITE	< 63	-	-	-	a) 20,70	12,12	3,46	4,41	0,71
"	"	-	-	-	b) 19,30	10,90	2,80	4,60	1,00
"	"	300	1 h	16 h	17,00	9,55	2,34	4,31	0,80
"	"	350	1 h	16 h	16,50	8,70	2,25	4,65	0,90
"	"	350	7 h	16 h	16,80	9,37	2,19	4,30	0,94
"	"	380	1 h	16 h	14,60	7,67	1,97	4,16	0,80
"	"	390	1 h	16 h	14,10	6,90	1,72	4,31	1,17
"	"	400	1 h	16 h	11,10	5,47	1,03	3,57	1,03
"	"	500	1 h	16 h	6,20	3,56	0,31	1,32	1,01
ATTAGEL	< 2	-	-	-	20,50	11,78	2,40	3,92	2,40
ATTAPULGUS	630-200	-	-	-	a) 13,00	6,80	1,43	3,50	1,27
"	"	-	-	-	b) 12,68	6,50	1,39	3,56	1,23
"	< 63	-	-	-	12,80	6,72	1,40	3,43	1,25
"	< 6,3	-	-	-	15,69	9,24	2,00	3,84	0,61
"	630-200	400	1 h	16 h	9,48	4,00	0,82	3,35	1,31
"	< 63	400	1 h	16 h	10,31	4,67	0,97	3,38	1,29
"	< 6,3	400	1 h	direct T.G.A.	3,73	-	-	2,91	0,82
"	< 6,3	400	1 h	16 h	12,33	6,50	1,19	3,53	1,11
"	< 6,3	400	1 h	40 h	12,44	6,90	1,20	3,40	0,94
"	< 6,3	400	1 h	10 h	13,13	7,40	1,23	3,53	0,97

Table 7 : Cation adsorptionx)

Sample	pretreatment		adsorption capacity in mequ. / 100 g. at pH=7				
	temp. °C	time	Na^+	K^+	Cs^+	Ca^{++}	Ba^{++}
ATTAPULGITE	-	-	-	12,2	14,9	-	19,5
"	300	1 h	-	11,7	14,4	-	21,5
"	350	1 h	-	11,0	10,5	-	22,1
"	380	1 h	-	9,1	8,5	-	26,0
"	400	1 h	-	16,8	23,0	-	42,3
"	450	1 h	-	-	-	-	43,7
"	500	1 h	-	18,3	28,9	-	44,8
"	600	1 h	-	15,6	24,1	-	47,2
"	700	1 h	-	-	-	-	44,3
"	800	1 h	-	-	-	-	13,7
"	1000	1 h	-	-	-	-	0,0
ATTAPULGUS 24-48 mesh	-xx)	-	10,1	12,6	16,2	22,1	35,2

x) values obtained by G. Gigli

xx) preheated already by the producer

Table 8 : Specific surface measurements

Sample	grain size μ ø	pretreatment		ethylene glycol retention mg. / g. clay	corresponding surface m^2 / g.
		temp. °C	time		
ATTAPULGITE	< 63	-	-	88,7	286,0
"	"	300	1 h	88,3	284,8
"	"	400	1 h	61,9	199,7
"	"	600	1 h	42,2	136,1
"	"	800	1 h	7,5	24,2
ATTAPULGUS	630-200	-x)	-	54,3	175,1
ATTAGEL	< 2	-	-	88,0	283,8

x) preheated already by the producer

Table 9 : Specific surfaces of several clay minerals (literature data)

Author / sample	ethylene glycol retention		B.E.T. (ethane)
	mg/g	m^2/g	m^2/g
DYAL and HENDRICKS:			
kaolinite	14,0	45,1	28,2
illite	58,0	187,1	89,6
montmorillonite from Wyoming	236,0	761,3	43,9
" heated to 400°C	137,0	441,9	
" " to 600°C	19,0	61,3	
HEYDEMANN:			
kaolinite from Zettlitz x)	19,6	63,2	
illite from Fithian x)	60,7	195,8	
montmorillonite from Upton/Wyoming x)	238,0	767,7	

x) <2 µ ⌀ fractions

Table 10 : Gaschromatographic analyses

Sample	ortho-	meta-	para-terphenyl
a) pure ortho-terphenyl			
as furnished	99,8 %	0,2	-
boiled for 5 h	99,5	0,5	-
boiled for 5 h + ATTAPULGUS	35,7	61,5	2,8
b) pure meta-terphenyl			
boiled for 5 h	-	98,2	1,8
boiled for 5 h + ATTAPULGUS	2,5	92,7	4,8
c) OM-2 (PROGIL)			
boiled for 5 h	23,3	74,0	2,7
boiled for 5 h + ATTAPULGUS	19,1	77,5	3,4

Table 11 : conditions of the two lab scale column experiments

	experiment A	experiment B
Circuit	closed	open
flow direction	up	down
velocity, kg/h	0,54	6,5
time of run, h	30	12
temperature, °C		
Column	135	300
tubes	150	300
containers	200	300
pressure, atm.	1	2-3
Column		
length, m	1,00	1,00
diameter, mm	18	40
material	glass	steel V4A
ATTAPULGUS 24-48 mesh		
pretreatment, °C/1h	300	400
quantity, g	130	780
terphenyl used	OM-2	OM-2
V/m	10	100
backup-filter pore size, μ	15 x 40	3

Table 12 : Granulometry and quantity of the breakdown material <200 µØ from column experiment A. (% of the initial sample weight)

Fraction		Top sample	Bottom sample
200 - 63 µ Ø	....	2,02 %	0,66
63 - 20	....	0,43	0,28
20 - 6,3	....	0,47	0,51
<6,3	....	0,64	0,66
<200 µ Ø	....	3,56 %	2,11 %

Table 13 : Dissolved fractions from the two column experiments

	Total ash	SiO_2	Al^{3+}	Fe^{3+}	Ca^{2+}	K^+
a) Experiment A						
OM-2 before run ..	–$^{x)}$	9 ppm	1	6	–$^{x)}$	7
" after 5 h ..	–	2	1	1	–	6
" " 15 h ..	–	2	1	1	–	6
" " 30 h ..	–	10	2	10	–	9
b) Experiment B						
OM-2 before run ..	1,0 ppm	–$^{xx)}$	–$^{xx)}$	0,2	0,7	–$^{x)}$
" after 3 h ..	1,4	–	–	0,3	1,0	–
" " 7 h ..	1,3	–	–	0,2	0,4	–
" " 12 h ..	0,9	–	–	0,2	0,7	–

x) not estimated

xx) not contained

Plates

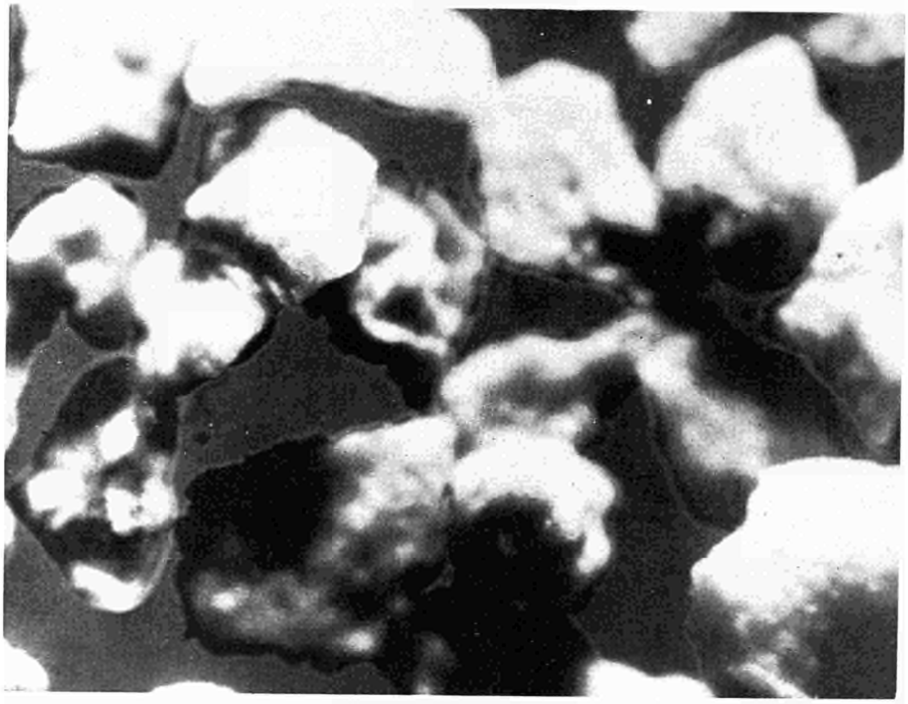


Plate 1 : ATTAPULGUS 24 - 48 mesh, as furnished

Plate 2 : ATTAPULGUS grains before (white) and after (black) terphenyl contact

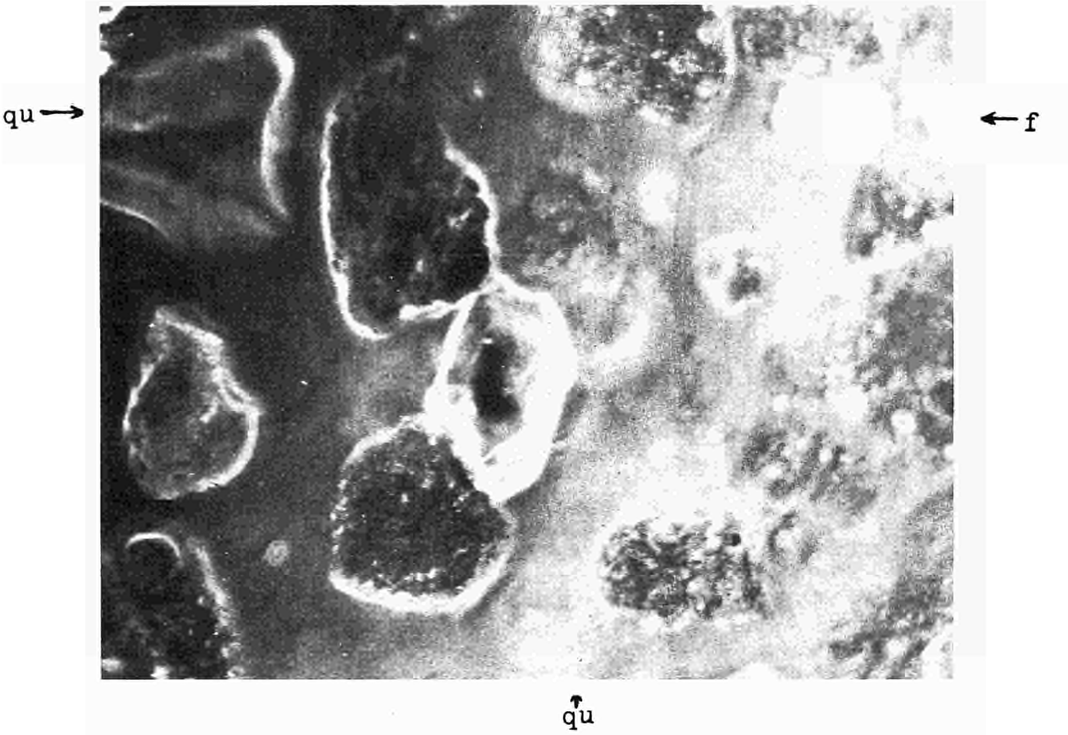


Plate 3 : ATTAPULGUS 200-63 µ Ø microscope fraction, containing quartz (qu), feldspar (f) and aggregates. 100 x, phase contrast

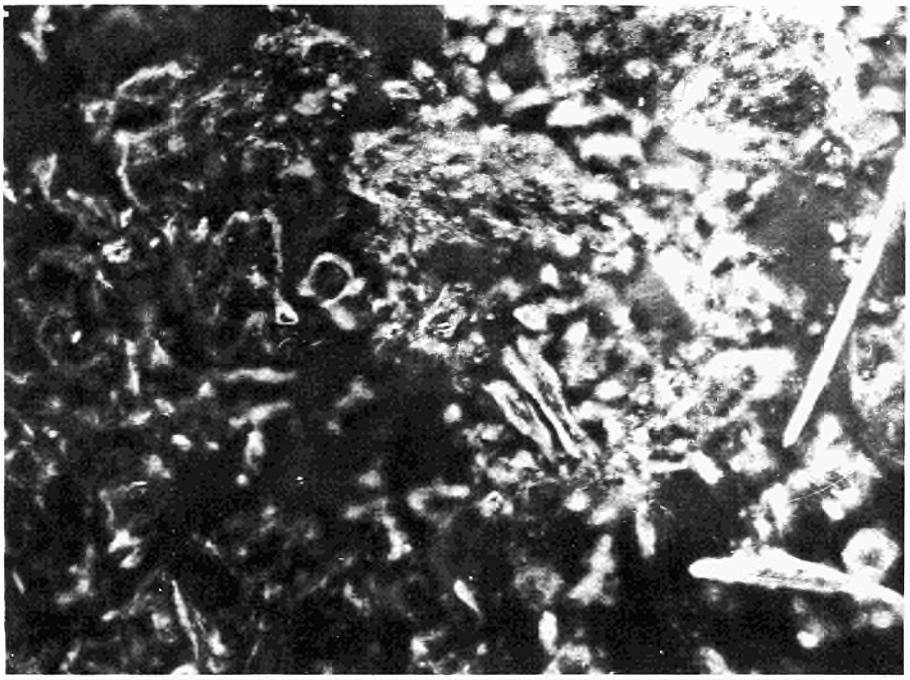
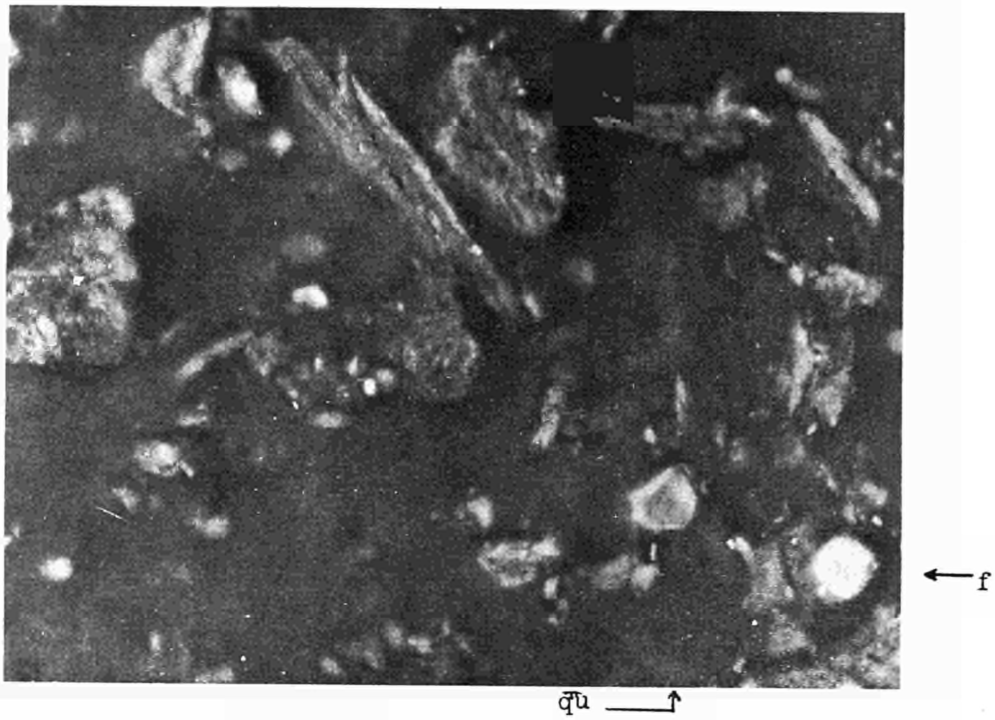
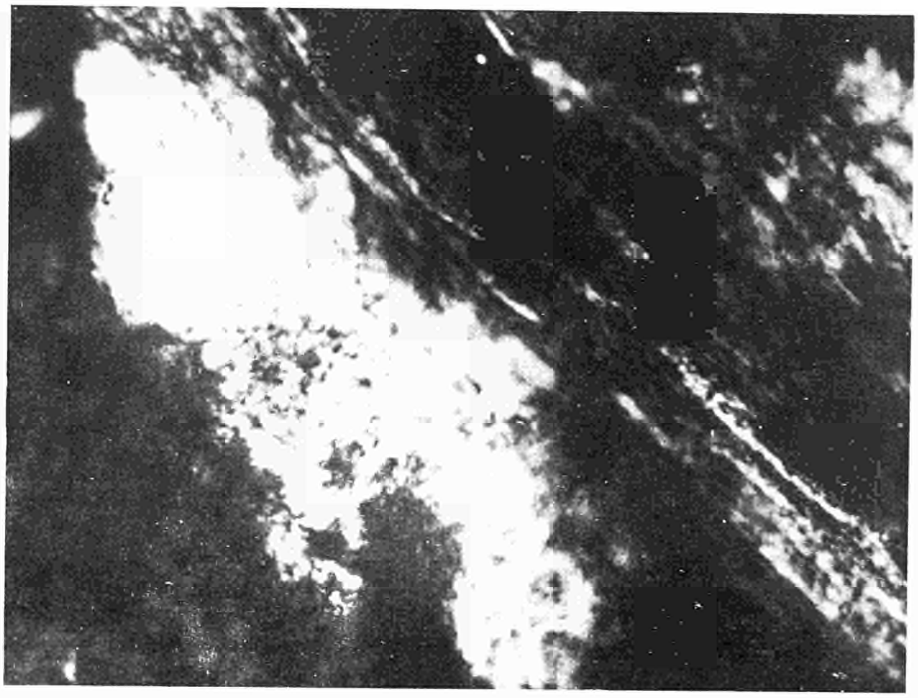


Plate 4 : ATTAPULGITE 63-20 µ Ø microscope fraction, aggregated particles. 100 x, phase contrast



<u>Plate 5 :</u> ATTAPULGITE 20-6,3 µ Ø microscope fraction, aggregates, quartz (qu), feldspar (f). 250 x, phase contrast



<u>Plate 6 :</u> ATTAPULGITE 20-6,3 µ Ø microscope fraction, internal aggregate birefringence due to parallel orientation of attapulgite fibres. 630 x, crossed nicols

Plate 7 : Electron micrograph, 15.000 x. ATTAPULGUS <2 /u 0

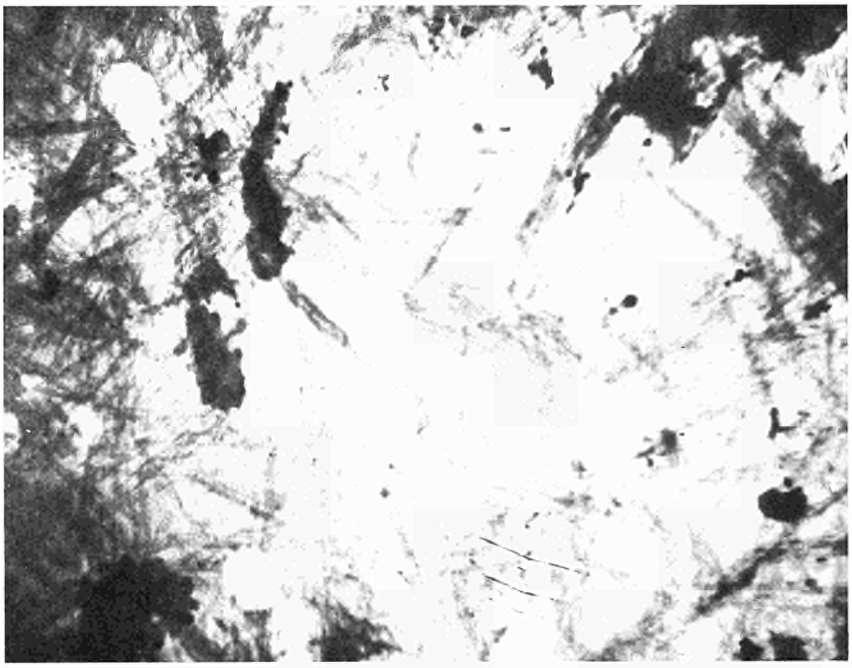


Plate 8 : Electron micrograph, 15.000 x. ATTAPULGITE <2 /u 0, not pretreated. Parallel and unoriented aggregation of attapulgite single fibres

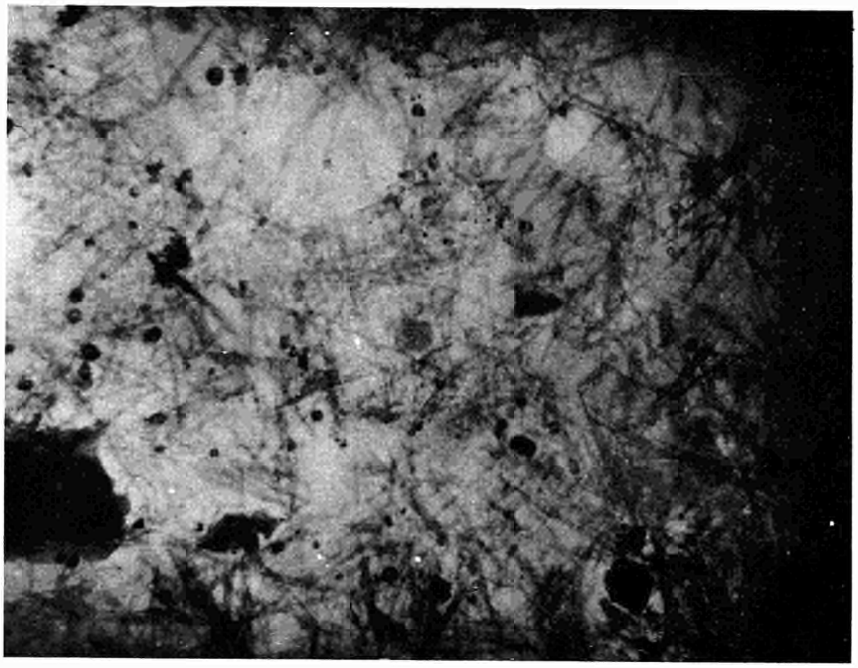


Plate 9 : Electron micrograph, 15.000 x. ATTAPULGITE preheated 1 h at 800°C. Attapulgite fibres, montmorillonite and kaolinite platelets

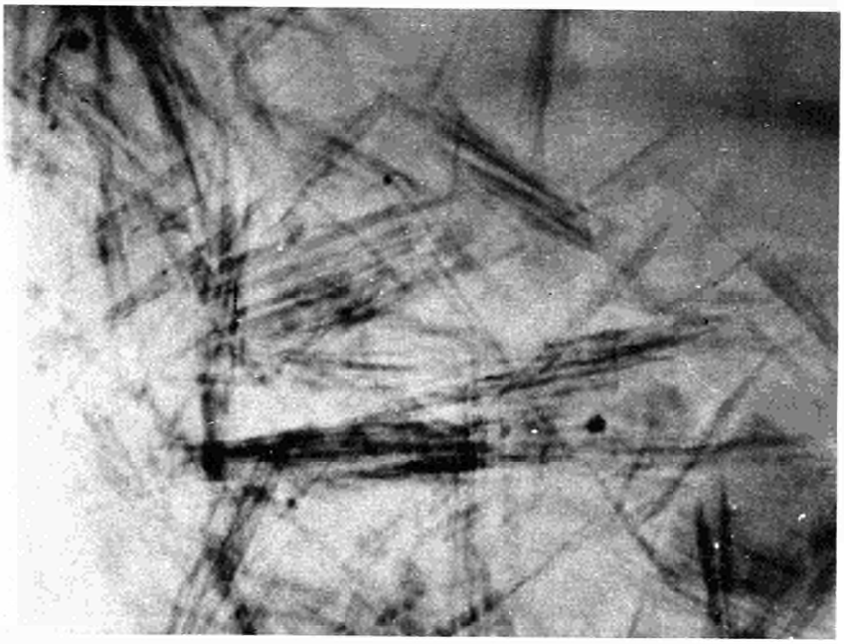


Plate 10 : Electron micrograph, 30.000 x. ATTAPULGITE, not pretreated

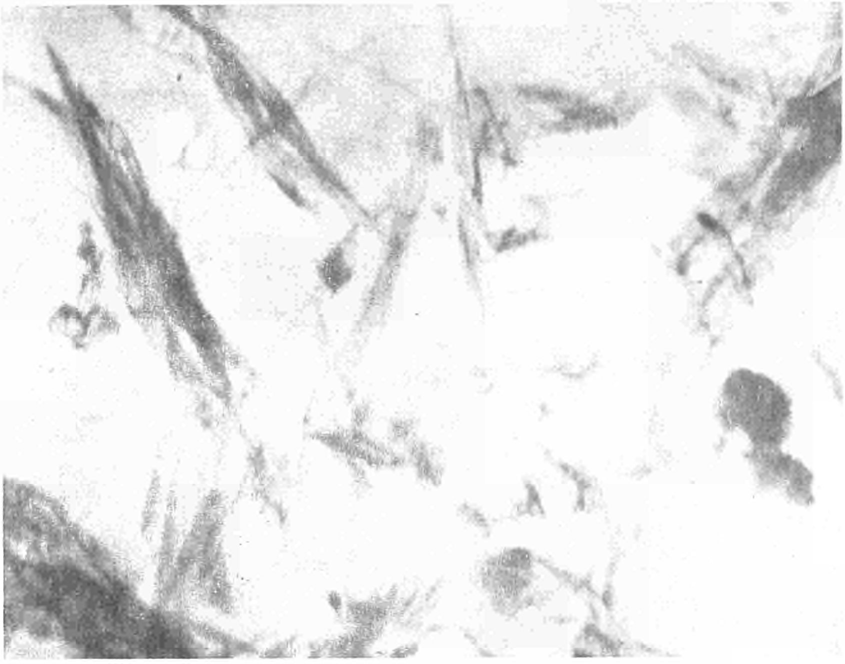


Plate 11 : Electron micrograph, 30.000 x. ATTAPULGITE, preheated 1 h at 600°C

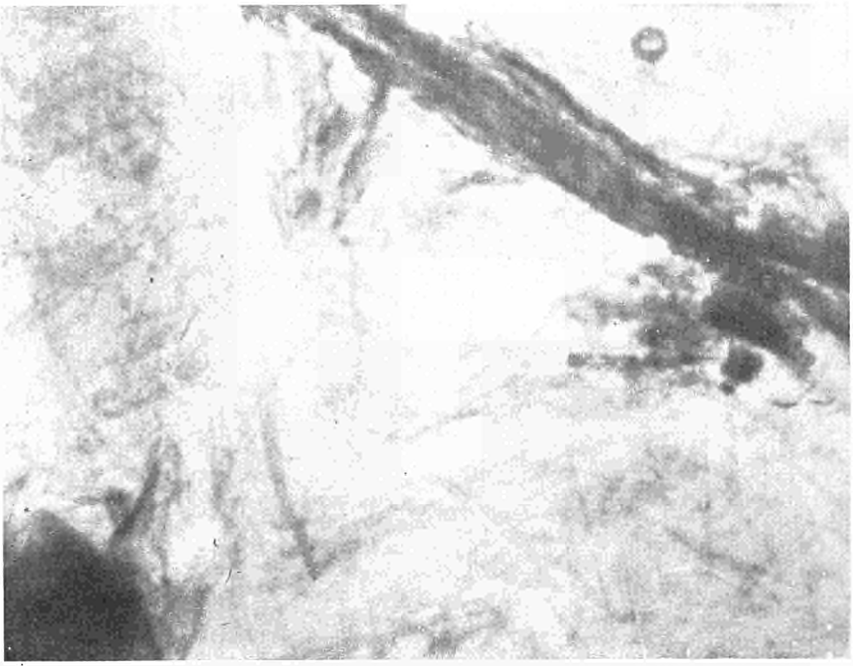


Plate 12 : Electron micrograph, 30.000 x. ATTAPULGITE, preheated 1 h at 800°C

Plate 13 : Electron micrograph, 45.000 x. ATTAPULGITE, preheated 1 h at 800°C and again heated under the microscope. Escape of gas bubbles (black points) and broadening of needles

Figure 1

PROJECTION ON (001) OF UNIT CELL OF ATTAPULGITE (BRADLEY 1940)

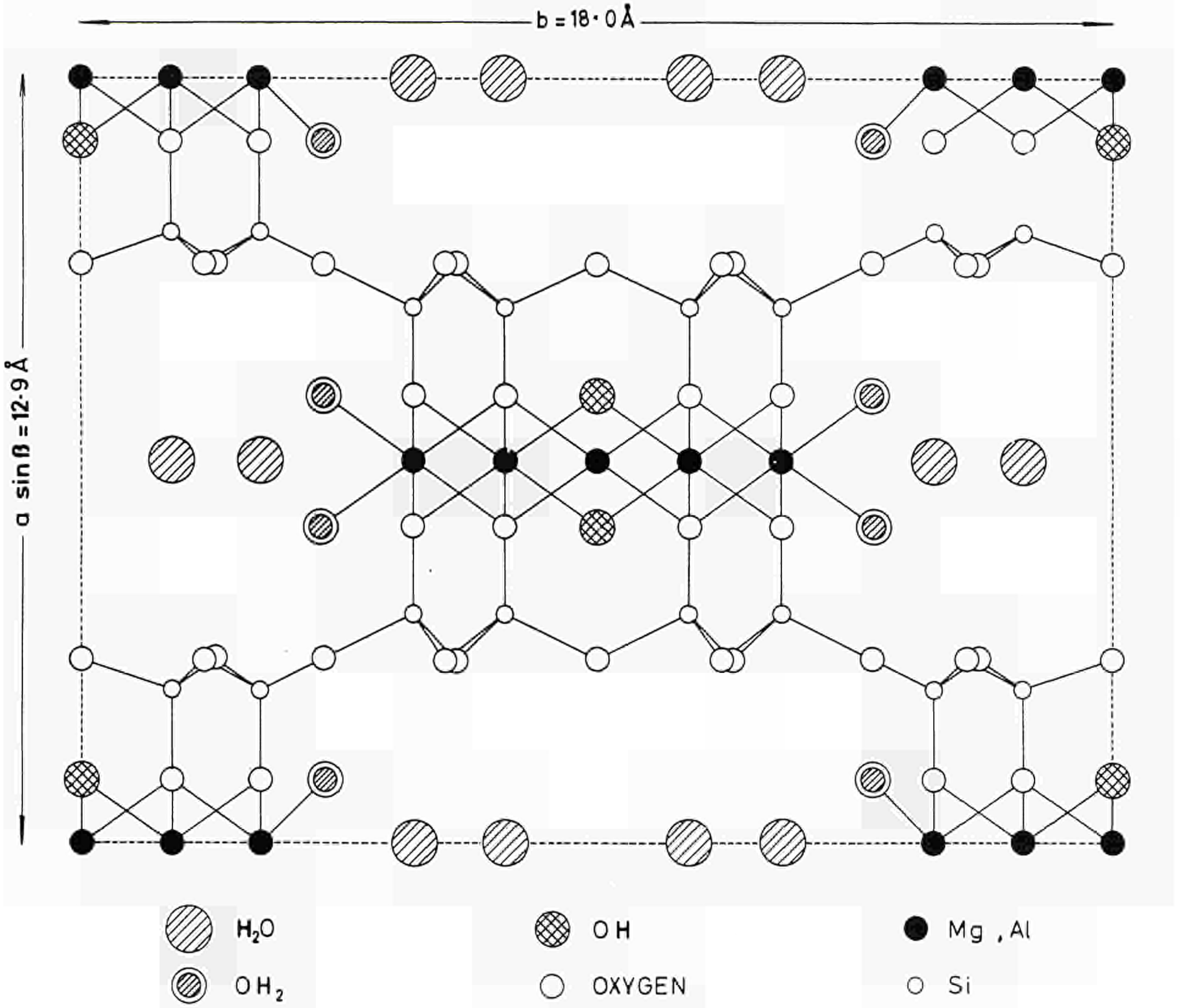


Figure 2

GRAIN SIZE DISTRIBUTION OF ACCESSORY MINERALS

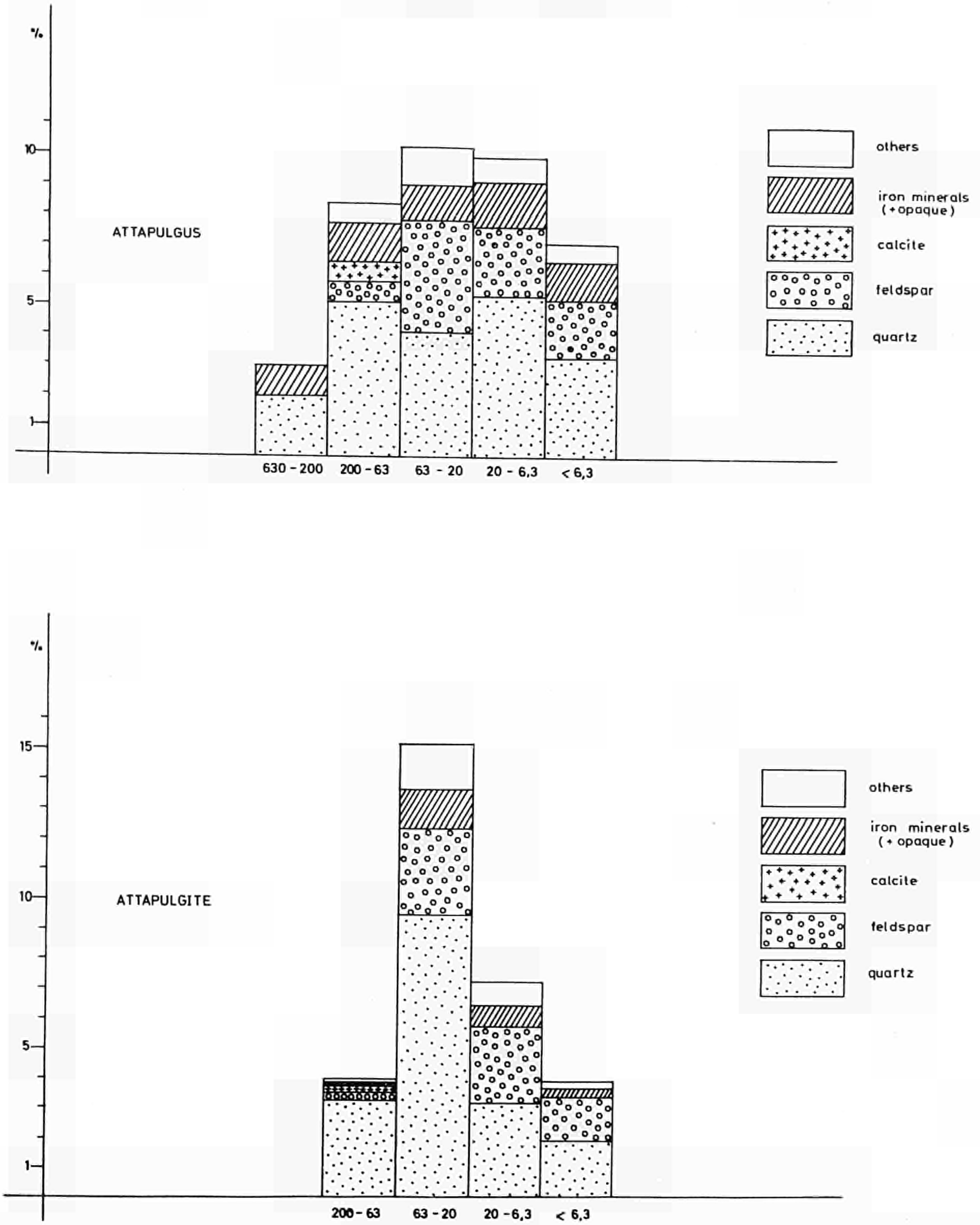


Figure 3

DIFFERENTIAL THERMAL ANALYSIS

(ΔT/T)

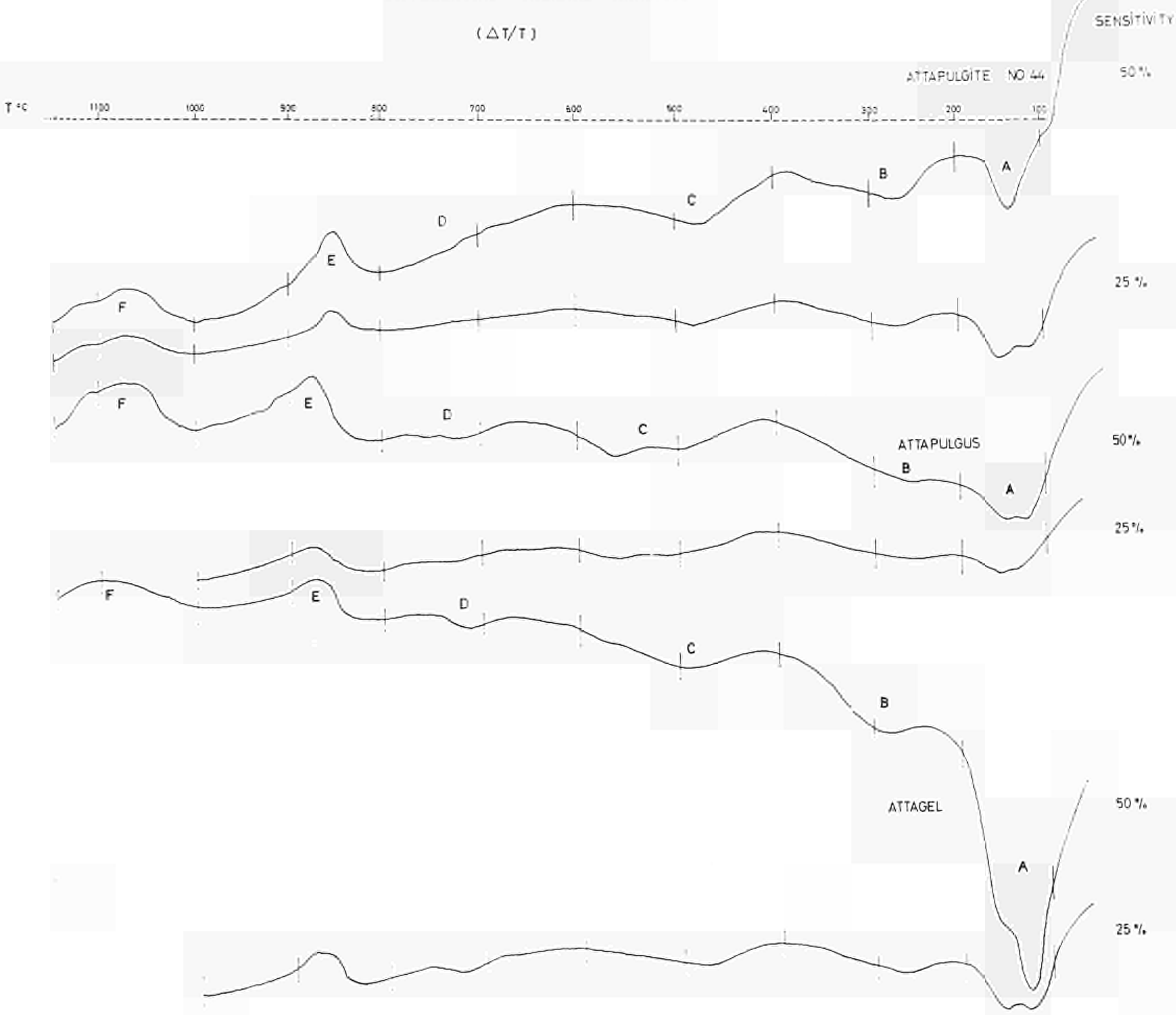


Figure 4

ATTAPULGITE N°44

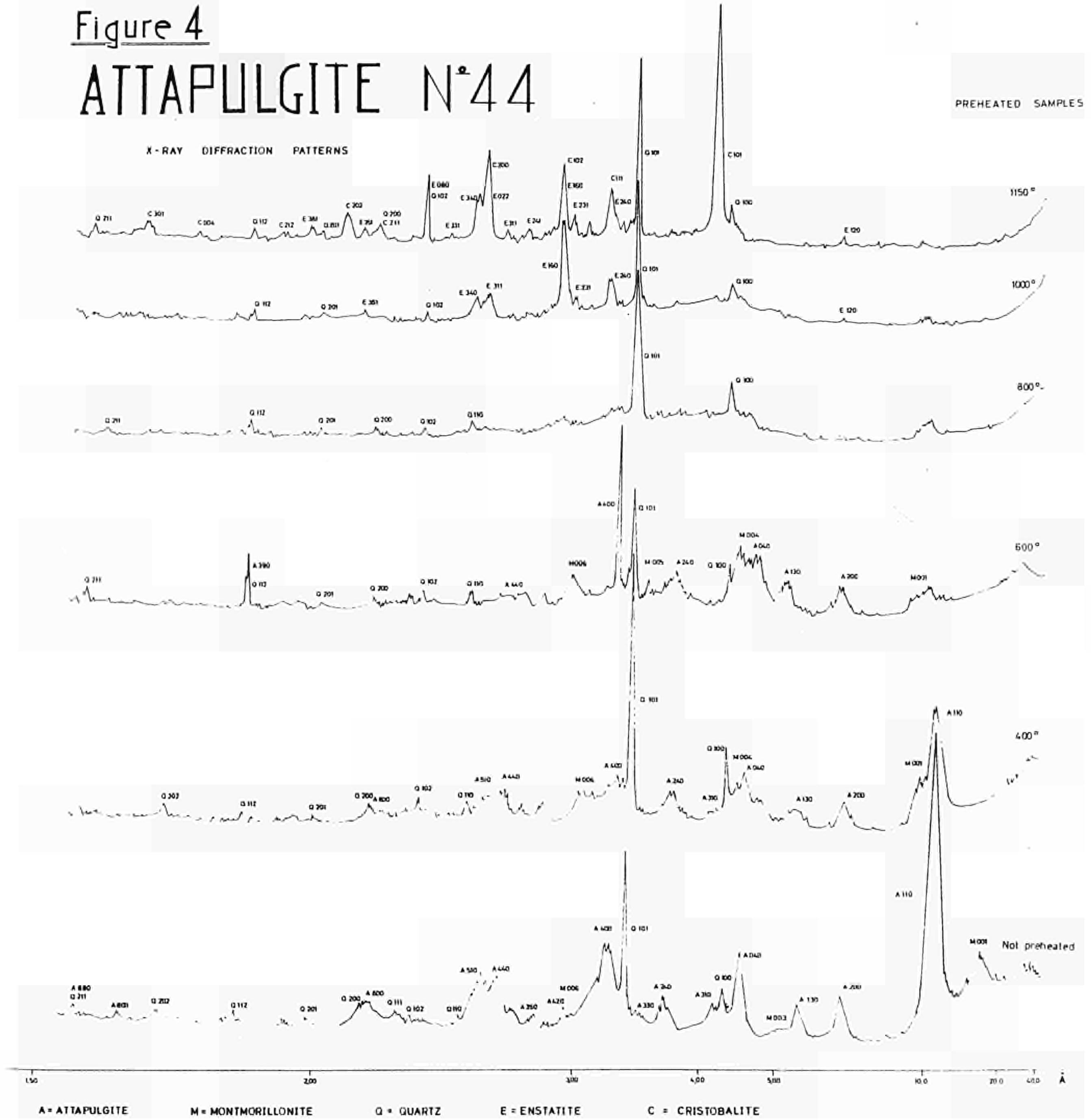


Figure 5

T G A : SINGLE REACTIONS

ATTAPULGITE

E = 0.500 g.

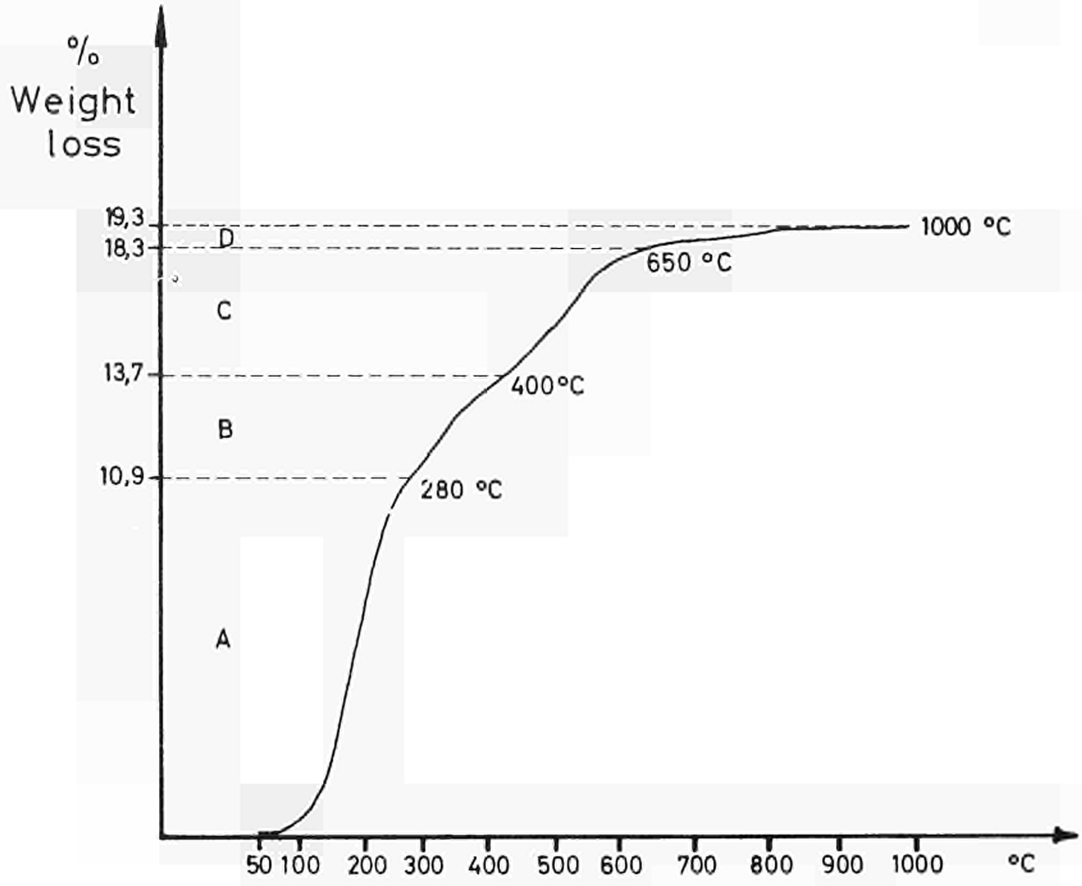


Figure 6

TGA :

REPRODUCIBILITY

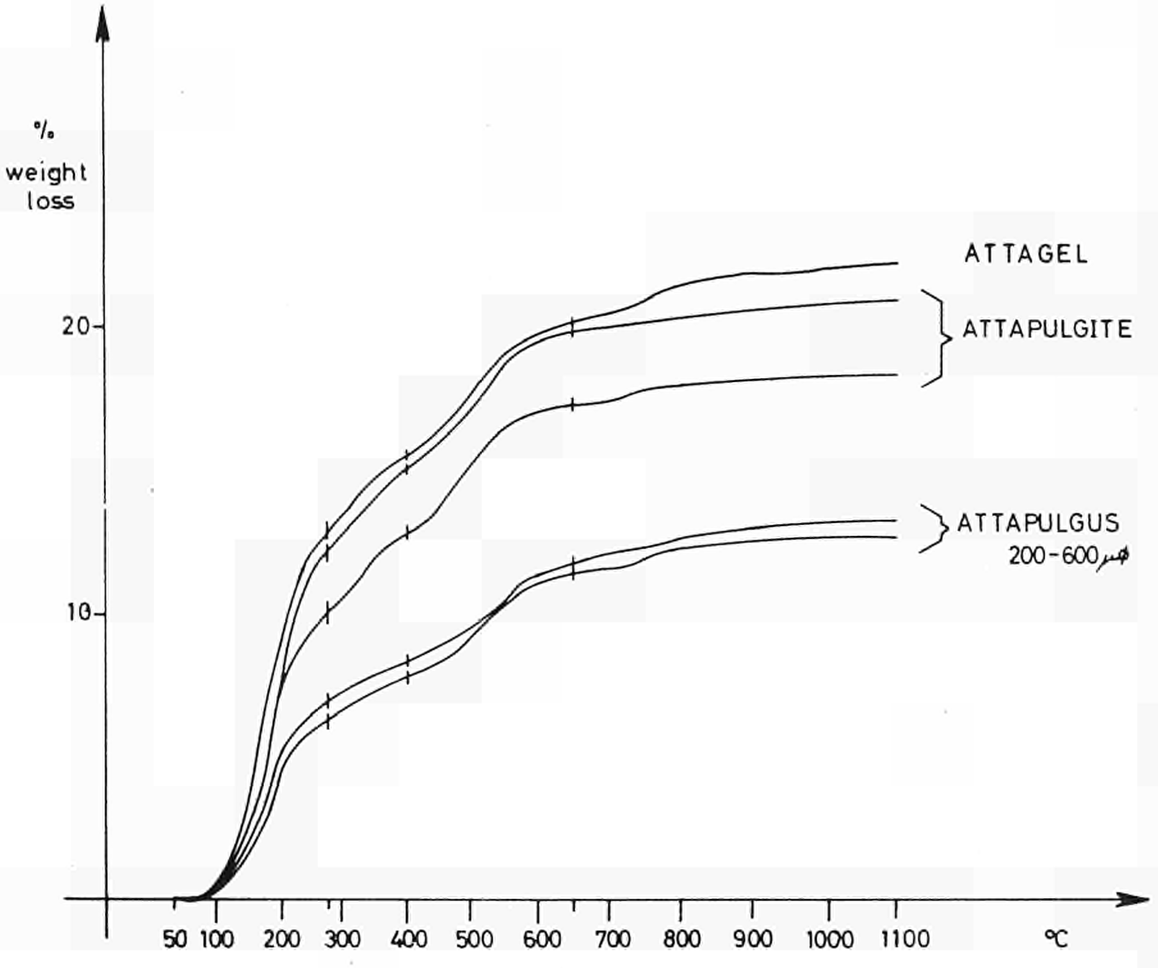


Figure 7

TGA :

GRANULOMETRIC EFFECT

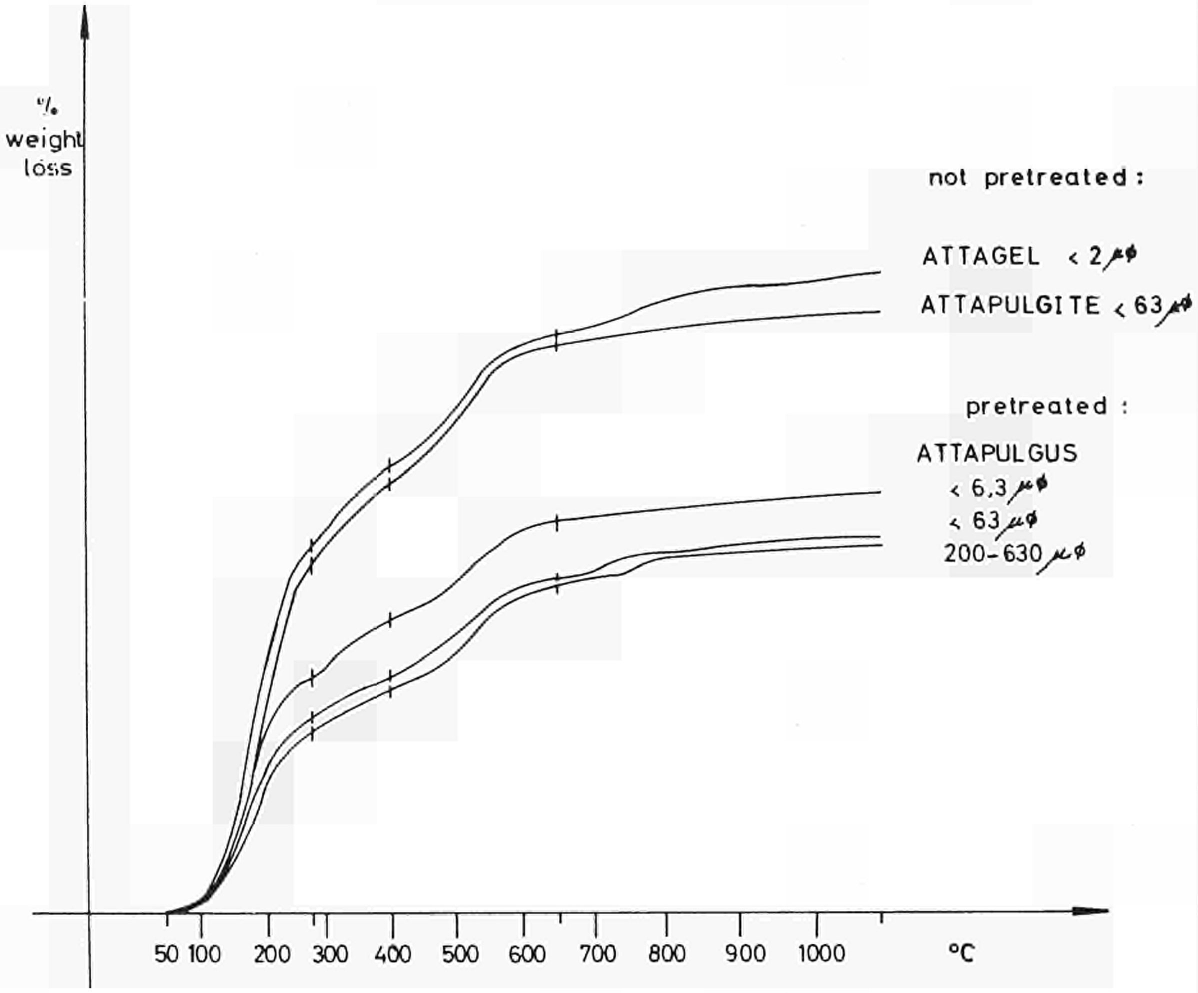


Figure 8

TGA :

GRANULOMETRIC EFFECT

all samples preheated 1h at 400°C

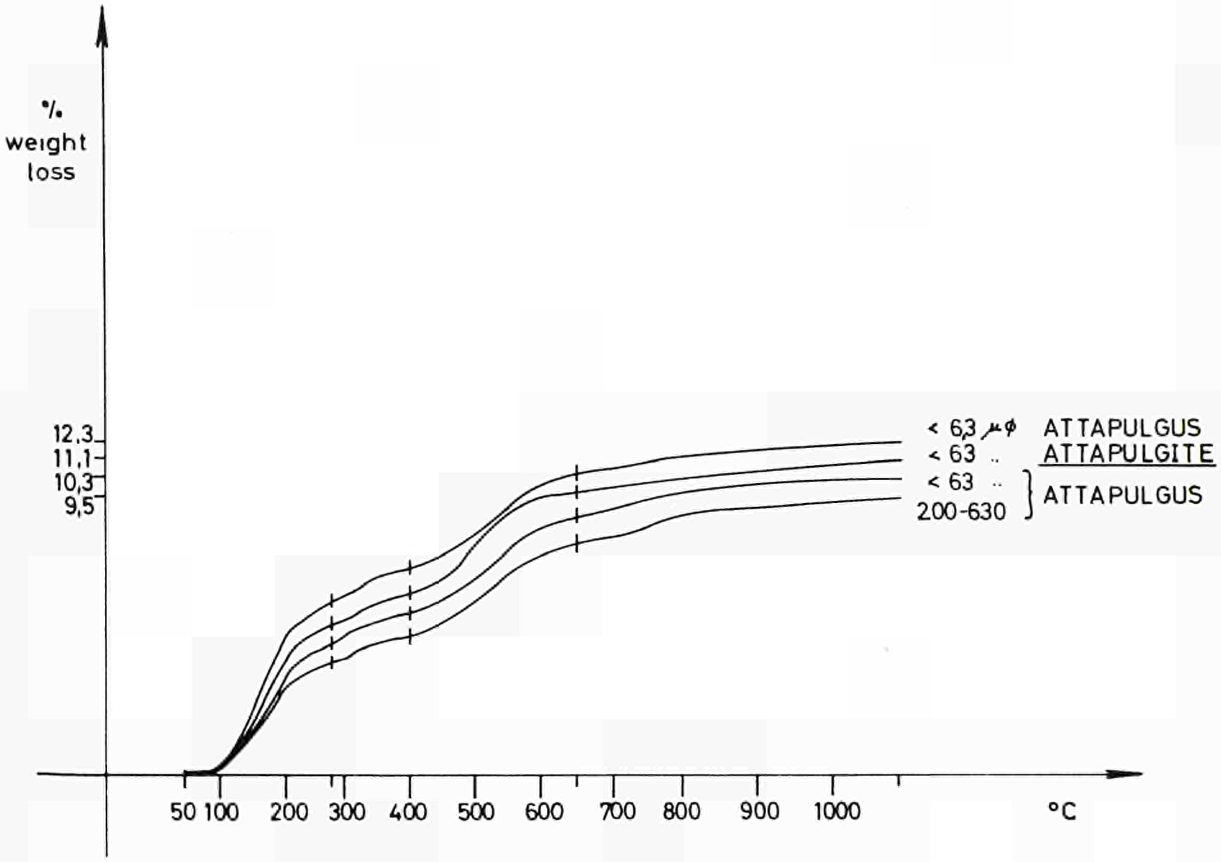


Figure 9

TGA : ATTAPULGITE

Preheated Samples

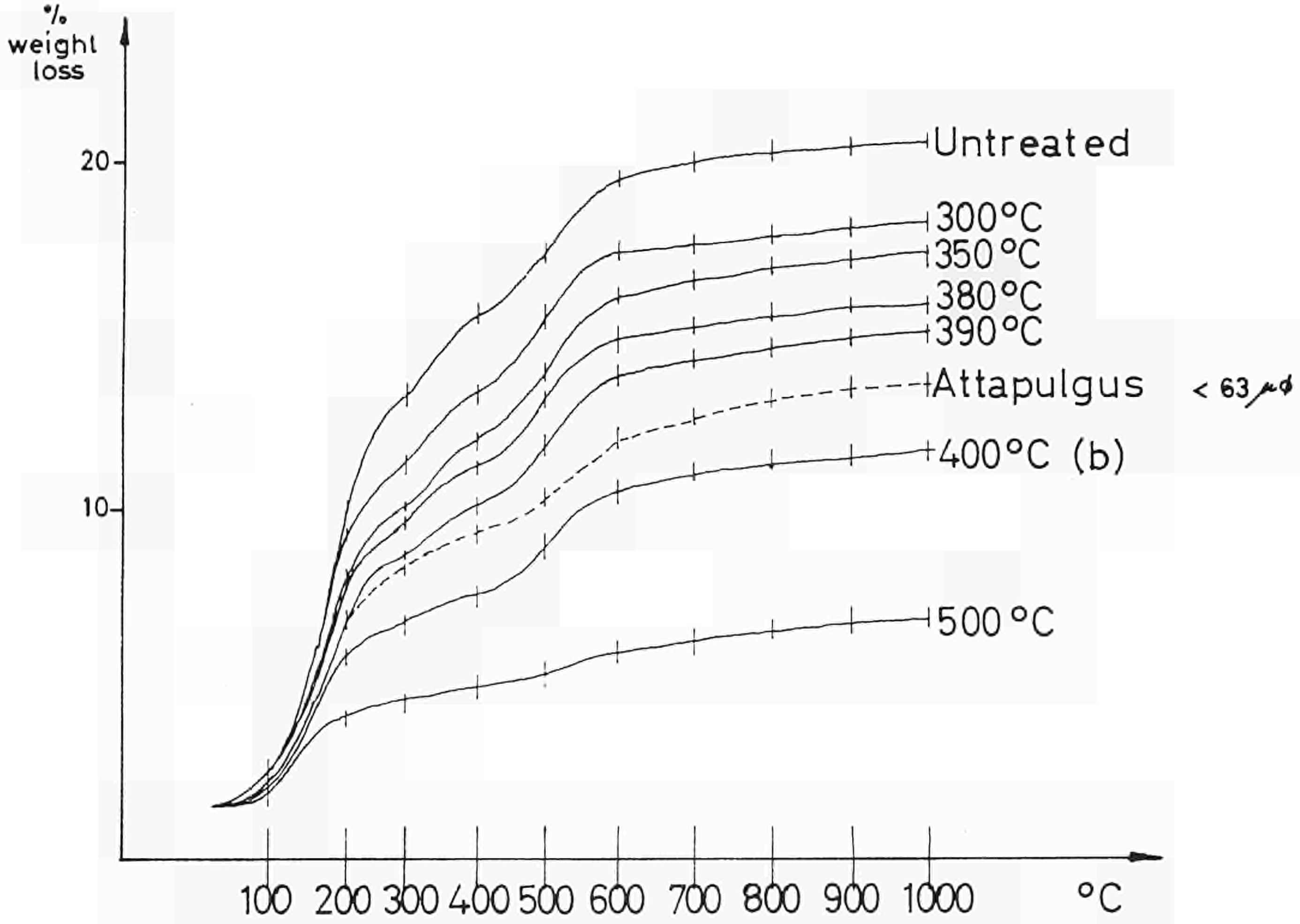


Figure 10

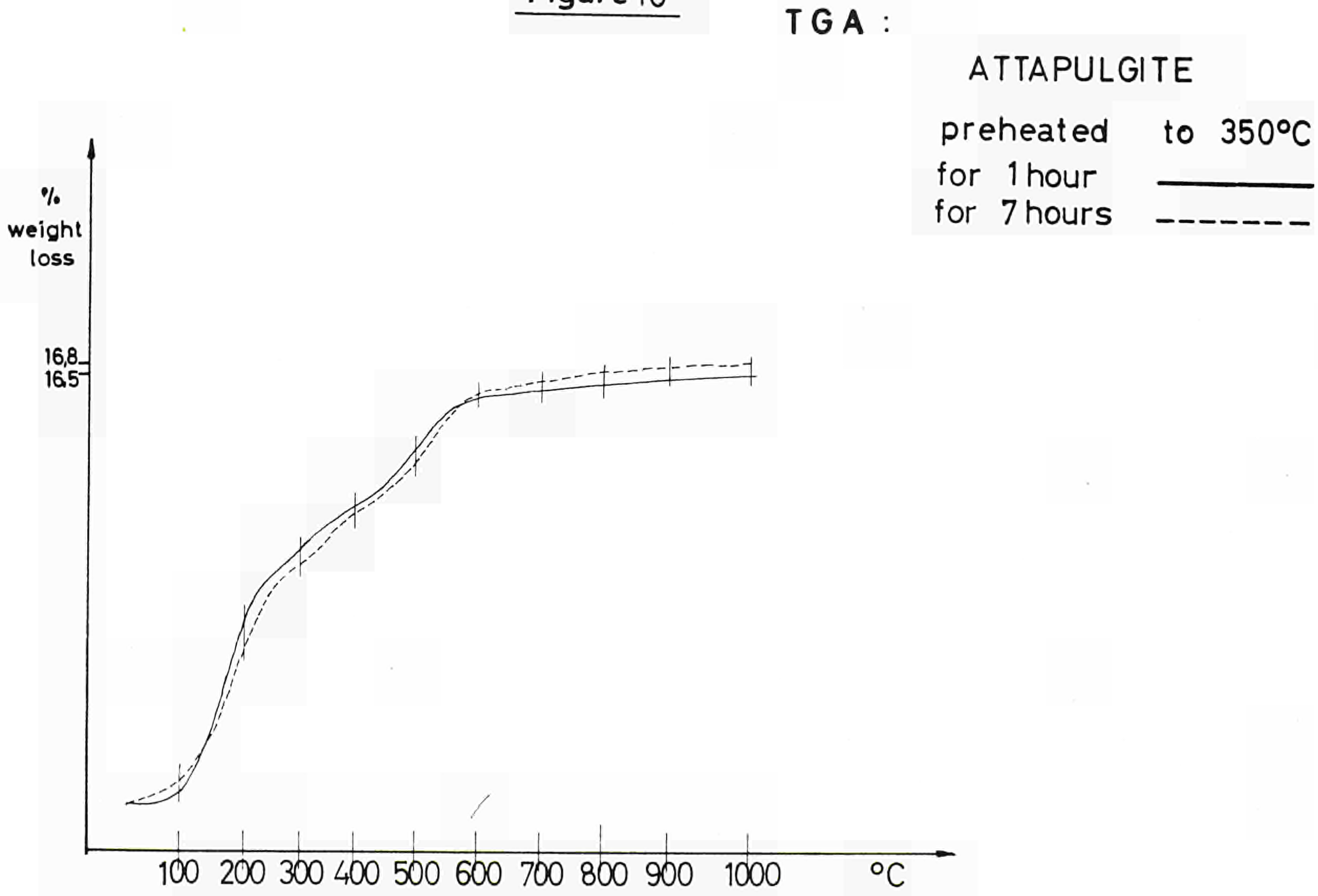

TGA :
ATTAPULGITE
preheated to 350°C
for 1 hour
for 7 hours
%
weight
loss
16,8
16,5
100
200
300
400
500
600
700
800
900
1000
°C

Figure 11

Influence of Thermal Pretreatment on TGA single reactions of ATTAPULGITE

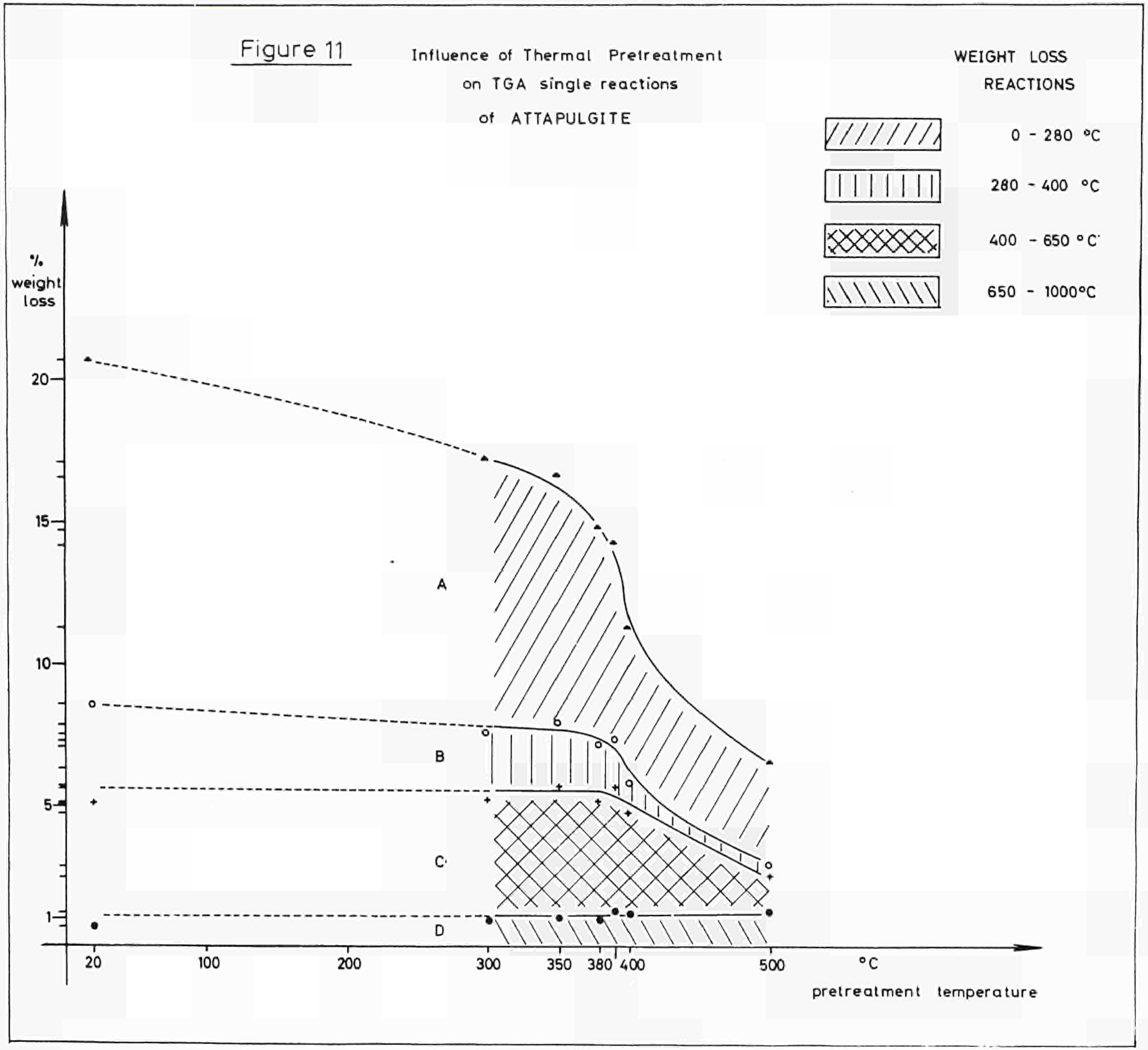


Figure 12 **TGA :**

REHYDRATION
after preheating 1h at 400°C
•
(ATTAPULGUS < 6,3 μ ϕ)

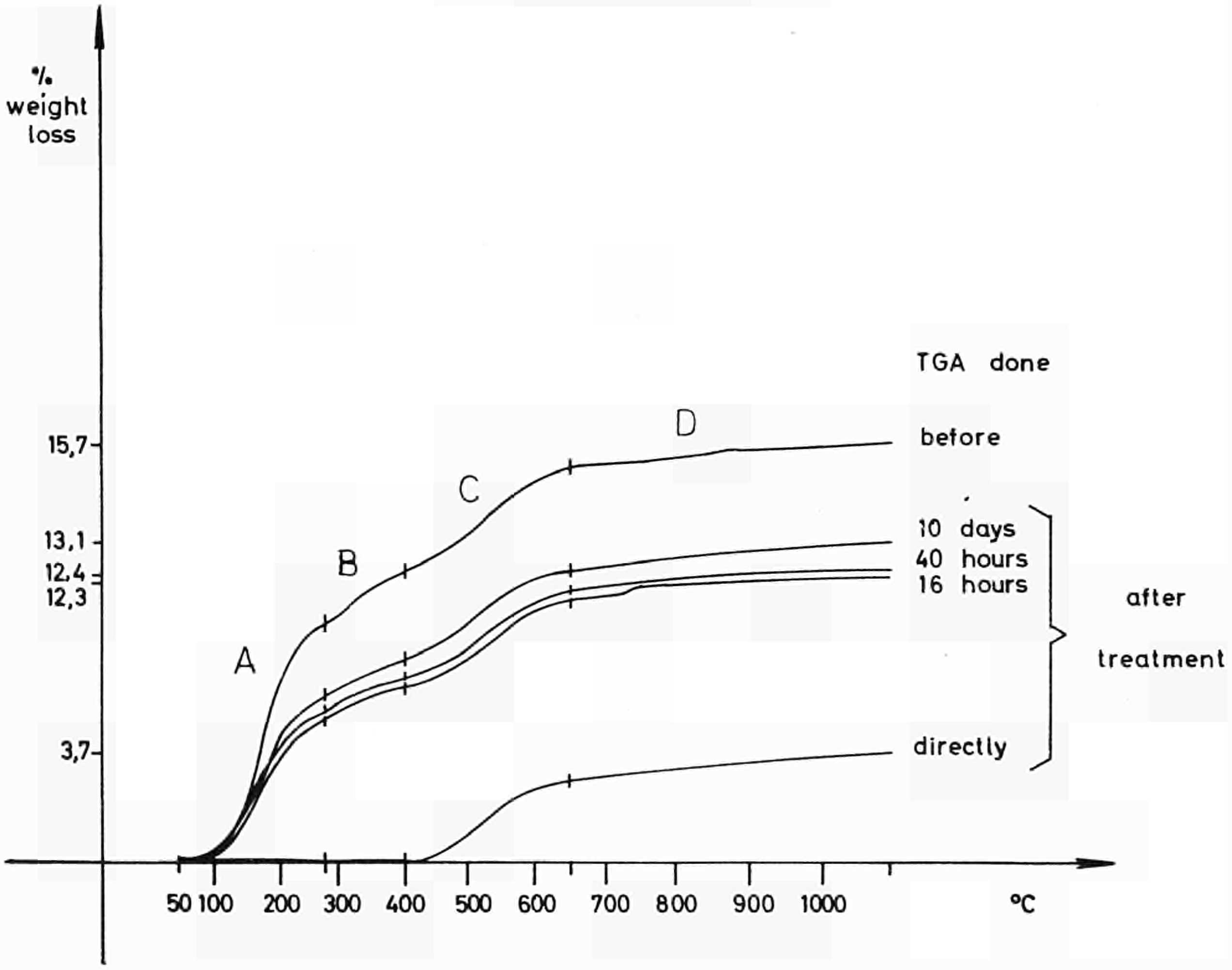


Figure 13

REHYDRATION after preheating 1h at 400 °C
TGA single reactions
of ATTAPULGUS < 6,3 µφ

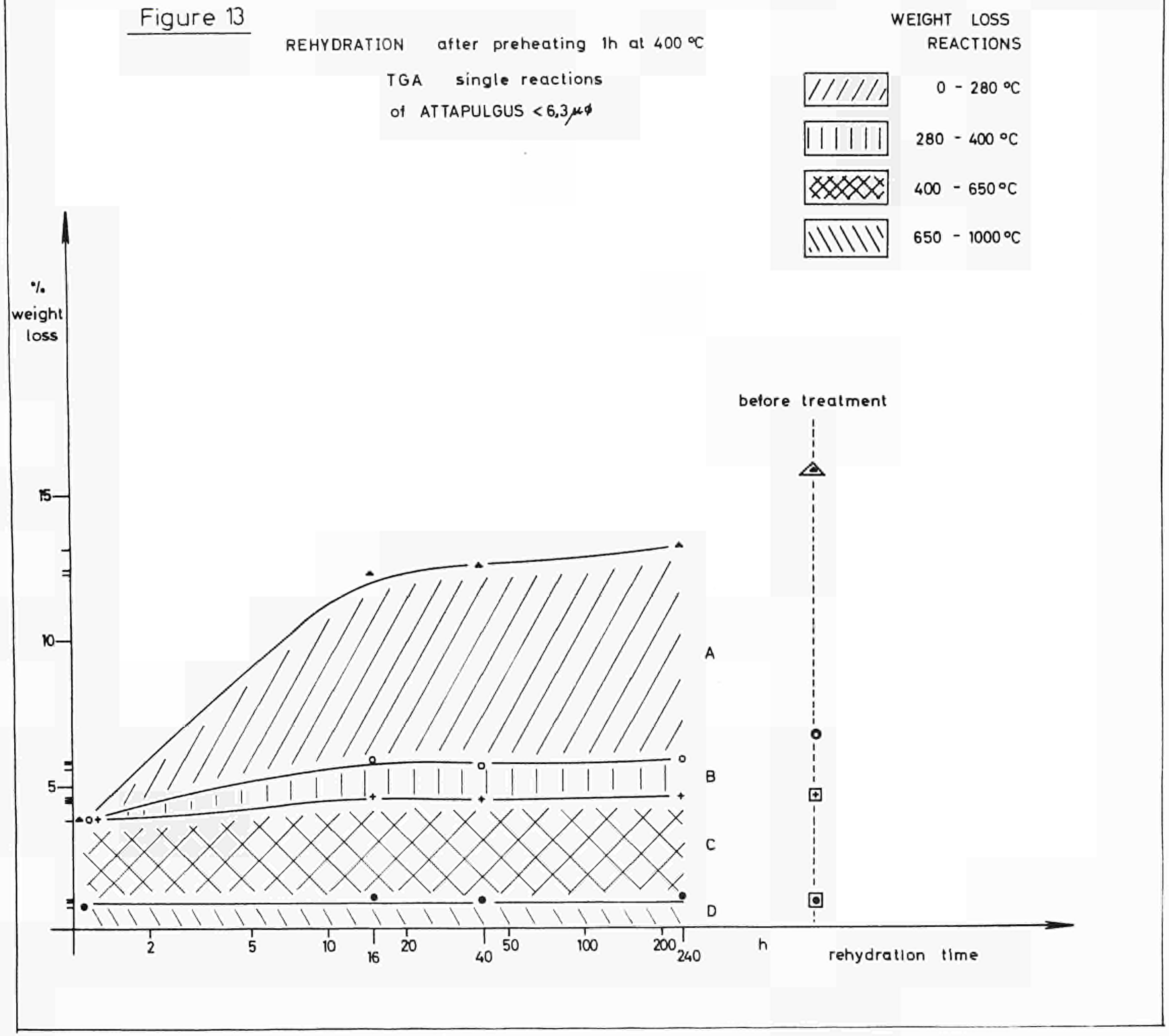


Figure 14

Cation adsorption on

ATTAPULGITE and ATTAPULGUS

depending from pretreatment temperature

(Estimated by G.GIGLI)

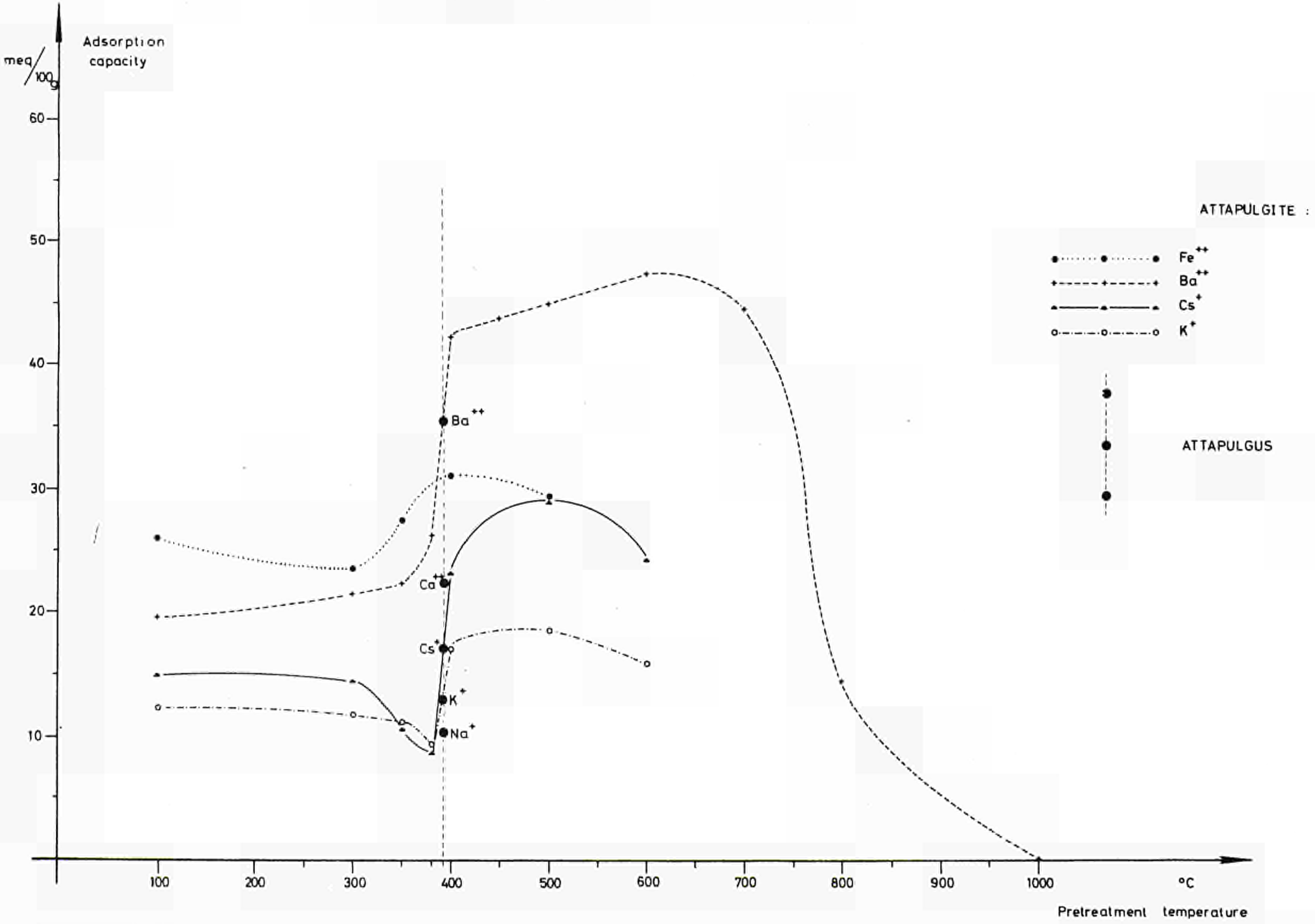
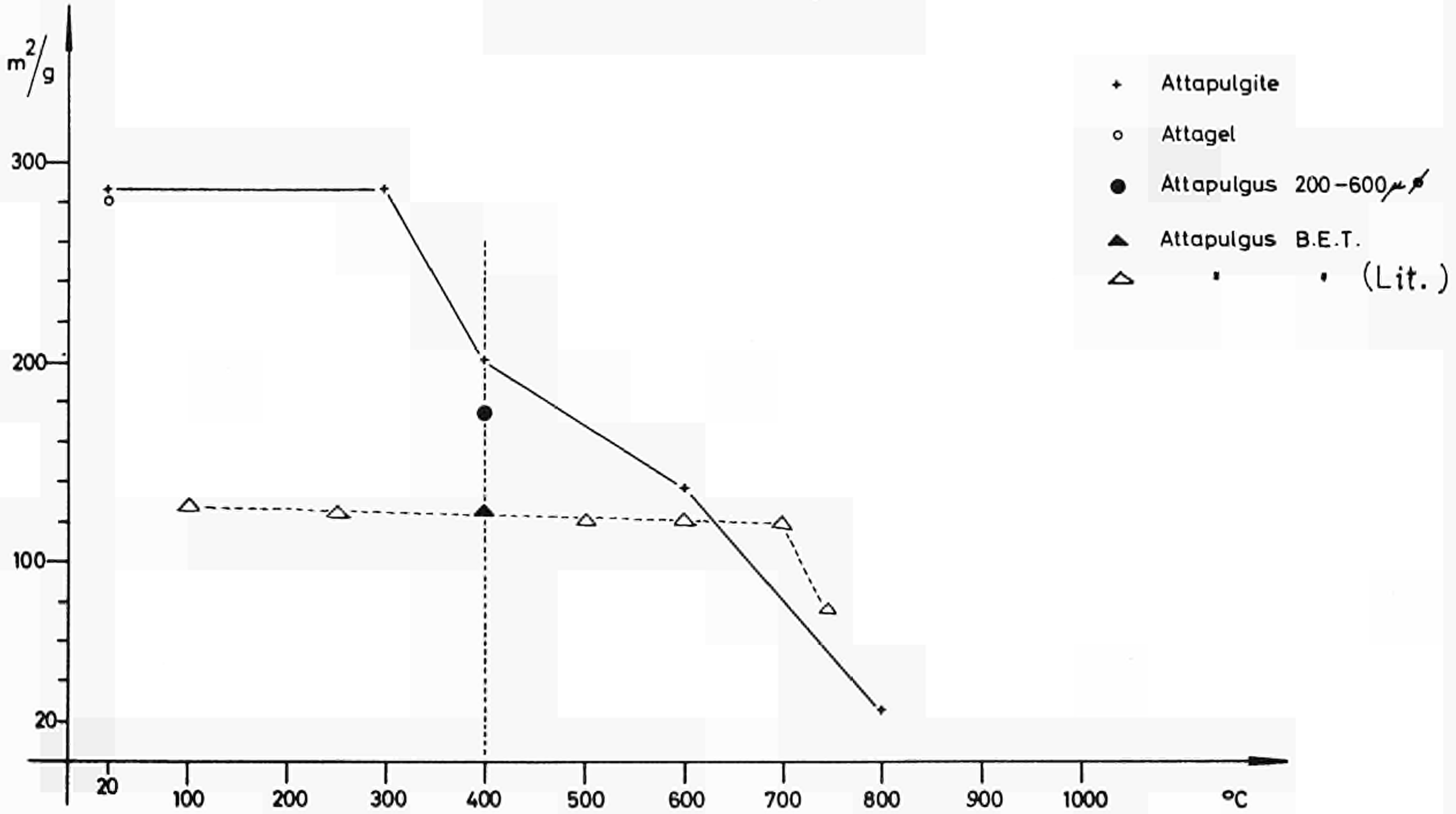
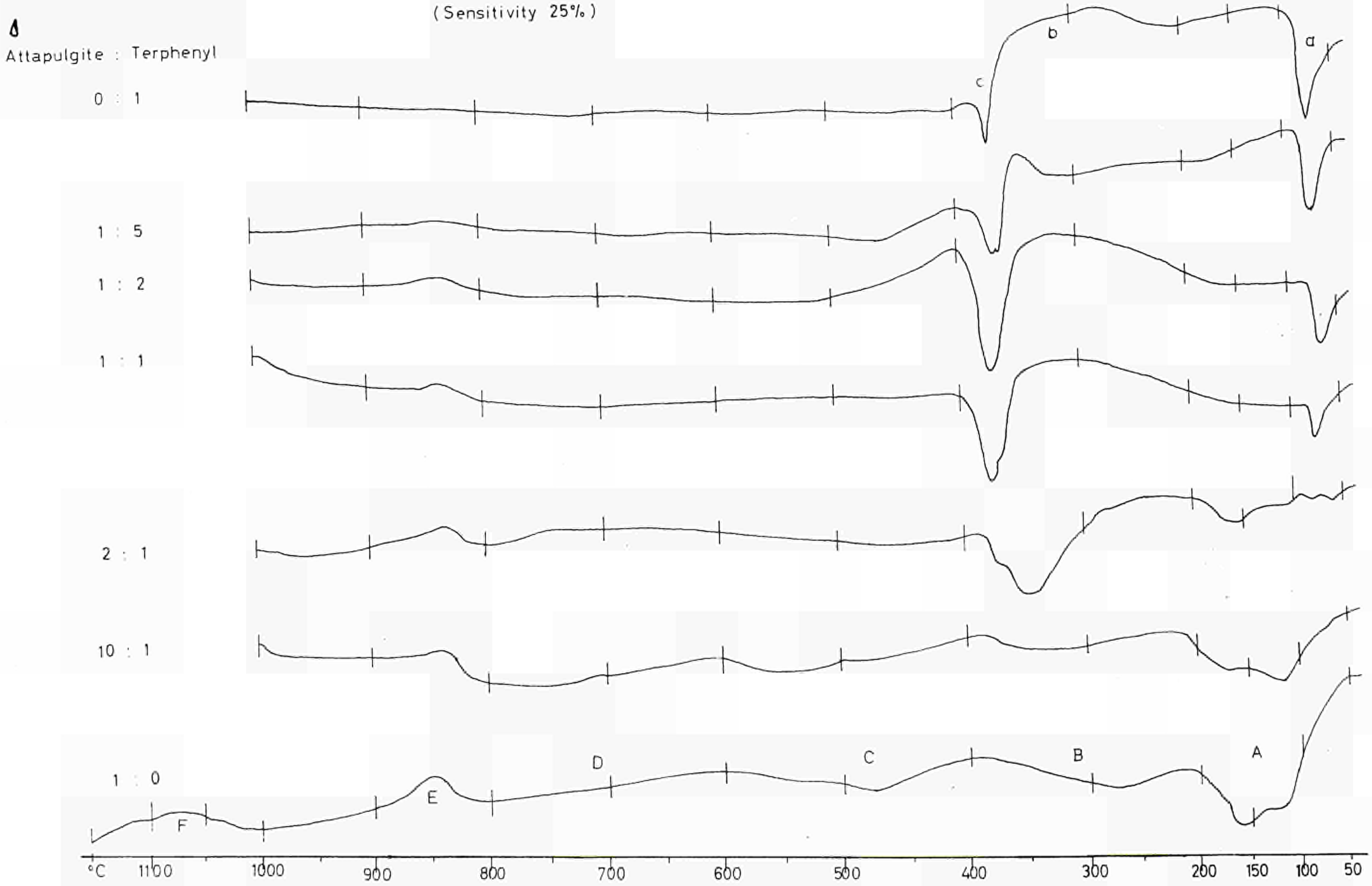


Figure 15 Ethylene Glycol Specific Surface versus Pretreatment Temperature



DTA : ATTAPULGITE - TERPHENYL MIXTURES

FIGURE 16

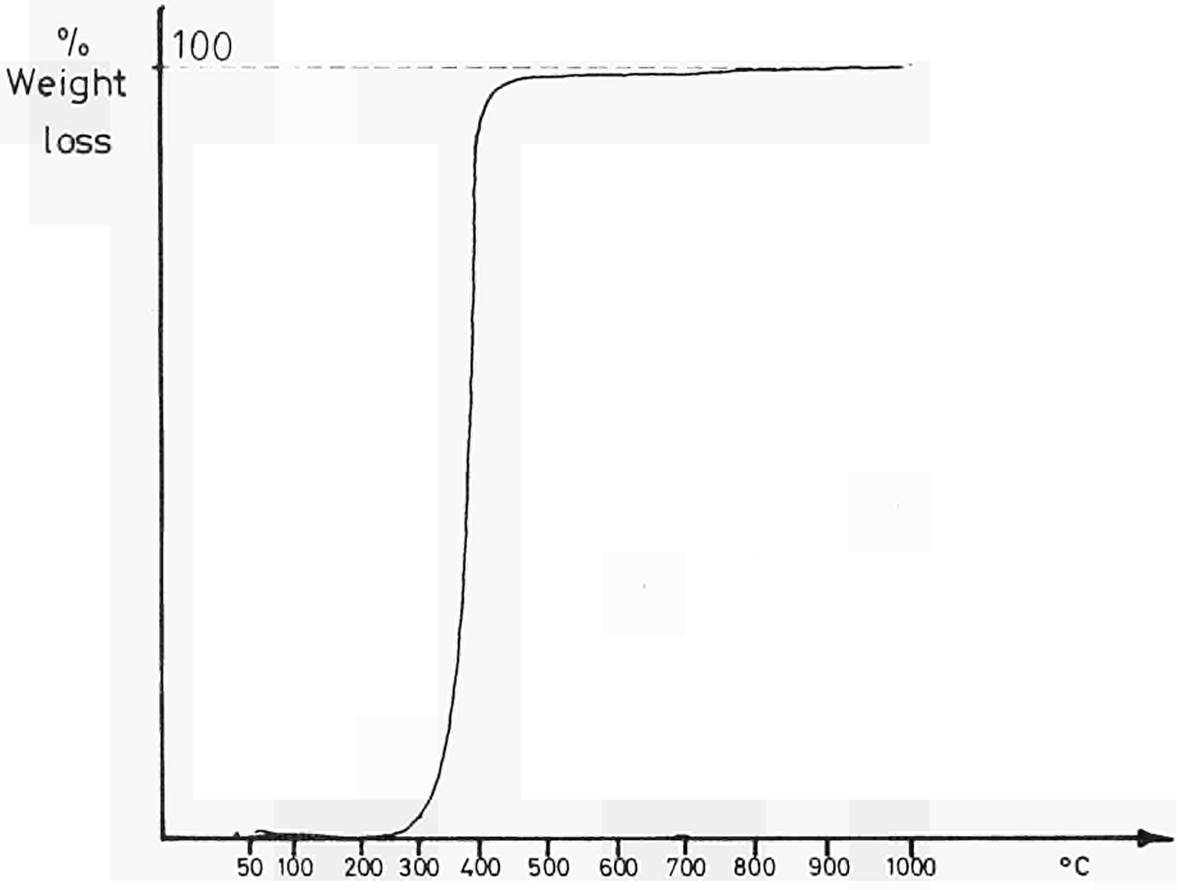


T G A :

Figure 17

TERPHENYL

E =0.117g.



T G A :

Figure 18

ATTAPULGITE - TERPHENYL MIXTURE (2:1)

E = 0.181 g.

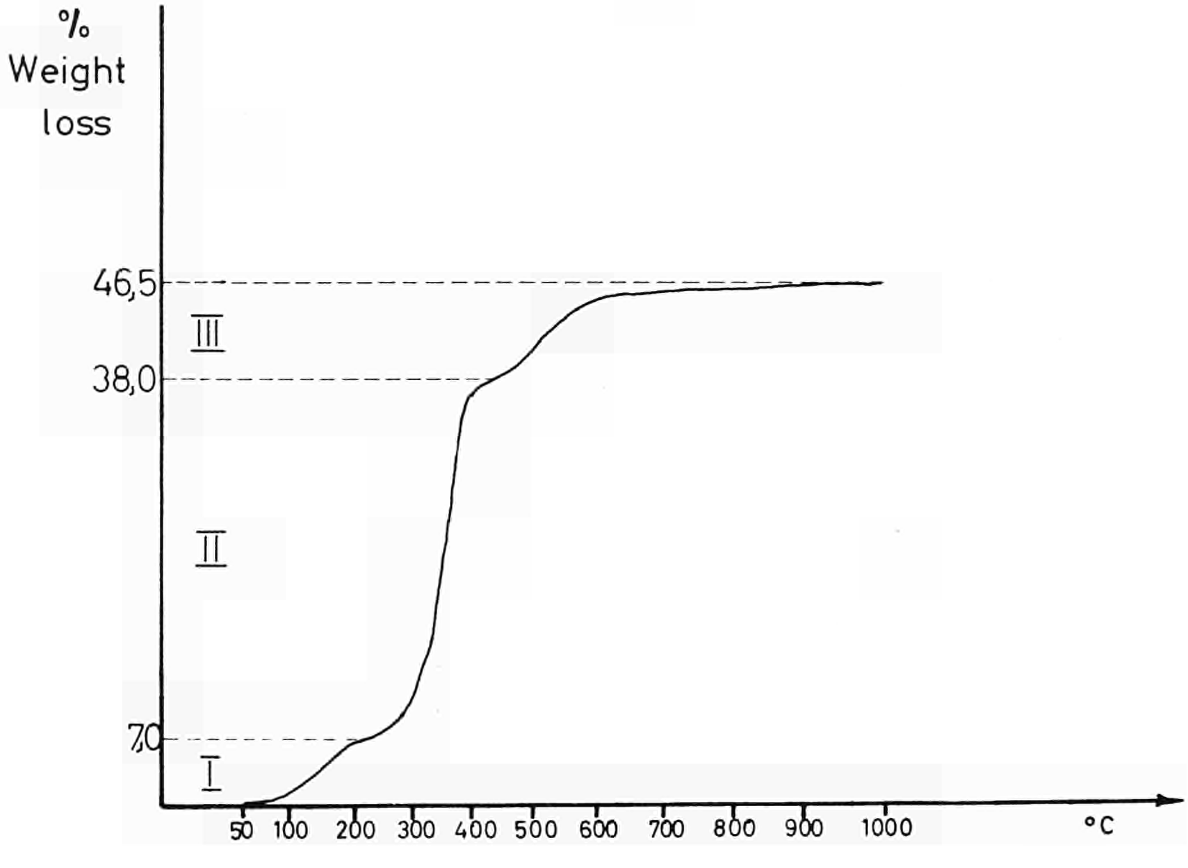


Figure 19 :

EFFECT OF REPEATED WETTING-DRYING TREATMENTS

T = 100 °C

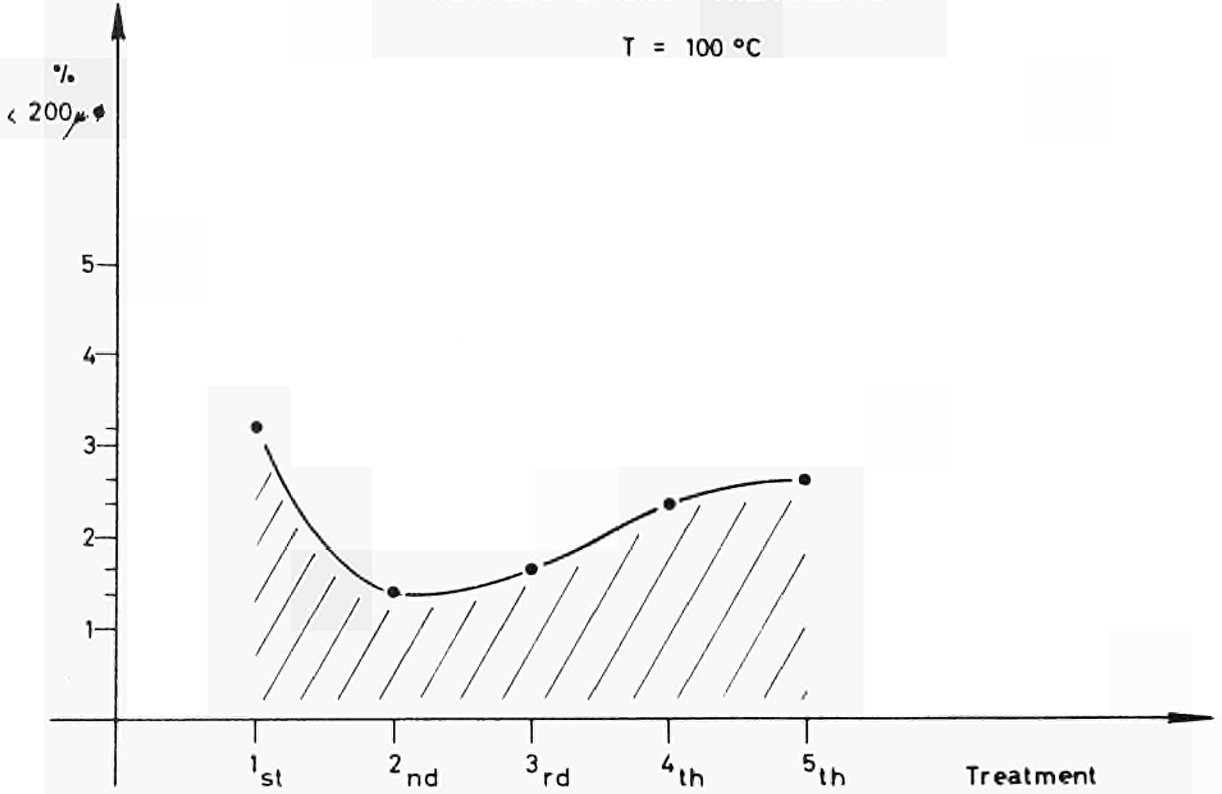


Figure 20 :

INFLUENCE OF THERMAL PRETREATMENT ON ATTAPULGUS GRAIN STABILITY

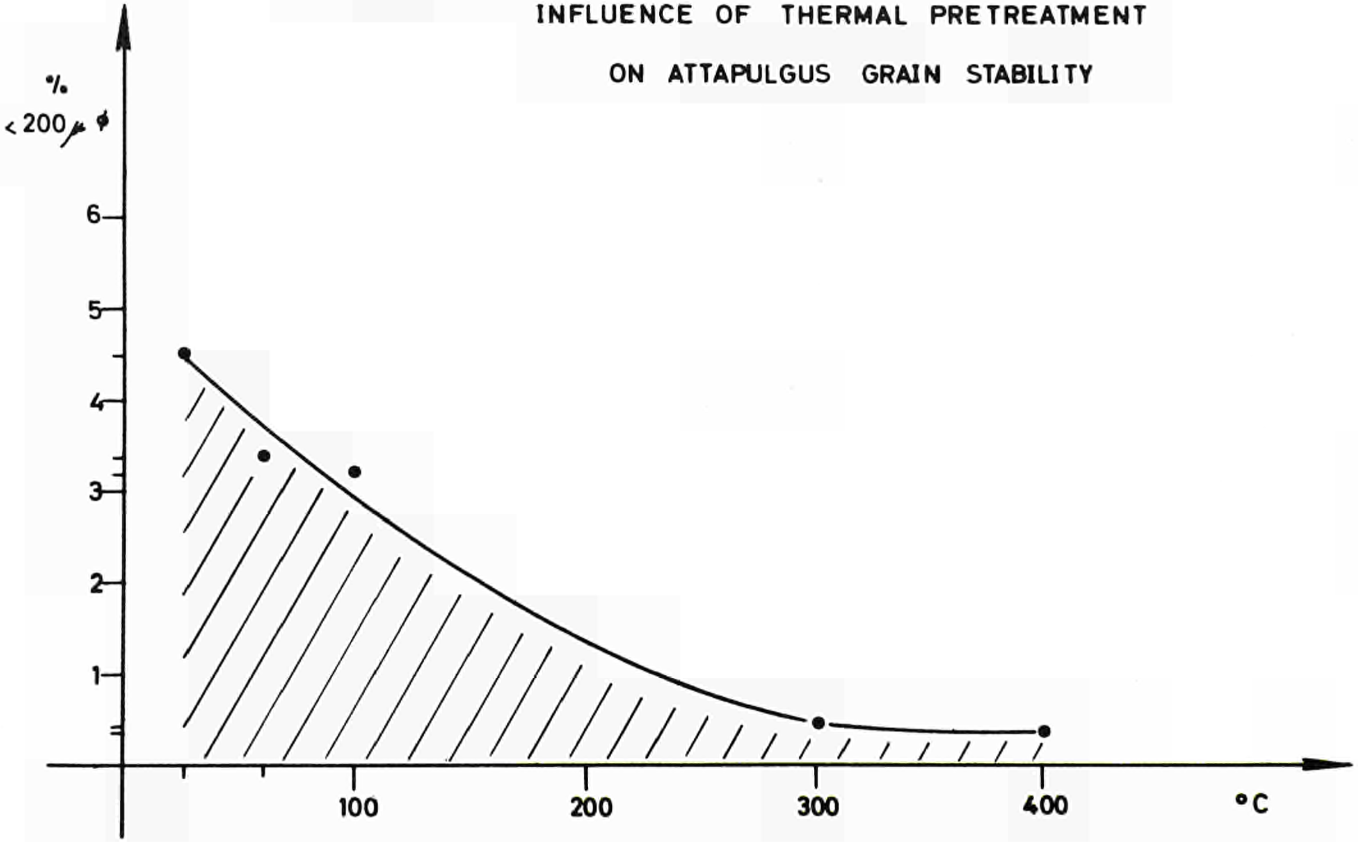


Figure 21 :

Influence of P_H values on grain stability

(11 days samples)

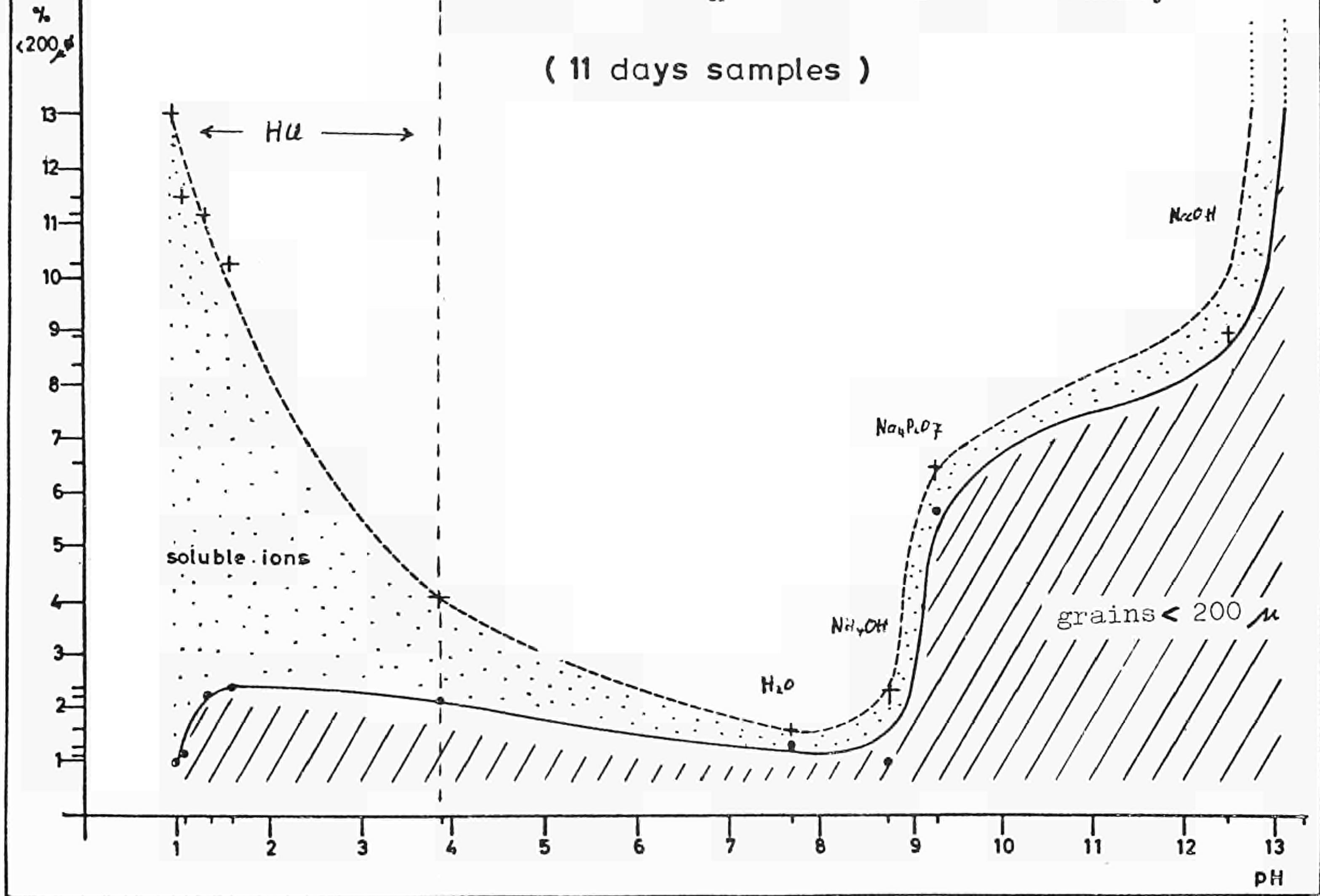
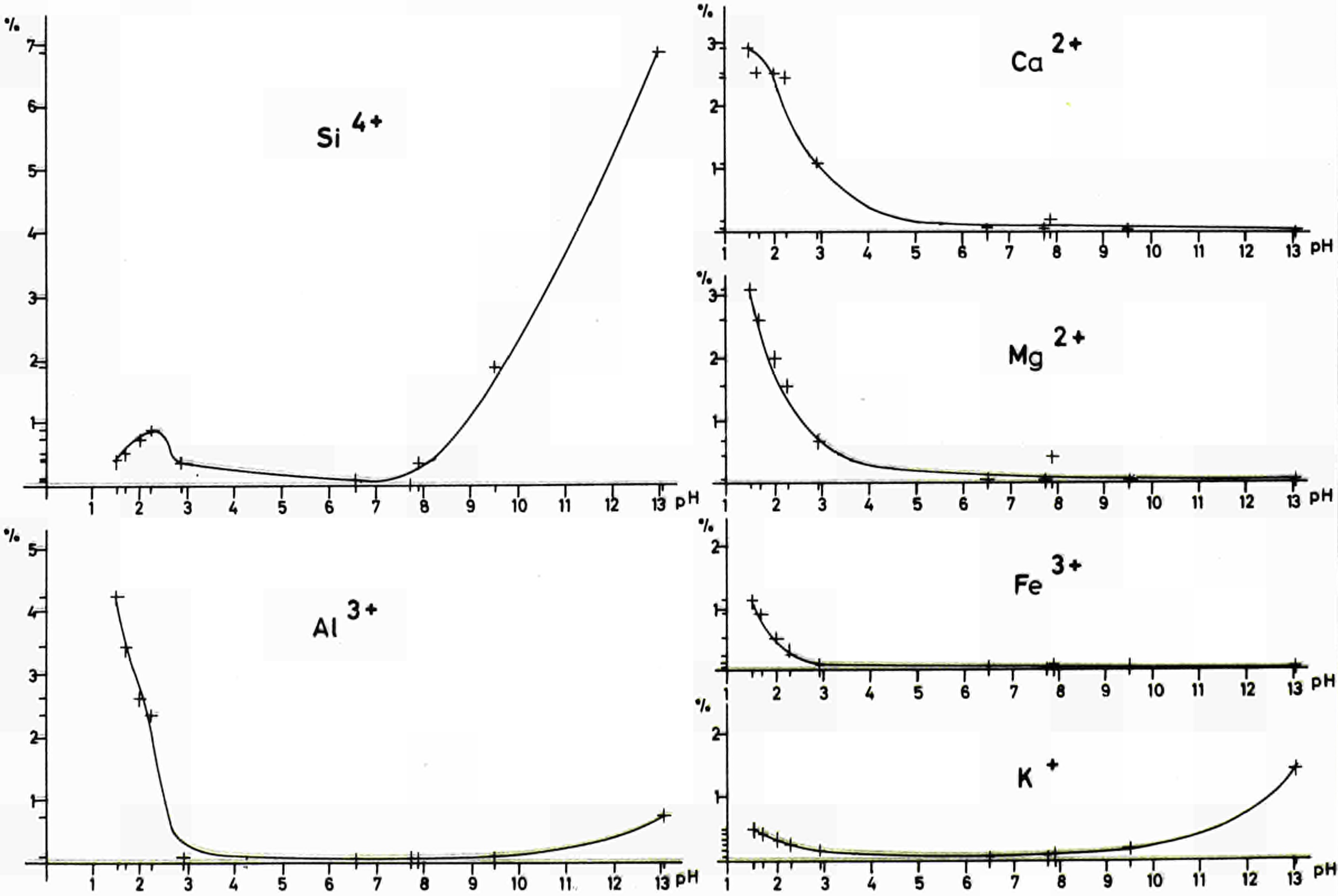


Figure 22 :

DIAGRAMM 5

Influence of pH values on Ions solubility (11 days samples)



To disseminate knowledge is to disseminate prosperity — I mean general prosperity and not individual riches — and with prosperity disappears the greater part of the evil which is our heritage from darker times.

Alfred Nobel

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Part III : The Interaction of Attapulgus Clay and Hydrogenated Polyphenylic Nuclear Reactor Coolant

by

R. LOPES CARDOZO and D. VAN VELZEN

1969

Joint Nuclear Research Center
Ispra Establishment - Italy

Chemistry Department
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Joint Nuclear Research Center - Ispra Establishment (Italy)
Chemistry Department - Organic Chemistry
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It is shown that the retention mechanism and the sorbate compounds are essentially the same in both cases.

The reaction rate constant and the retention capacity of the clay with hydrogenated polyphenylic coolants are superior to the corresponding values for

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KEYWORDS

ADSORPTION
CLAYS
POLYPHENYLS
ORGANIC COOLANT
HYDROGENATION
REACTION KINETICS
CATALYSIS
CRACKING
POLYMERIZATION
ISOMERS
CHEMICAL REACTIONS

CONTENTS

1. INTRODUCTION (*)

One of the major problems in the development of an organic cooled reactor is the control of fouling on fuel elements. A process for the elimination of fouling inducing constituents is sorption on Attapulgus Clay.

Initially some promising results have been obtained in batch experiments in the United States and Canada [1,2]. Afterwards Attapulgus Clay sorption systems were installed and operated in a by-pass loop at the OMRE during Core III-B and III-C [2], in the U-3 and X-7 loop at Chalk River and finally in the WR-1 reactor at Whiteshell (A.E.C.L.).

In a preceding study it has been proved that the purifying action of Attapulgus Clay consists of irreversible chemisorption of a very high molecular weight part of the coolant [3]. These products often contain oxygenated compounds, so that Attapulgus Clay treatment also causes a certain deoxygenation of the coolant.

The studies upon which the above statements are based, have been performed with blends of OM-2*) and High Boilers from OMRE Core III-A. The OMRE facility (Organic Moderated Reactor Experiment) consisted of a 5 to 6 MWt reactor, cooled and moderated by a mixture of terphenyls, generally at a temperature of 310°C. During Core III-A the organic liquid used consisted of Santowax OMP, a terphenyl blend of about 12 %w o-, 60 %w m- and 28 %w p-terphenyl. During this period the reactor operated at an average HB concentration of approximately 5 %w.

The only organic cooled reactor which is actually in operation, is the WR-1 reactor in Whiteshell (Canada). This reactor is an organic cooled, heavy water moderated experimental reactor with a thermal power of approximately 35 MW. The coolant used in this reactor consists of a mixture of partly hydrogenated terphenyls (40-60 % of saturation) which is manufactured by Monsanto under the name of HB-40. This coolant has a much more naphtenic character than the purely aromatic coolants, OM-2 and Santowax OMP. This fact may have its influence on the chemical nature of the very high molecular weight products sorbed by the Attapulgus Clay.

It is therefore of interest to investigate whether the mechanism proposed for OM-2 based coolants is also valid for HB-40 based coolants.

This complementary study was made feasible by the availability of about 400 kg of actual WR-1 coolant, dated 20/3/68, at the C.C.R. Ispra. The coolant is an equilibrium coolant obtained at a reactor temperature of 325-350°C. The HB content (determined according to the microdistillation method in use at Whiteshell [7]) has been maintained between 30 and 35 %w for nearly 8 months. The average molecular weight of the HB is 690, the autoignition temperature 420°C and the kinematic viscosity of the coolant is 0.80 cS at 300°C.

---

*) A terphenyl mixture consisting of approximately 25 %w o-, 70 %w m- and 5 %w p-terphenyl.

*) Manuscript received on 24 April 1969

2. NATURE OF THE REACTING IMPURITIES

In analogy with the preceding study [3] the Heavy High Boiler (HHB) and the oxygen content of the coolant were used as a yardstick for the detection of the nature of the reacting impurities.

The HHB content is defined as the percentage of the product which is insoluble in dodecane at room temperature. The method of determination is essentially the same as before, except that presently dodecane is used as a solvent instead of decane. The analytical procedure has been described in [3].

The oxygen content has been determined by activation analysis [4]. The experimental studies were carried out in a 4 cm diameter stainless steel column. The HHB and the oxygen content of the feed and of each percolation fraction has been determined. The clay used was the sieve fraction between 50 and 70 mesh from Attapulgus AA/LVM 30/60 obtained from the Minerals and Chemicals Philipp Corporation. It has been pretreated at 150°C, 10 cm Hg for 2 hours. Data, results and conditions of these experiments are given in Table I.

It appears that also in the present case an appreciable amount of HHB is retained on the Attapulgus Clay column. The effect rapidly decreases with increasing contact time.

Contrary to the results obtained with OM-2 based coolants, no sorption of oxygenated products can be observed.

Practically all deviations of the oxygen content are within the limit of error of the determination, which is approximately ± 50 ppm.

The conclusion is that the very high molecular weight compounds present in the WR-1 coolant are sorbed on Attapulgus Clay, but that these products are apparently free from oxygenated compounds.

3. THE SORPTION PROCESS

3.1. Retention Capacity

The retention capacity of Attapulgus Clay in contact with the WR-1 coolant has been determined by means of the same technique as has been used formerly.

It involves drying of the clay to constant weight before use under standard conditions (10 cm Hg and 150°C), thorough elution and washing after a percolation run and subsequent drying of the spent clay to constant weight under the same standard conditions. The resulting increase in weight is considered as the quantity of sorbate retained.

Elution is performed at working temperature by passing virgin HB-40 through the bed until the brown colour of the eluate has completely disappeared. This usually requires a quantity of 5 to 10 times of the bed weight. Subsequent washing of the bed is done with xylene at 130°C to 140°C until the solvent passes colourless and finally with 5 times the bed weight of benzene or toluene in order to remove all xylene.

TABLE I

Percolation experiments on Attapulgus Clay.

Flow direction	Downflow				Downflow			
Column diameter (cm)	4.0				4.0			
Bed weight (g)	320				320			
Temperature (°C)	185				315			
Feed rate (g.min-1)	18				18			
Feed	WR-1 coolant				WR-1 coolant			
HHB content of feed (%w)	13.7				13.7			
Oxygen content of feed (ppm)	480				480			
Contact Time (min)	Weight (g)	E/A	HHB Content (%w)	Oxygen Content (ppm)	Weight (g)	E/A	HHB Content (%w)	Oxygen Content (ppm)
16*) - 20	70	0 -0.2	7.9	480	68	0 -0.2	3.5	540
20 - 35	281	0.2-1.1	8.9	370	230	0.2-0.9	7.3	450
35 - 50	268	1.1-1.9	10.5	480	265	0.9-1.8	10.5	490
50 - 65	264	1.9-2.7	11.2	490	282	1.8-2.6	11.6	560
65 - 80	272	2.7-3.6	12.0	440	280	2.6-3.5	12.0	580
80 - 95	273	3.6-4.4	12.6	460	279	3.5-4.4	12.9	500

---

*) First drop **appears** after 16 minutes from start.

The percolation runs have been carried out in a glass column, internal diameter 12 mm, length 530 mm. The feed was introduced by means of a calibrated metering pump. Contact time was varied from 10 to 120 minutes. The results and conditions of these experiments are given in Table II and Fig. 1.

Fig. 1 shows that the sorption curve for the WR-1 coolant has the same nature as the curves for the reaction controlled chemisorption for OM-2 based coolants. These are given as a reference in the same figure. It is noted that the saturation capacity of Attapulgus Clay is substantially higher for the WR-1 coolant than for HB obtained from Santowax OMP (Core IIIA HB). This effect may be due to a higher average molecular weight and/or to a possible difference in chemical nature of the active compounds.

3.2. Estimation of the Reaction Rate Constant

In the preceding study [3] it has been shown that the sorption rate is either reaction or diffusion controlled.

The process is reaction controlled at relatively high impurity concentrations and diffusion controlled at low concentrations.

Evidently the impurity concentration in the WR-1 coolant is rather high, so that the process in this case is reaction controlled. The shape of the sorption curve (Fig. 1) and the high HHB content of the coolant (13.7 %w) bring this statement into evidence.

It follows that the available data only permit the evaluation of the reaction rate constant. The law governing the process can be expressed as:

$$-\ln(1-W/Q) = \frac{K_R t}{Q}, \quad \text{or}$$

$$K_R = -\frac{Q}{t}\ln(1-W/Q) \quad \text{in which}$$

W = sorbate concentration, integrated over the bed height
Q = saturation capacity
t = contact time
K_R = reaction rate constant.

The saturation capacity has been estimated as 15 %w (Figure 1). The calculated value for the reaction rate constant becomes 5.0×10^{-3} min^{-1}, all values being comprised between 6.9×10^{-3} and 3.0×10^{-3} min^{-1}. This value is higher than the one found for OM-2 based coolants (2.0×10^{-3} min^{-1}), but is still of the same order of magnitude.

The expression for the exit impurity concentration for the reaction controlled case is:

$$C_x = C_o - \frac{AK_R}{L}\exp\left(-\frac{K_R t}{Q}\right) \quad \text{in which}$$

C_x = exit impurity concentration
C_o = initial impurity concentration
A = total weight of clay
L = feed flow rate.

With this expression it is possible to calculate the HHB concentration of the percolated coolant as a function of contact time. The exit HHB concentration is equal to:

$$(HHB)_x = (HHB)_o - (C_o - C_x)$$

$$= (HHB)_o - \frac{AK_R}{L} \exp\left(-\frac{K_R t}{Q}\right)$$

The evolution of the HHB content with contact time has been calculated for the two percolation runs in the 4 cm diameter stainless steel column (Table I).

The calculated lines together with the experimental points are given in Fig. 2.

It is concluded that the experimental data agree quite satisfactorily with the calculated lines and that the increase in temperature from 185°C to 315°C shows little effect. Similar conclusions have been drawn in the preceding study.

TABLE II

Percolation experiments in glass columns.

Column diameter : 12 mm
Temperature : 175°C
Feed rate : 13 $g.min^{-1}$
Feed : WR-1 coolant

Contact Time	Bed Weight		W*)
	In (g)	Out (g)	
(min)			(%w)
15	26.90	28.92	7.5
25	28.42	31.03	9.2
45	26.70	29.69	11.2
85	30.00	33.66	12.2
125	28.32	32.41	14.4

---

*) W = the percentage weight increase of the clay bed, i.e. the weight of the sorbate retained.

4. ISOMERISATION AND CRACKING

It has precedently been proved that Attapulgus Clay has not only a sorptive, but also a catalytic action, which strongly increases polymerisation, cracking and isomerisation reactions. It has been shown that at approximately 350°C pure o-terphenyl has been decomposed for more than 60 % in 5 hours, mainly to m-terphenyl. It was also reported that the o-terphenyl content of OM-2 decreased from 23.3 to 19.1 %w, during the same contact time [5].

Pyrolysis experiments with o- and m-terphenyl in quartz capsules at 451°C showed an approximately two fold increase of the formation of benzene, diphenyl and HB, a strong isomerisation and a 50 times increased gas formation rate in presence of Attapulgus Clay [6].

In the present study the stability of HB-40 and the Canadian reactor coolant in the presence of Attapulgus Clay has been investigated. The liquids under investigation were boiled under reflux with and without addition of the clay. The resulting products were submitted to a fractional distillation analysis, during which a sample of 50 g has been divided into 3 fractions:

- One with a boiling point lower than 150°C at 20 mm Hg.
- One with a boiling point between 150 and 240°C at 20 mm Hg.
- One with a boiling point higher than 240°C (the residue).

In some cases the top temperature of 240°C at 20 mm Hg has not been attained; in these cases the distillation was stopped when the bottom temperature reached 360°C. The reflux ratio is 3, the distillation bottom has constantly been heated at a rate of 135 W and the column is a Vigreux column of 40 cm effective length.

The results of these analyses are given in Table III. This table also contains the fractional distillation analyses of the percolation fractions from the experiments summarised in Table I.

It appears that non-irradiated and irradiated HB-40 behave quite differently in the presence of Attapulgus Clay. The original product shows a poor stability: about 20 %w are converted into lighter products (in the range of diphenyl) and at the same time about 25 %w are polymerised. Besides, a strong isomerisation occurs, which qualitatively appears from the gaschromatographic analyses illustrated in Fig. 3.

Apparently the reaction is practically terminated after 2 hours. No sensible difference between the 2 and 5 hours experiments could be shown with the actual method of analysis.

Contrary to the behaviour of the original product, the irradiated coolant does not show a distinct change in composition upon Attapulgus Clay contact. Only the very first fraction of the percolation at 315°C apparently shows a formation of light products. However, this effect may be due to a chromatographic effect which gives rise to an enrichment in light products of this fraction during percolation.

All other samples shows a light decrease of 3 to 6 %w in the diphenyl-fraction, which points to a moderate polymerisation of the light products. Generally, also a light decrease of the residue content is observed. The fact that part of the HB are chemisorbed by the Attapulgus Clay, accounts for this decrease. Besides, it should be kept in mind that the precision of the fractional distillation analysis is very limited and permits a very general evaluation only.

By gaschromatographic means no isomerisation could be shown, see Fig. 4.

Subsequently it has been investigated, if also in the case of OM-2 based coolants a difference in the behaviour of the original and irradiated coolants upon Attapulgus Clay treatment could be observed.

Virginal OM-2 and two irradiated products from irradiation experiments in the BLO-4 loop in the SILOE-reactor (Grenoble, France) were included in this investigation. The two irradiated products were near-equilibrium coolants from feed-and-bleed experiments of the following main characteristics:

	Sample I	Sample II
Run	C5-41-420	C2-41-320
HB-content	13.5 %w	43.1 %w
Temperature of irradiation	427°C	328°C
Dose intensity in irradiating vessel	1.4 $W.g^{-1}$	2.8 $W.g^{-1}$
Fast neutron fraction of energy deposited in the coolant	0.195	0.28

The liquids were boiled under reflux for 2 and 5 hours, with and without Attapulgus Clay addition.

The resulting products were analysed by gaschromatography. The results are given in Table IV.

Also in this case a substantial difference between unirradiated and irradiated coolants is observed. Under the actual experimental conditions (360°C) no formation of low boiling or polymerised products can be shown, neither with irradiated nor with original coolants. The isomerisation of o-terphenyl into m-terphenyl is very important in the case of the original coolants, as has been shown precedently [5]. The o-terphenyl content decreased from 23.7 to 17.0 %w in 2 hours and to 14.7 %w in 5 hours. A slight increase in p-terphenyl content could be observed, but the major part of the o-terphenyl changes into m-terphenyl.

These isomerisation effects are much less important for the two irradiated coolants. The experiments with the coolant containing 13.5 %w HB showed a decrease from 17.2 to 16.4 %w of o-terphenyl in 2 hours and to 15.2 %w in 5 hours, whereas in the experiments with the C2-42-320 sample containing 43.1 %w HB the decrease in o-terphenyl content is even smaller: from 11.2 to 10.5 %w in 5 hours.

TABLE III

Polymerisation and cracking of HB-40 in presence of Attapulgus Clay.
200 g of HB-40 have been boiled under reflux in presence of 50 g of Attapulgus Clay.

Boiling Time	Fraction Ø$_2$*) (%w)	Fraction Ø$_3$*) (%w)	Residue*) (%w)
	Virginal HB-40, ex Monsanto		
Original product	0.0	96.0	4.0
5 h without clay	0.0	87.3	12.8
2 h with clay	19.1	48.7	29.5
5 h with clay	22.3	50.9	26.6
	Coolant ex A-loop WR-1 reactor, d.d. 20/3/68		
Original product	13.5	44.6	40.9
2 h with clay	7.7	50.3	40.2
5 h with clay	10.0	50.0	39.5
Fraction n°	Fractions of the percolation run (Table I) at 185°C		
1	8.6	45.4	44.9
2	7.1	56.8	33.6
3	8.9	58.7	32.4
4	10.3	50.5	34.6
5	9.2	53.2	36.5
6	9.2	Lost	Lost
Fraction n°	Fractions of the percolation run (Table I) at 315°C		
1	29.5	Lost	Lost
2	13.5	46.8	36.6
3	9.7	50.1	40.5
4	8.6	51.3	36.9
5 and 6 combined	10.3	51.7	36.4

---

*) Fraction Ø$_2$: Boiling point less than 150°C/20 mm Hg.
Fraction Ø$_3$: Boiling point comprised between 150 and 240°C/20 mm Hg.
Residue : Boiling point superior to 240°C/20 mm Hg.

For the difference in behaviour of irradiated and unirradiated coolants in contact with Attapulgus Clay, two main causes can be responsible:

1) The high molecular weight products in the irradiated coolants are rapidly chemisorbed on the clay surface; the active spots are covered and the clay soon looses its catalytic activity.
2) In the case of HB-40 based coolants, the less stable compounds which were initially present, have precedently been decomposed and replaced by more stable products during the irradiation process.

TABLE IV

Polymerisation and cracking of OM-2 in presence of Attapulgus Clay.
200 g of coolant have been boiled under reflux in presence of 50 g of Attapulgus Clay.

Boiling Time	Diphenyl	Terphenyls			HB
	(%w)	ortho (%w)	meta (%w)	para (%w)	(%w)
	Virginal OM-2				
Original product	-	24.1	70.4	5.2	0.3
5 h without clay	-	23.3	69.8	4.9	2.0
2 h with clay	-	17.0	73.9	6.4	2.7
5 h with clay	-	14.7	75.9	7.3	2.1
	Sample C5-41-420				
Original product	1.3	17.1	63.6	4.6	13.4
5 h without clay	1.2	17.2	63.3	4.6	13.7
2 h with clay	1.5	16.4	63.4	4.8	13.9
5 h with clay	1.3	15.2	64.6	5.3	13.6
	Sample C2-42-320				
Original product	0.8	11.2	41.9	3.0	43.1
5 h without clay	0.7	11.2	41.6	3.1	43.4
2 h with clay	0.7	10.8	42.4	3.3	42.8
5 h with clay	1.0	10.5	42.4	3.5	42.6

5. CONCLUSIONS

The present complementary study has shown that the action of Attapulgus Clay in the presence of hydrogenated polyphenyl based coolants consists of irreversible chemisorption of impurities from the HHB range of the coolant. This is also the case with the action of this material in contact with non-hydrogenated polyphenylic coolants [3].

Contrary to the polyphenylic case, no decrease in the oxygen content upon Attapulgus Clay treatment could be observed for a hydrogenated coolant.

For an actual coolant from the WR-1 reactor the overall sorption rate is determined by the rate of reaction; diffusion and adsorption rates can be neglected.

The reaction rate constant has been determined as 5×10^{-3} min^{-1}. This value is superior to the corresponding constant for the polyphenylic coolant, which is 2×10^{-3} min^{-1}.

The saturation capacity of the clay is approximately 15 %w, which is also superior to the saturation capacity of Attapulgus Clay in contact with polyphenylic coolants, i.e. 5-10 %w.

It has been shown that Attapulgus Clay causes very important cracking, polymerisation and isomerisation reactions in virginal HB-40. The irradiated reactor coolant only undergoes minor changes in composition.

It has been proved that this last conclusion is also valid for OM-2 based coolants.

NOTATION

All dimensions are given in terms of weight (w), time (t) and length (l).

A	:	total weight of sorbent	(w)
C_o	:	initial sorbate concentration	(-)
C_x	:	final sorbate concentration	(-)
$(HHB)_o$	:	initial HHB concentration	(-)
$(HHB)_x$	:	final HHB concentration	(-)
K_R	:	reaction rate constant	(t^{-1})
L	:	liquid flow rate	$(w.t^{-1})$
Q	:	saturation capacity	(-)
W	:	sorbate concentration on sorbent, integrated over bed height	(-)

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Figure 1

ATTAPULGUS CLAY SORPTION

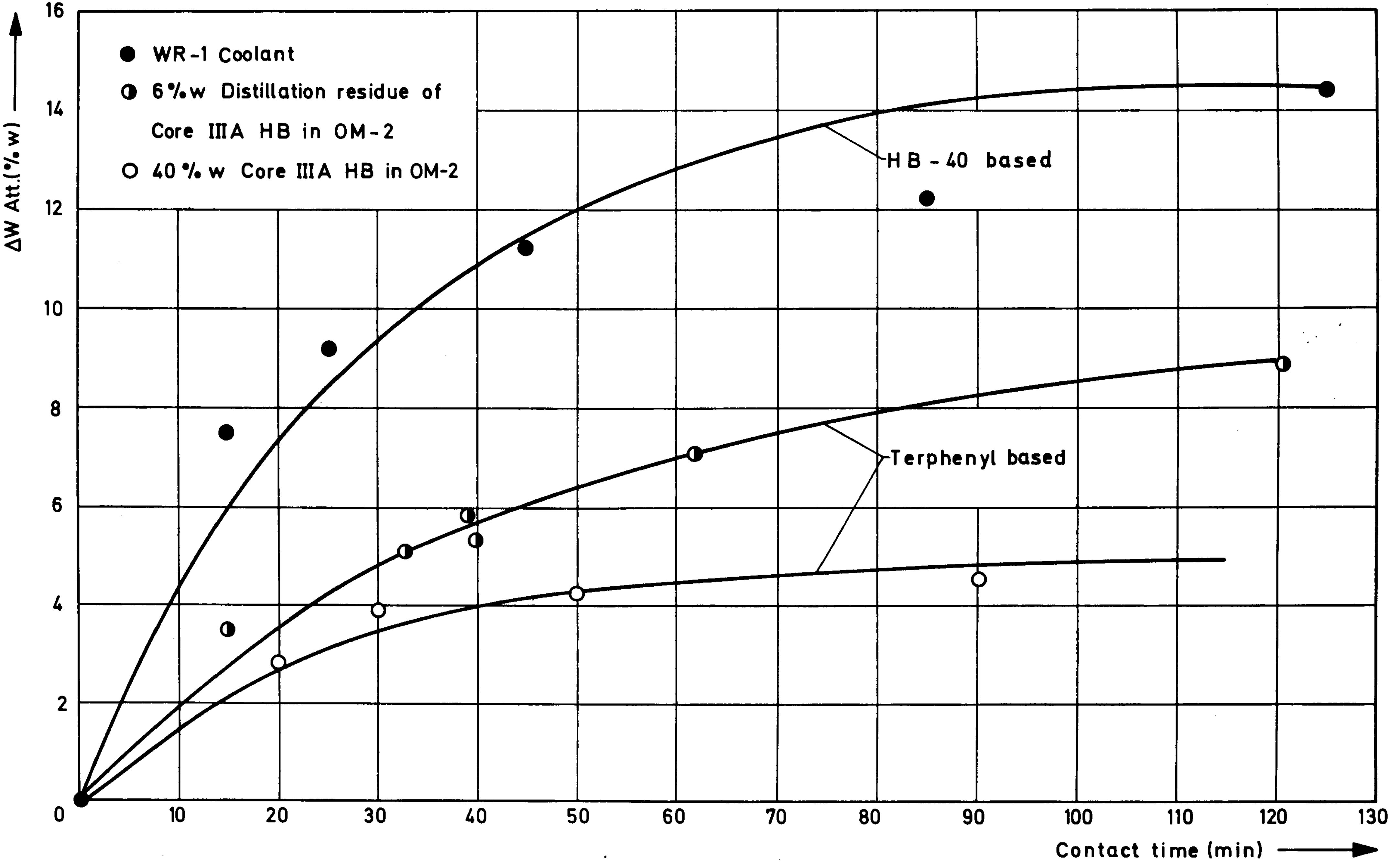


Figure 2

SORPTION ON ATTAPULGUS CLAY OF WR-1 COOLANT EXPERIMENTAL AND CALCULATED RESULTS

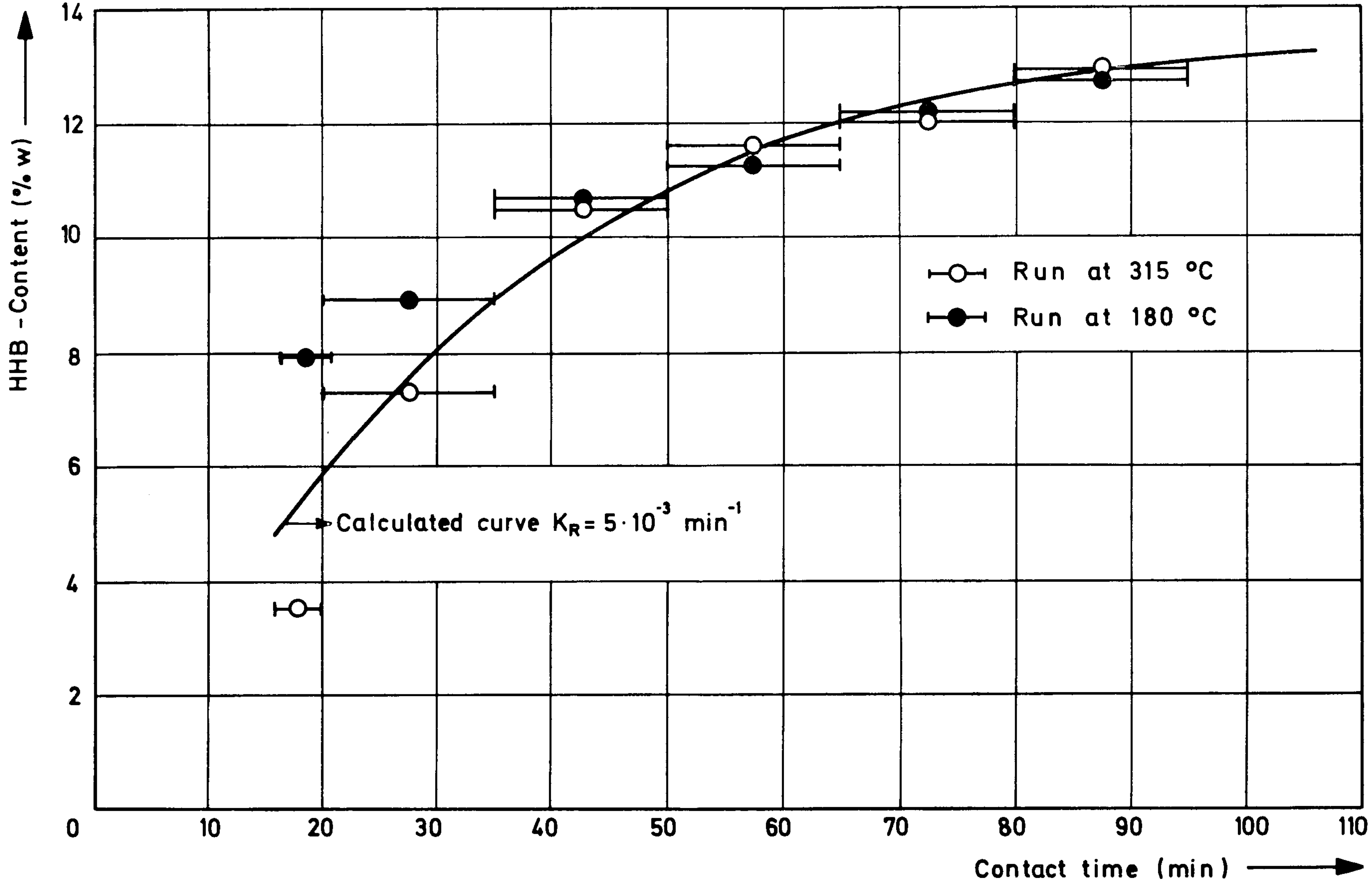


Figure 3

CHROMATOGRAM OF UNIRRADIATED HB-40 ON DIASPORT S+10% DOW 11

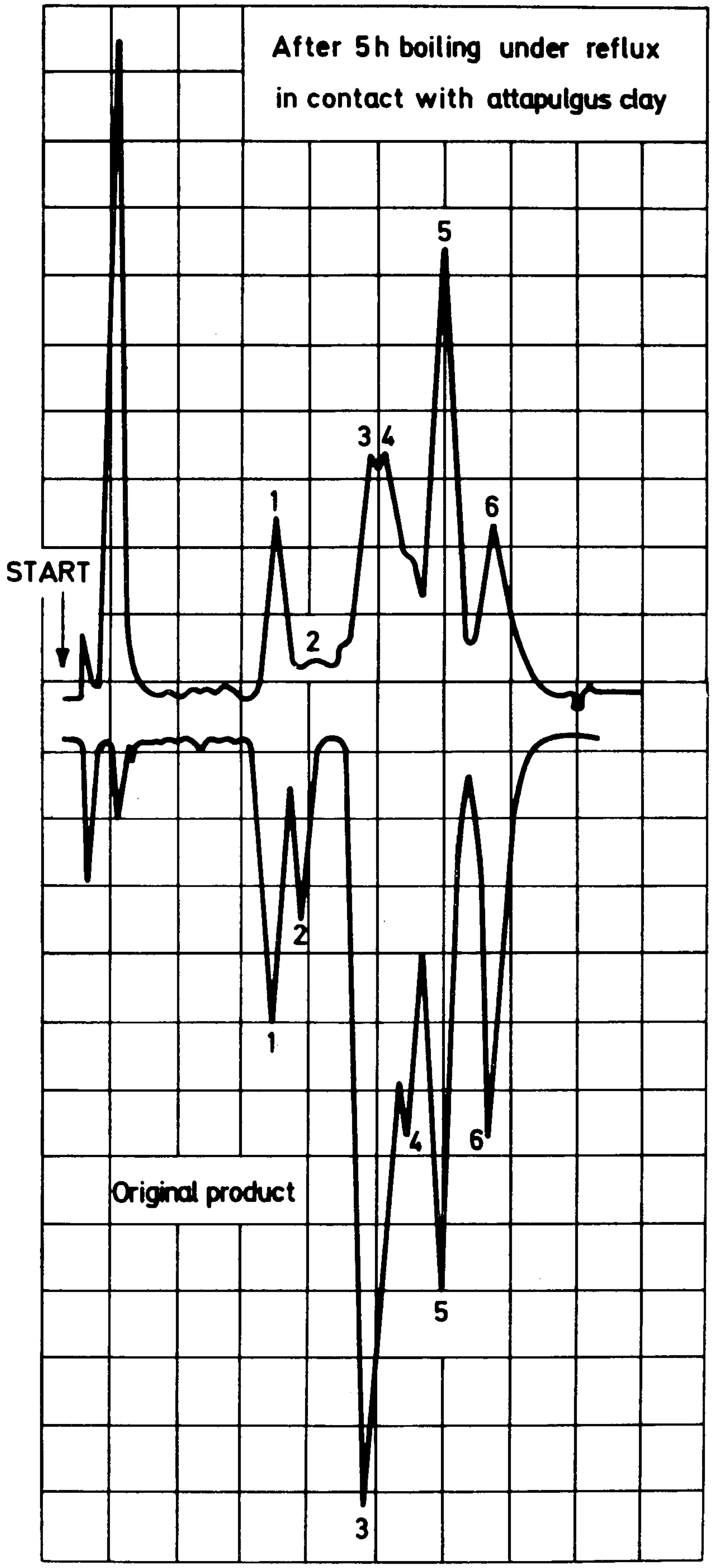
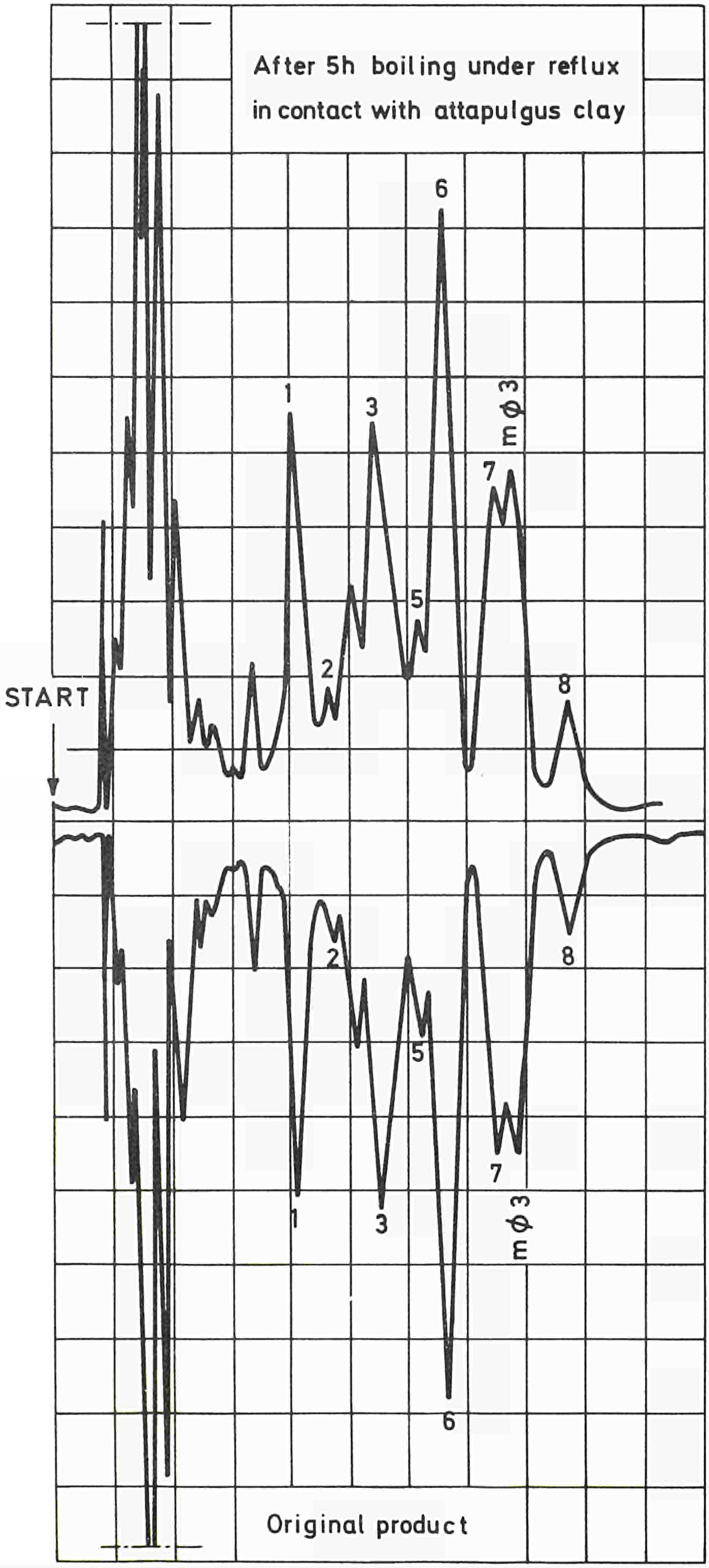


Figure 4

CHROMATOGRAM OF IRRADIATED HB-40 (WR-1-COOLANT) ON DIASPORT S+10% DOW 11



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