

SURFACE CHEMICAL STUDIES
OF ASBESTOS MINERALS

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by

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ABSTRACT

Surface chemical properties of three asbestos minerals (chrysotile, amosite and crocidolite) have been investigated with special reference to the occupational disease asbestosis.

Kinetics of leaching of these minerals in distilled water at 37°C have been determined under both static and dynamic conditions. Adsorption of inorganic ions (Ca^{2+} , Na^{+}) from concentrations comparable with those in human serum on to chrysotile was studied. The extent was found to be small and appears unlikely to be physiologically significant.

By thermogravimetric and X-ray analysis, a Canadian chrysotile (Bells) was proved to contain 5% brucite as impurity. By hydrothermal heat treatment with added silica, this was converted to a stoichiometric chrysotile.

Zeta-potentials of various asbestoses were measured by electrophoresis. Chrysotile from different sources showed variable mobilities. The electro-osmotic method was also tried for measurement of zeta-potential but gave much lower values because of high surface conductivity of chrysotile.

Adsorption of water vapour on chrysotile was studied. The water vapour adsorption isotherm showed a hysteresis loop. The amount of benzene adsorbed on chrysotile pre-saturated with water was much less than on dry chrysotile.

Adsorption of aminoacids from concentrations present in human blood on the three types of asbestos have been determined. With chrysotile a Langmuir type of isotherm was obtained; but with amphiboles adsorption never came to saturation. It was ascertained that amino acids (like other

surfactants) produce defibrilization. This phenomenon appears to be an example of the "Rehbinder effect".

Adsorption of albumin and γ -globulin on the three types of asbestos was found to form approximately a monolayer coverage. Interaction of lipid with asbestoses and other related minerals has been studied by a simple phase-transfer experiment. All three asbestoses were found to adsorb lecithin : but asbestos which had previously adsorbed some protein failed to adsorb lecithin.

An attempt has been made to correlate the present findings with the current theory of asbestosis put forward by Allison. But partly owing to the uncertainty as to the actual mechanism by which the asbestos particles arrive at the lung proper, no firm conclusions can be drawn. It appears that more physiological data are needed before it can be ascertained whether the surface-chemical effects now known to occur on asbestos particles do actually play any significant part in the problem of asbestosis or mesothelioma.

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CHAPTER I
GENERAL INTRODUCTION

I.1 Nature of "asbestos" - different types of asbestos

Asbestos is a general name given to the naturally occurring inorganic minerals which when crushed or processed break down into fibres. They are mainly hydrated silicates having true crystalline structure which determines their wide range of physical and chemical properties. The naturally occurring fibres differ from the man-made fibres (such as glass, silica, aluminosilicate fibres, etc.) in that the latter have random non-crystalline structure and cannot be sub-divided. Most natural fibres can be sub-divided into fibrils almost until molecular dimensions are achieved (though chrysotile asbestos is a remarkable exception - see below). Since ordinarily the name asbestos is associated with those fibres of technological importance, some authors use the term "asbestiform minerals" to be more descriptive. The chief forms of asbestiform minerals with their chemical formulae are tabulated below.

Classification of asbestiform minerals

Mineral class	Specific name	Chemical formula (ideal)
serpentine	chrysotile	$3\text{MgO}, 2\text{SiO}_2, 2\text{H}_2\text{O}$
amphiboles	amosite actinolite anthophyllite crocidolite tremolite	$5.5\text{FeO}, 1.5\text{MgO}, 8\text{SiO}_2, \text{H}_2\text{O}$ $2\text{CaO}, 4\text{MgO}, \text{FeO}, 8\text{SiO}_2, \text{H}_2\text{O}$ $7\text{MgO}, 8\text{SiO}_2, \text{H}_2\text{O}$ $\text{Na}_2\text{O}, \text{Fe}_2\text{O}_3, \text{FeO}, 8\text{SiO}_2, \text{H}_2\text{O}$ $2\text{CaO}, 5\text{MgO}, 8\text{SiO}_2, \text{H}_2\text{O}$

Altogether six different species of asbestiform minerals are known (1).

They come under the two classes, serpentine and amphiboles. Chrysotile is the only asbestiform member of the serpentine group. The amphibole group consists of five recognised varieties of asbestiform minerals: crocidolite, amosite, anthophyllite, tremolite and actinolite. The names anthophyllite, tremolite and actinolite apply equally to the fibre and crystal form of these minerals; the name crocidolite is given to the fibrous form of riebeckite and amosite to the fibrous form of grunerite (2). Another rare asbestiform mineral not included in the general classification is palygorskite ($\text{Si}_8\text{Mg}_5\text{O}_{20}(\text{OH})_2(\text{OH}_2)_{4.4}\text{H}_2\text{O}$). Because of its fibrous nature it has been classified as asbestiform mineral (3). There is considerable controversy as to whether it should be classified as a chain silicate or sheet silicate. It is mined in Alaska, Brazil, U.S.S.R. Sepiolite ($2\text{MgO}, 3\text{SiO}_2, 2\text{H}_2\text{O}$) another magnesium silicate is sometimes found to form fibres. It has a talc-like structure and the fibrous variety is called α -sepiolite (3).

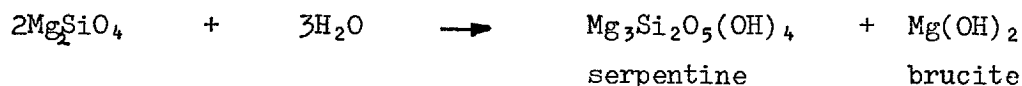
The present work is confined to three most commonly used asbestoses : chrysotile, amosite and crocidolite. Therefore in the subsequent chapters it is the surface chemistry of these three minerals that will be discussed.

I.2 Chrysotile, $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$

I.2(a) Geological origin

Chrysotile is commercially the most important type of asbestos and accounts for almost 90% of the total output. The most valuable deposits occur in serpentine formed by the hydrothermal alteration of ultrabasic rocks such as dunite, peridotite, pyroxenites (4). The work of Bowen and Tuttle (5) on the phase equilibria in the system $\text{MgO} - \text{SiO}_2 - \text{H}_2\text{O}$ threw

much light on this complicated process of "serpentinisation". They have shown that below 400°C serpentines can be formed by the action of water on forsterite (anhydrous magnesium orthosilicate, Mg_2SiO_4) whereas above 500°C serpentine is unstable but talc (3MgO , 4SiO_2 , $2\text{H}_2\text{O}$) may form up to about 800°C. They further suggested that olivine and pyroxene are first intruded in crystalline state and come in contact with water vapour from the wet rocks below 500°C. When forsterite undergoes the process of serpentinisation, it forms brucite ($\text{Mg}(\text{OH})_2$) as well



Consequently many serpentine contain brucite. However, serpentinisation of forsterite may also take place with addition of silica and water, in which case the brucite phase disappears, and with excess silica, some talc may be formed.

Hendry in 1965 (6) explained the formation of chrysotile in the ultrabasic rocks. According to him the emplacement and subsequent alteration of an ultrabasic rock took place under the earth's crust. This then underwent structural deformation due to folding, faulting and shearing processes. The serpentine was then shattered in places through which hot water entered. This water dissolved serpentine until it became super-saturated due to fall of temperature and pressure. The crystals of magnesium silicate (chrysotile) started growing at the fractured places. The crystals grew on both the walls and sprouted inward towards the centre; thus the width of the fracture is equal to the length of the fibres.

Chrysotile formed by the natural processes is always associated with impurities which may include (in different localities) pyroxene, calcite,

brucite, talc, magnetite, chromite etc.

The world's two biggest deposits of chrysotile are in eastern Quebec (Canada) and the Urals in Russia. Besides these, considerable deposits of high quality fibres are known in the Shabani mines in Rhodesia and Cassiar mines in British Columbia. Smaller deposits are found in U.S.A., Italy, China, Greece, India, Brazil.

In appearance, native chrysotile is seen to consist of tightly packed bundles of parallel fibres, which can be teased apart with needles. Microscopic examination shows that the fibrous units are exceedingly thin and thread-like; indeed, the optically visible threads are still composite and electron microscopy is needed to resolve the ultimate fibrils (see below). The bundles of fibrils do, however, give sharp X-ray diffraction.

I.2(b) Crystal structure

The structural determination of chrysotile was first attempted by Warren and Bragg (7) in 1930 by X-ray analysis. They proposed that chrysotile is composed of Si_4O_{11} chains similar to the chains in amphiboles (see below). Between the sets of chains are sections of Mg and OH arranged as in brucite. However, in a subsequent paper in 1941, Warren and Hering (8) ruled out the above structure and proposed a layer structure, analogous to that of the corresponding aluminium silicate, kaolin. The layers in chrysotile are in the sequence of 3 O, 2Si, 2O OH, 3Mg, 3OH. Consideration of their proposed structure in relation to kaolinite structure suggests that a part of the layer is a pseudo-hexagonal network of linked SiO_4 tetrahedra (pointing one way). To this siloxane sheet is joined a brucite layer on one

side of which only two out of every three hydroxyl groups are replaced by apical oxygen atoms of SiO_4 tetrahedra, the distance between the composite layers being $7.3 \text{ \AA}$. Consideration of the dimensions of the brucite layer and the silica layer shows that there is mis-fitting of the two layers when superimposed, the brucite layer being slightly bigger than the silica layer. This mis-matching might be avoided by the replacement of bigger Mg atoms by smaller atoms in octahedral brucite layer or by the replacement of smaller Si atoms in tetrahedral layer by bigger atoms. But it could also be avoided either by distortion of ideal octahedral or tetrahedral network or by the curvature of the composite sheet with the tetrahedral component on the inside. Many of the experimental results favour the curvature in chrysotile lattice. This remarkable curved layer structure was supported by Whittaker later (9). A schematic diagram of the cross-section of layer structure is shown in fig. 1.

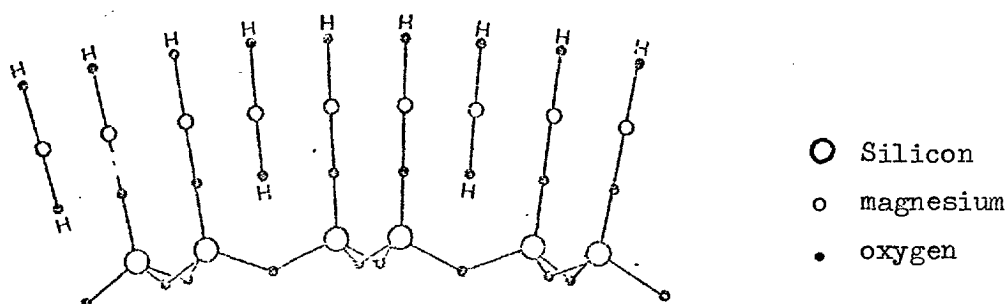


Fig. 1 Schematic diagram of a cross-section of the chrysotile structure on (010) plane.

From the figure it is evident that out of eight hydroxyl groups per unit cell six are exposed externally and two are associated with internal oxygen layer.

In 1950 Bates, Sand and Mink (10) published electron micrographs of both synthetic and natural chrysotile showing that chrysotile fibrils have a hollow tubular structure. Many more electron micrographs have been published since that time showing the same structure (11, 12). Subsequently there was considerable controversy regarding the morphology of chrysotile. Pundsack (13) pointed out that a hollow tubular structure could not be accepted in view of the experimental density value of solid blocks of fibre. He suggested a distorted ribbon-like structure. Whittaker (14) in 1957 suggested that "the interfibrillar voids are filled by layers in the form of cylindrical arcs coaxial with the adjacent fibres and the intra-fibrillar voids are filled by layers in the form of cylindrical arcs oriented parallel to but not coaxial with the walls of the fibre; but a small proportion of the fibres are hollow".

The final answer as to the real nature of the tubular structure was given by Yada (15) in 1967. By means of high resolution electron microscopy he was able to take electron micrograph of microfibrils of chrysotile from two directions, parallel and perpendicular to the fibre axis. He showed that most of the fibres are hollow tubes but some fibres are solid and show an unusual growth pattern. Not all the tubes observed were simple cylindrical ones, some consisted of spirally wound layers.

Depending upon crystallographic structure, Whittaker (16, 17, 18, 19, 20) classified the chrysotile into three types - clino-, ortho- and para-. In clino-chrysotile the successive sheets all have the same orientation whereas in ortho-chrysotile alternate sheets are reversed right and left. In para-chrysotile the atomic arrangement is analagous to ortho-chrysotile but in this the sheets curve in such a way that the b-axis becomes the fibre axis. Clino-chrysotile is the most common form; the amount of

ortho-chrysotile varies from 0-50% in different samples whereas para- is a very rare form.

I.2(c) Properties and chemical composition

Chrysotile fibres are very often silky but sometimes they become "greasy", harsh and brittle in nature. Colour is mainly white but the bundles of original fibres commonly show a light greenish shade.

The chemical compositions of various chrysotiles from different sources have been published in the literature (1, 4, 21). One due to Harington (21) is quoted here.

TABLE I
Chemical composition of chrysotile

Compounds	Percentage (wt)
SiO ₂	39.15
Al ₂ O ₃	2.15
Fe ₂ O ₃	1.18
FeO	1.33
MgO	40.32
CaO	1.09
Na ₂ O	0.09
K ₂ O	0.15
- H ₂ O	0.60
+ H ₂ O	13.09
MnO	0.07

The chemical compositions of different chrysotiles show that the common impurities are small amounts of Fe^{3+} , Fe^{2+} and Al^{3+} . It is assumed by some authors that these atoms are substituted in the crystal lattice for Mg and Si atoms. Others associate them with external impurities (which can sometimes be detected). However, no confirmed information is available regarding the distribution of impurities.

Since the exposed surface of rolled chrysotile fibrils is similar (from a crystal-chemical point of view) to that of brucite, most of its surface properties are supposed to resemble those of brucite. Several authors have published information regarding the surface chemical properties of chrysotile; these will be discussed later.

1.3 Amphiboles

The amphibole series of minerals are complex silicates of mainly iron, magnesium and calcium, though some contain sodium and aluminium. Their chemical analysis can vary because of extensive isomorphous replacement of basic constituents. Despite the analytical variations, the amphibole minerals have a common crystallographic structure and occur in similar rocks (6). They are of metamorphic origin, being derived from basic igneous rocks, but the host rock may be sedimentary. The zones within the strata at which crocidolite occurs are soda-rich, unlike the zones at which amosite occurs. It is believed that crystallisation took place in situ under moderate pressure and temperature in the presence of moisture from surrounding rocks. This is described as a metamorphic process with a recrystallisation to fibrous form.

I.3(a) Amosite

The name was derived from the initial letters of the asbestos mines in South Africa. Vermaas (22) proved from X-ray diffraction and differential thermal analysis that amosite belongs to cummingtonite-grunerite solid solution series in which the bases are Mg^{2+} and Fe^{2+} in varying proportions with very little Ca^{2+} or Na^+ . Amosite can be considered as the fibrous modification of the monoclinic amphibole grunerite having the general formula $(Fe^{2+}, Mg)_7(Si_8O_{22})(OH)_2$. The fibres are long, somewhat harsh, brownish-yellow to almost white, depending on quality. It is used widely for asbestos cement and heat insulating products and is mined in South Africa. A typical variety of amosite has the approximate chemical formula 1.5 MgO, 5.5 FeO, 8 $SiO_2 \cdot H_2O$ - i.e. it is principally a (high-iron) ferrous magnesium silicate (23) though with typical variability.

I.3(b) Crocidolite

Crocidolite comes under the sub-group riebeckite, which has the general chemical formula $Na_2 Fe_3^{2+} Fe_2^{3+} Si_8O_{22}(OH)_2$. It similarly forms a monoclinic crystal (2). Crocidolite yields fine resilient fibres of characteristic blue colour (the colour is sometimes explained by the $Fe^{2+} - Fe^{3+}$ association in the crystal structure). It is largely mined in South Africa but also in Australia and in Bolivia. It is a strong "fast filtering" fibre used in the production of asbestos cement sheets and pressure pipes. A typical analysis is approximately $Na_2O, 3FeO, Fe_2O_3, 8 SiO_2, H_2O$ (i.e. sodium ferroso-ferric silicate) (23).

I.3(c) Crystal structure of amphiboles

The crystal structure of tremolite was first determined by Warren (24) in 1929, and that structure serves as the model for all the amphiboles. The structure, which is schematically shown in fig. 2, consists of a ribbon formed from two silicon-oxygen chains (comprising fused Si_4O_{11} ring units), separated by a band of cations. The basal unit of each cell consists of seven cations; two hydroxyl groups are attached at the central cation of each unit cell and are contained in the cell.

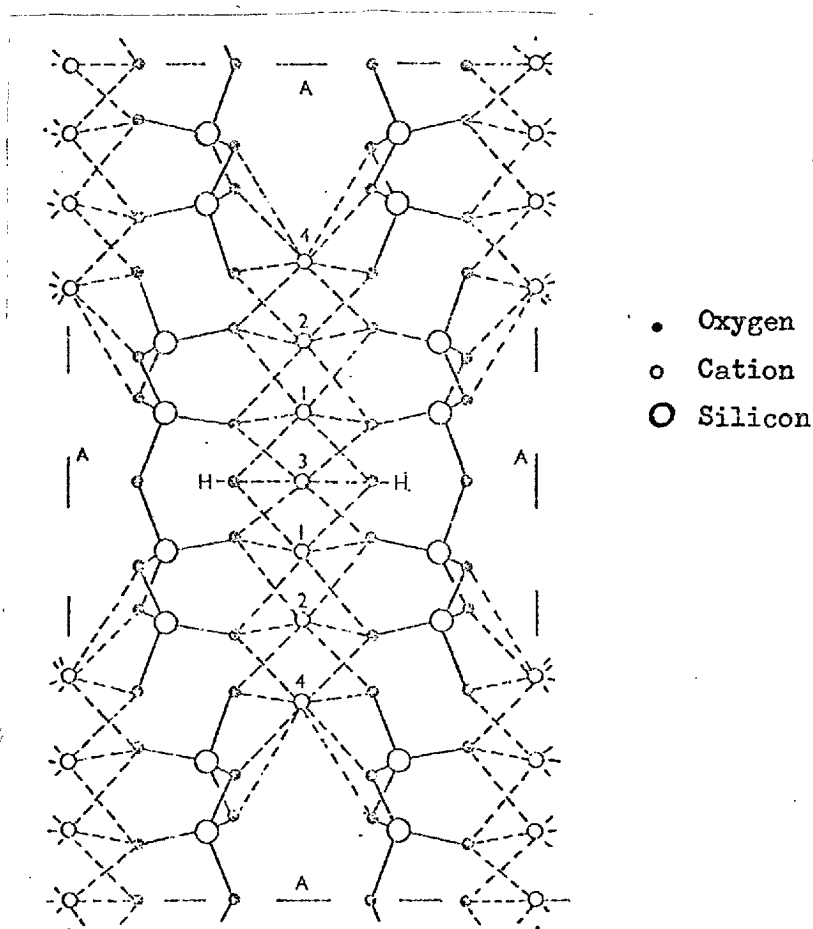


Fig. 2 Schematic diagram of the structure of amphibole on (001) plane, fibre axis is normal to the plane of the paper.

In order to explain the blue colour of crocidolite, Hodgson (1) argued that it is due to resonance $\text{Fe}^{3+} \rightleftharpoons \text{Fe}^{2+}$ between the so-called adjacent M_2 and M_3 sites in the crystal structure. He has further pointed out that intensely dark blue crocidolite contains minimal Mg^{2+} in M_3 sites while pale blue crocidolite contains a proportion of Mg^{2+} . Similar resonance is supposed to be responsible for the blue colour of Prussian blue (25). The resonance theory has, however, been discounted by Gibb & Greenwood(26) on the grounds of Mossbauer spectroscopic data.

I.3(d) Chemical composition

The percentages of different constituents in amosite and crocidolite vary widely, depending on the variety. Typical ranges of main constituents are given in table 2.

TABLE 2

Chemical composition of amosite and
crocidolite

	amosite	crocidolite
SiO_2 (%)	49 - 53	49 - 53
MgO	1 - 7	0 - 3
FeO	34 - 44	13 - 20
Fe_2O_3	-	17 - 20
Na_2O	-	4 - 8.5

I.3(e) Surface properties

Spiel and Leinweber (27) reported that chemically the surface of amphiboles is similar to that of silica. It is polar in nature, the electrokinetic charge being negative. Iso-electric points have not been well established although it is assumed by these authors that charge would become positive at low pH.

Not much information is available regarding the chemical reactivity of amphiboles. Hiscock (27, 1) studied the decomposition of different asbestos in 4N HCl and found the following relative order of resistance to attack:

crocidolite > amosite >> chrysotile

Thompson (27) made some studies on chemical reactivity of crocidolite and amosite with water and acid and obtained results in agreement with those of Hiscock. Addison and Addison and Sharp (28, 29, 30) have done extensive work on the high temperature oxidation and reduction of crocidolite. They have shown that the oxidation of crocidolite at 450°C involves the simultaneous oxidation of ferrous and hydroxyl ions with a secondary surface reaction. The reaction takes place on the surface and is maintained by the migration of electrons and protons through the crystal. They have further shown that crocidolite loses all, or nearly all, its hydroxyl groups without structural breakdown when heated at 615°C in vacuo. Reduction of fresh dehydroxylated and oxidised crocidolite follows a different mechanism but in each case elementary iron is formed.

Hodgson, Freeman and Taylor (31, 32, 33) carried out extensive work on the thermal decomposition of different amphiboles. Their results on the decomposition of crocidolite in an oxidising atmosphere were explained by Addison's theory of dehydrogenation and oxidation. They concluded that

the decomposition of amphiboles comprises three fundamental stages - loss of physically bound water, loss of chemically bound water and breakdown into simple products, the main one of which is pyroxene.

Harington (21) was able to extract both primary and secondary oils from native crocidolite and amosite. He obtained 0.32% of extractable material from crocidolite and 0.28% from amosite. Besides these, he detected low levels of polycyclic aromatic hydrocarbons in these two amphiboles.

1.4 The disease asbestosis

Asbestosis is a form of diffused fibrosis of the lungs (35) which results from long exposure to air carrying asbestos dust. The dominant symptom is a shortness of breath, of gradually increasing intensity and often associated with a dry cough. In the early stages physical signs are absent or slight; in the later stages there is frequent clubbing of the fingers. "Asbestos bodies" are found in the sputum. Where the disease is much advanced, there are large areas of fibrosis in the lungs, the alveolar walls are thickened and the characteristic asbestos bodies are found.

This disease is mainly confined to the people who handle asbestos. Many authors have published information based on statistics of asbestosis cases in different countries (36, 37, 38). Investigation by different workers revealed that the maximum latent period from exposure to onset of the disease was 33 years and the minimum was 7 years and there is remarkable variation in susceptibility in different persons. Although many attempts have been made to explain the mechanism by which the asbestos bodies are formed and the disease is caused no definite answer has yet been established

to this question. Another comparatively new but more dangerous disease is "mesothelioma". This is a newly recognised form of tumour of pleura of lungs which is rapidly fatal. It has been claimed by various authors that in most cases the patient suffering from mesothelioma has had a history of exposure to "blue asbestos" (crocidolite). However, it has definitely been established that asbestos dusts are responsible for both the above diseases.

I.5 Object of the present work

The aim of the present project is to contribute basic information from the standpoint of surface chemistry of asbestos minerals towards the understanding of the serious industrial disease asbestosis. There is no intention (or possibility) of engaging in research on the biological aspects. An enormous amount of work has been done on living systems in an attempt to understand the relationship between the asbestos minerals and the disease; but not much information is available regarding the nature of the surface and its interaction with the physiologically active materials. Therefore this project starts with a plausible hypothesis that the disease may have a chemical or physico-chemical origin, (rather than a purely mechanical one). Inside the human lungs a physiological response may be set in motion by the release of material from the mineral surface to the surroundings or by the adsorption of surrounding material on the mineral surface. Starting from the above idea, it is proposed to confine the project to the reactions between asbestos minerals and aqueous solutions of substances that might be found in human lungs. All the experimental work has therefore been carried out at body temperature (37°C)

In studying the surface chemistry of any mineral/water system two

aspects must be considered - firstly, the interaction of the mineral with water alone and secondly, chemical reactions involving dissolved or dispersed substances (including adsorption processes). The surface chemistry of minerals is not confined to instantaneous effect of the initial outer-most layer. Silicates are mainly unstable in water; surface groups chemisorb water and certain components dissolve out. Moreover, the silicates have no true solubility and a theoretical equilibrium constant is not known for ordinary temperatures. Study of the literature on chrysotiles has revealed that it is relatively unstable in water. Therefore this material is not an inert adsorbent only, as it will release some material to its surroundings. For these reasons study of the leaching process has been taken as an essential first step for the present research.

Secondly, since the surface of chrysotile is unstable, the metallic ions in its lattice may undergo ion-exchange reaction when brought into contact with the inorganic ions. Since the human blood and serum contain inorganic salts as their constituents, these may either exchange for the metallic ions in the crystal lattice or undergo simple adsorption on the surface. Study of the adsorption of inorganic ions like Ca^{2+} , Na^{+} etc has therefore been considered.

Finally, amosite and crocidolite have silica-like surfaces (27); chrysotile after leaching may produce silica-like surface as well and the interaction of silica with the physiologically active materials like albumin and globulin are well known. Therefore it has been thought essential to study the interaction of the three different asbestos surfaces with physiologically active organic materials such as amino acids, proteins and lipids. Hence the whole project includes

- (1) Study of the leaching of chrysotile, amosite and crocidolite in water at 37°C .

- (2) Ion-exchange processes of chrysotile in dilute electrolyte solutions.
- (3) Interaction of fresh and leached asbestos surface with organic materials such as amino acids, proteins and lipids. .

CHAPTER II

LEACHING OF CHRYSOTILE IN WATER AT 37°C.

It has been mentioned previously that silicates like chrysotile are not perfectly stable in aqueous media. Their surfaces change because of the dissolution of various ions. Therefore, one of the important steps in the surface chemical studies of these minerals will be the study of the leaching kinetics.

Clark and Holt (39, 40) studied the leaching of chrysotile with water, acid and alkali at different temperatures. They observed that chrysotile yields very little monosilicic acid compared to Mg at low temperature (25°C). But when the extract was heated to 90°C the amount of molybdate-reactive silica increased. They further observed that release of Mg from chrysotile was less at 90°C than at 25°C. This they explained from the solubility of magnesium hydroxide which decreases with increase of temperature.

From the above discussion and also from the chemical formula of chrysotile ($\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$) it is evident that the main constituents of leaching product of chrysotile are Mg and SiO_2 . Therefore the first step in the study of leaching at 37°C would be to establish accurate methods for the determination of Mg and SiO_2 .

II.1 Determination of magnesium and silica

Magnesium was determined by atomic absorption spectrophotometry according to the method described by David, D.J., Wallace, and Willis (41, 42, 43). In the determination of magnesium, by atomic absorption, the presence of silica was found to cause serious interference. Even 1 p.p.m. of silica

decreases the absorbance due to Mg considerably. It was suggested by David (41) that this interference can be best removed by the addition of 1500 p.p.m. of Sr solution. This method was tried with success. By this method magnesium could be determined within the range of 0.2 - 2.5 p.p.m. with a sensitivity of 0.05 p.p.m., even in the presence of 10 p.p.m. silica.

Silica was determined by a colorimetric method described by Jeffery and Wilson (44). In this method, soluble monomeric silica is first converted to yellow silico-molybdate by adding ammonium molybdate. This yellow compound is then reduced to blue silico-molybdate in presence of oxalic acid with the help of a reducing agent (1-amino-2 naphthol-4-sulphonic acid + sodium metabisulphite + sodium sulphite). The blue silico-molybdate thus formed has a strong absorption at 650 nm. The colour is quite stable after half an hour and is not affected by light. It has been experimentally observed that presence of Mg does not interfere with the silica estimation. This method works quite satisfactorily within the range of 0.2 - 2 p.p.m. of SiO_2 with a sensitivity of 0.03 p.p.m.

For the estimation of total silica (monomeric, polymeric and colloidal) the method was slightly modified. The solution containing silica was first boiled with NaOH at a pH around 12 for about an hour (45). By this treatment any polysilicic acid depolymerises, colloidal silica and other silicate particles dissolve as Na-silicate which on subsequent acid treatment forms molybdate-reactive monosilicic acid and can be estimated as usual. The silica estimation (including the boiling) was always done in polypropylene bottles in order to avoid the introduction of any silica from the vessel itself.

II.2 Preparation of samples of chrysotile

Chrysotile samples were kindly provided by Turner Brothers Asbestos Co. Ltd. They supplied both rocky minerals as well as highly "opened" fibres of commercial use. The opened fluffy fibres were chosen for the leaching tests. A portion of the fibres was ground in a vibratory steel mill to a fine powder for some of the experimental work.

II.3 Effect of grinding on release of magnesium

An experiment was made to compare the release of Mg from the highly opened fibres ("Bells") and some of the same material that was ground. It was observed that the initial release of Mg (in 1 day) was more in the case of ground than from non-ground fibres. But after 7 days the net release was the same in both the cases.

II.4 Location of release of alkali

Some fibres of chrysotile were set into agar gel saturated with phenolphthalein and examined under a microscope. In the case of Bells chrysotile, all fibres quickly developed a pink colour more or less uniformly. On the other hand with fibres carefully extracted from virgin rock, it was quite clear that the pink colour was localised at the tips of the fibre bundles and at points where the fibres have been crumpled or kinked during extraction. Similar experiments with silver nitrate showed dark stains of Ag_2O at points of release of alkali.

From the above two experiments (II.3 and II.4) it can be concluded that the release of Mg is facilitated by mechanical damage to the crystal structure.

II.5 Static leaching of chrysotile fibres with time

For this experiment highly opened fluffy fibres of Bells chrysotile were chosen. Two sets of experiments have been studied.

Experiment A : In two separate polypropylene bottles 2.0 g of chrysotile was kept suspended in 400 ml water at 37°C. The bottles were continuously shaken. 20 ml of the suspension was taken out every day, the pH determined and the amount of Mg and silica released were determined by the methods specified above.

Experiment B : In each of several separate polypropylene tubes 0.2 g of chrysotile was kept suspended in 40 ml water (the same suspension concentration as in series A). The polypropylene bottles were continuously shaken at 37°C. One bottle was taken out every day to determine the pH and the amount of Mg and silica released. This experiment was performed in duplicate.

The results of pH determination and Mg estimation are given in Table 3.

TABLE 3
Leaching data.

0.5% suspensions of Bells chrysotile fibres in distilled water
gently agitated at 37°C.

[Mg^{2+}] given in millimoles/litre.

Leaching time (days)	Experiment A		Experiment B	
	pH	[Mg^{2+}]	pH	[Mg^{2+}]
1	9.5	0.15	10	0.15
2	-	-	9.9	0.16
3	-	-	9.9	0.17
4	9.8	0.17	10.0	0.18
5	9.8	0.18	10.0	0.19
6	10.0	0.18	10.1	0.19
8	10.0	0.20	10.1	0.22
11	10.0	0.22	10.3	0.22
15	10.1	0.23	10.1	0.23
21	10.1	0.26	10.1	0.23
27	10.0	0.29	10.3	0.22
32	10.1	0.32	10.3	0.23
39	10.0	0.38	10.3	0.23
53	9.9	0.46	10.0	0.29

In both series A and B replicate samples gave the same type of results.

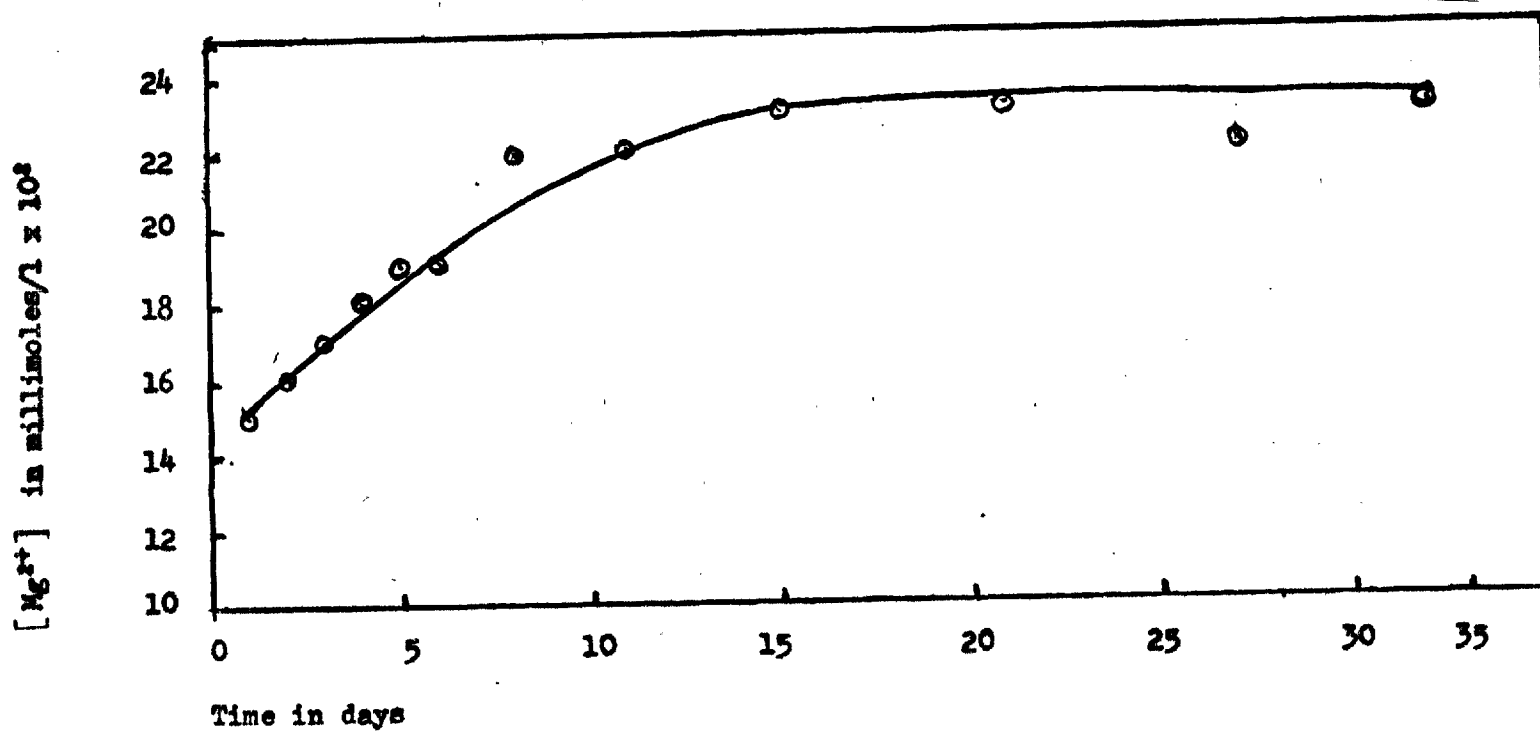


Fig. 3. Release of magnesium from chrysotile with time (static leaching- 0.5% suspensions)

Release of silica

In these two experiments silica was determined as monomeric (dissolved) silica and as total silica (monomeric + polymeric + colloidal) according to the methods described earlier.

The results show that the level of monomeric and total silica in the extract did not change with time; only some random variations were observed. Typical results are as follows.

Experiment A : Test conditions : 2 g chrysotile suspended in 400 ml water at 37°C
the final pH = 10 ± 0.1

Concentration of monomeric silica = 18 μ moles/l

Concentration of total silica = 230 μ moles/l

Experiment B : Test conditions : 0.2 g of chrysotile suspended in 40 ml water at 37°C; final pH = 10.1 ± 0.1

Concentration of monomeric silica = 12 μ moles/l

Concentration of total silica = 280 μ moles/l

From the results of these experiments the following significant points can be noted:

(i) The water starting at pH 6 (due to a trace of CO₂) quickly rises in pH to approximately 9-10 and remains practically constant. In case of experiment 'A' the pH was slightly lower; this may have been due to introduction of a trace of CO₂ while opening the bottles frequently.

(ii) The release of Mg is found to be progressive with time and continues still even after two months. This suggests that the whole of Mg associated with chrysotile fibre cannot be washed out by this process of leaching.

The comparatively high amount of Mg leached out suggests that it is not

merely the thin outermost layer of $\text{Mg}(\text{OH})_2$ from the fibrils which comes out during leaching.

(iii) The level of silica recorded is surprisingly lower than the actual solubility of amorphous silica in water. Moreover, the amount of silica released did not have any relation with the amount of Mg released. No data for the solubility product of pure "magnesium silicate" at 37°C are available in the literature surveyed recently. However, experiments on the leaching of magnesium silicate, MgO , SiO_2 , MgO in presence of excess of SiO_2 and SiO_2 in presence of excess of MgO have been carried out to explain the apparent anomaly (pages 31, 32, 33).

II.6 Leaching of chrysotile - dynamic flow experiment

This experiment was intended to study the leaching in a way more close to that which might take place inside the human lungs. Presumably asbestos fibres inside the lungs will be subjected to continuous buffering action of the body fluids and a constant renewal of the leaching medium. Both of these phenomena will prevent the pH rising high. Therefore it has been thought that a more relevant test condition of leaching would be leaching in a flowing system.

Experimental

In the actual experiment a small multiple line pump (Watson Marlow "Delta" pump) was used. This electrically operated mini-pump is provided with silicone rubber tubes of different bore. As the pump works, liquid is pumped at different rates the lowest rate being 13 ml/24h and the highest rate being 123 ml/24h. In this present experiment five different rates

have been employed. The asbestos containers used here were some specially made glass cells, each provided with a sintered glass filter of porosity 3. One end of each of the glass cells was connected to a small water reservoir and the other end to the pump. The water reservoir and the glass cells with the asbestos were kept in a thermostat at 37°C. As the pump worked, water flowed at different known rates through the asbestos in the different cells. Water passing in every 24 h through the asbestos beds was collected in separate vessels. These were then analysed for Mg and total silica. The results are shown in table 4.

The significant result of this experiment was that the release of Mg in the first 24 h was very high but dropped on the second day and then followed a uniform decrease until it came to a constant rate. The same effect was observed in all different rates employed. The initial release of high Mg suggests that either the surface Mg of the chrysotile lattice is very easily leached, or the damaged chrysotile leaches first, or the sample is contaminated with brucite.

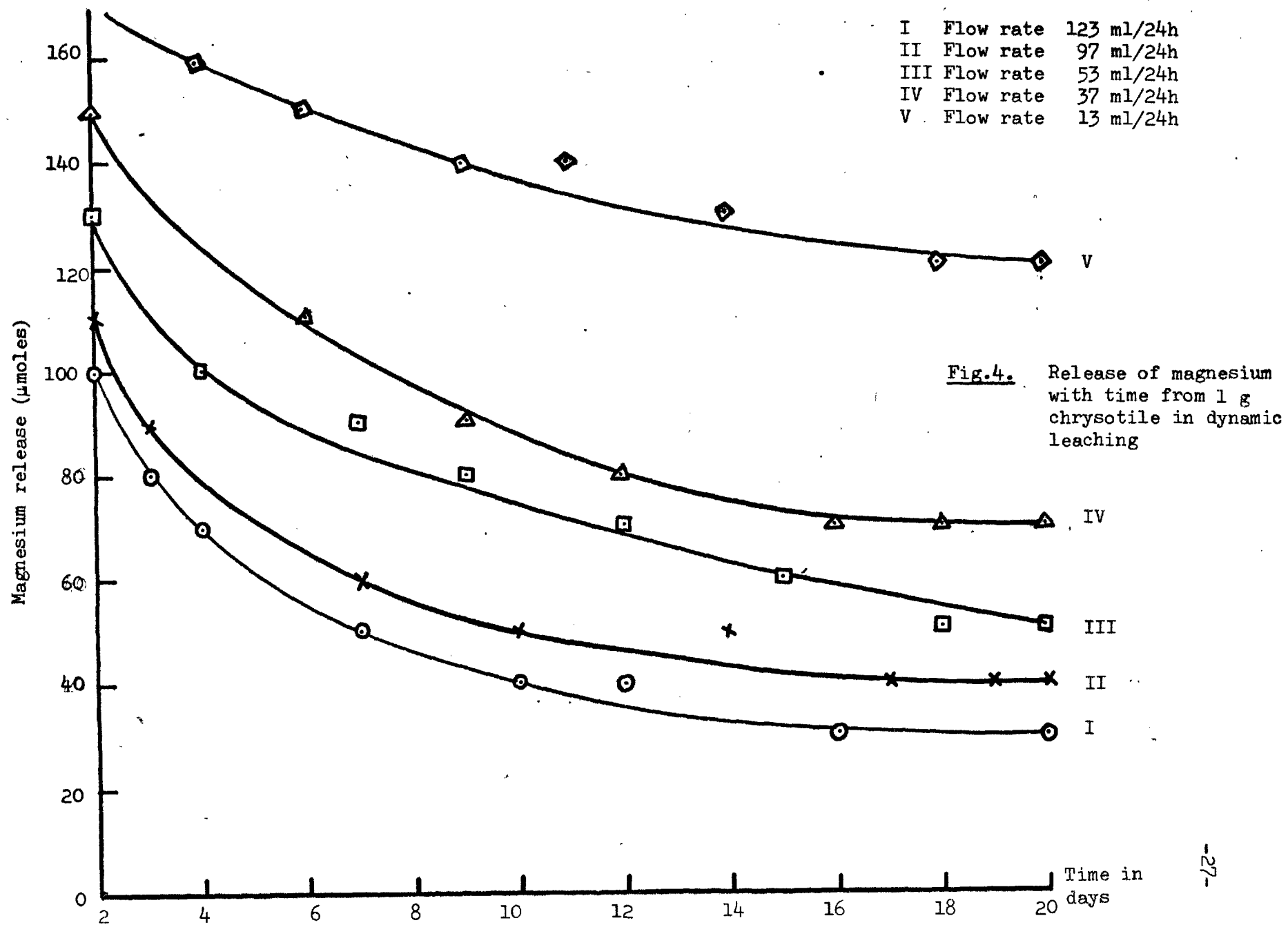
The release of silica in this process was exceptionally high in comparison with the release of Mg.

TABLE 4 : Release of Mg^{2+} and SiO_2 from chrysotile in dynamic leaching at $37^\circ C$.

No. of Days	Flowrate 123ml/24h			Flowrate 97ml/24h			Flowrate 53/24h			Flowrate 37ml/24h			Flowrate 13ml/24h		
	pH	[Mg^{2+}]	[SiO_2]	pH	[Mg^{2+}]	[SiO_2]	pH	[Mg^{2+}]	[SiO_2]	pH	[Mg^{2+}]	[SiO_2]	pH	[Mg^{2+}]	[SiO_2]
1	8.7	240	80	7.7	250	90	7.9	440	90	7.8	560	80	7.6	1770	130
2	8.3	100	90	7.7	110	80	7.7	130	80	7.8	150	140	7.6	220	140
3	7.7	80	120	7.6	90	130	7.6	120	130	7.6	120	130	7.5	160	140
4	7.5	70	120	7.4	60	160	7.6	100	130	7.5	110	140	7.7	160	170
5	7.6	60	250	7.1	60	240	7.4	100	230	7.2	110	230	7.8	160	280
6	7.2	70	260	7.2	60	260	7.2	100	280	7.3	110	230	7.5	160	370
7	7.0	50	320	7.3	60	300	7.3	90	320	7.3	100	340	7.6	150	420
8	7.2	50	330	7.1	50	320	7.2	80	380	7.3	90	330	7.3	150	430
9	7.1	50	-	7.1	50	300	7.3	80	350	7.3	90	370	7.5	150	410
10	7.1	40	300	7.1	50	330	7.2	70	350	7.3	80	450	7.5	140	440
11	7.2	40	310	7.2	50	370	7.3	70	360	7.3	80	470	7.6	140	480
12	7.0	40	320	7.1	50	390	7.1	70	440	7.3	80	430	7.3	140	480
13	7.2	40	340	7.0	50	420	7.4	70	450	7.3	80	420	7.2	140	460
14	7.1	40	370	7.1	50	440	7.2	60	460	7.2	70	450	7.5	130	450
15	7.0	40	410	7.2	50	440	7.1	60	420	7.3	70	470	7.5	130	470
16	7.0	30	390	7.0	50	440	6.9	60	400	7.3	60	46	7.5	130	470
17	7.1	30	380	7.1	40	430	7.3	50	440	7.3	70	450	7.5	130	480
18	6.8	30	390	7.0	40	420	7.2	50	450	7.3	70	450	7.5	120	480
19	6.9	30	400	7.0	40	440	7.1	50	450	7.3	70	460	7.5	120	480
20	7.0	30	400	7.0	40	440		50	450	7.3	70	460	7.5	120	480

[Mg^{2+}] = μ moles of Mg^{2+} released in 24h from 1 g of chrysotile

[SiO_2] = μ moles of SiO_2 released in 24h from 1 g of chrysotile



As Mg release was decreasing silica was increasing till it came to a constant rate. From the formula of chrysotile the ratio of $[Mg] : [SiO_2]$ should be 1.5 : 1 but the experimentally found values are much higher than the theoretical values. This may be due to two reasons - (i) the chrysotile fibres might have been broken down to fine particles which passed through the filter and dissolved when the solution was boiled with NaOH, to give a high value of total silica, (ii) the silica released may be in the form of colloidal silica which is not involved in chemical equilibrium.

In view of the first assumption an experiment was carried out in which the solutions were boiled with moderately concentrated HCl for almost an hour in order to dissolve the fragments of chrysotile, if any, and then Mg was estimated on the extract. The results are given in table 5.

TABLE 5
Results of Mg release before and after boiling
with HCl

Flow rate : 123 ml/24 hrs	Mg before boiling (mg/l)	Mg after boiling (mg/l)
1	1.33	1.50
2	1.06	1.25
3	1.00	1.15
4	0.95	1.05

The above results show that by boiling with HCl the amount of Mg released is slightly increased, though the increase is not very significant. Therefore the possibility of some chrysotile fragments passing through the filter cannot be ruled out; but the major part of the silica must be released as colloidal silica.

Another feature observed in this process of dynamic leaching is that the pH never went above 7.6, whereas in case of static leaching process the pH of the solutions were almost constant at the range of 9.9-10.2 (It is because of the constant renewal of the leaching medium, the building of pH cannot take place).

II.7 Leaching experiment with initially dispersed fibres

This experiment was performed in order to see if the Mg leached out was coming off the surface of individual fibril or from the outer surfaces of the fibre bundles and also to get some idea whether the fibres are contaminated with the common impurity mineral, brucite.

Experimental - In this experiment 4 g of chrysotile fibres suspended in 100 ml of water was treated in a "Silverson mixer" for 15 minutes. The defibrilated fibres were then filtered, washed with more water and dried at 120°C. 0.2 g of this fibre was then suspended in 40 ml water in a series of separate polypropylene tubes kept shaken continuously at 37°C. Two tubes were taken out everyday and the amount of Mg released was determined in the usual way by atomic absorption spectrophotometry. The results are given in table 6.

TABLE 6

Leaching of Mg from dispersed
fibres at 37°C .

(The following results correspond to 0.5% suspensions)

Leaching time (days)	pH	$[\text{Mg}^{2+}]$ released (millimoles/litre)
1	9.8	0.12
2	9.8	0.13
3	9.9	0.15
5	9.9	0.16
6	9.9	0.16
7	9.9	0.17
8	9.9	0.17
9	9.9	0.17
12	9.9	0.17

Comparison of these results with the leaching results of the original fibres shows the following facts.

- (i) The equilibrium pH of the original fibre suspension (10.2) is significantly higher than in case of defibrilated fibre suspension (9.9)
- (ii) The initial (0.15 mM) and "equilibrium" (0.22 mM) release of Mg is slightly higher in ^{the} case of original fibre suspension than in case of defibrilated fibres (0.12 mM and 0.17 mM respectively).

II.8 Solubility of MgO, Mg-trisilicate, SiO₂ and mixtures of MgO and SiO₂ .

In order to check the solubility of silica in presence of excess of Mg²⁺ ions the following experiments were carried out.

Solubility of MgO at different pH - MgO was kept suspended in water with different amounts of acid and alkali at room temperature. After about 20 days the pH of the suspension was measured and the amount of Mg²⁺ ions in the supernatant solution was measured by atomic absorption spectrophotometry. The results for the solubility product are given in table 7.

TABLE 7
Solubility product of Mg(OH)₂

pH	- log [Mg ²⁺]	- log [OH ⁻]	- log K _s K _s = [Mg ²⁺][OH ⁻] ²
9.8	2.2	4.2	10.6
10.3	3.0	3.7	10.4
10.5	2.5	3.5	10.5
11.0	4.1	3.0	10.1

The results are quite comparable to the published values for the solubility product of Mg(OH)₂, 10^{-11.15} at 25°C (46).

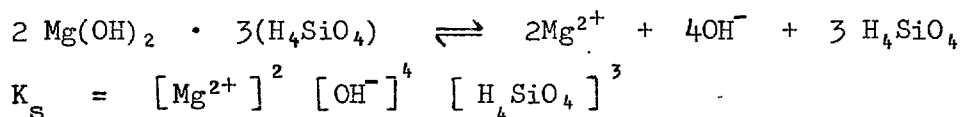
Solubility of precipitated silica - A suspension of pptd. silica in water was found to have pH 7.6 at room temperature. The amount of soluble

silica measured by the molybdate blue method was found to be 98 p.p.m. which is quite comparable to published values of 100 p.p.m. at pH 7 (45).

Solubility of pure Mg-trisilicate

"Magnesium trisilicate" (used as medicine) is supposed to have a composition $2\text{MgO} \cdot 3\text{SiO}_2$ with some molecules of water. A suspension of this Mg-trisilicate at room temperature was found to have a pH of 8.8 and the concentrations of Mg^{2+} and silica were $[\text{Mg}^{2+}] = 0.411$ millimoles/l; $[\text{SiO}_2] = 0.680$ millimoles/l.

If we consider the following equilibrium existing in this reaction of Mg-trisilicate with water



For the above reaction

$$[\text{Mg}^{2+}] = 10^{-3.39} : [\text{OH}^-] = 10^{-5.2} : [\text{H}_4\text{SiO}_4] = 10^{-3.17}$$

Hence

$$-\log K_s = 37.1$$

Mixtures of MgO and SiO_2 (1:1 by wt.) gave the following results at different pH.

TABLE 8

Solubility product of Mg-silicate

pH	$-\log[\text{Mg}^{2+}]$	$-\log[\text{OH}^-]$	$-\log[\text{H}_4\text{SiO}_4]$	$-\log K_s$ $K_s = [\text{Mg}^{2+}][\text{OH}^-]^4[\text{H}_4\text{SiO}_4]^3$
8.9	2.3	5.1	3.0	34.1
9.1	3.8	4.9	2.9	35.1
9.7	4.2	4.3	2.8	34.2
10.0	4.4	4.0	2.8	33.2

For want of any published literature on the solubility of pure Mg-silicate the results could not be compared.

Solubility of SiO_2 in excess of MgO

A mixture of pptd SiO_2 and MgO in the ratio of 1:10 was kept suspended in water for at least 20 days at room temperature. The pH of the suspension was found to be 10.3. The solubility of silica measured by the molybdate blue method was 55.2 p.p.m.

The solutiblity of amorphous silica at pH 10.26 is 490 p.p.m. (45). This shows that there is a strong depression in the solubility of silica due to the presence of excess MgO. This fact requires explanation; formation of a compound is indicated.

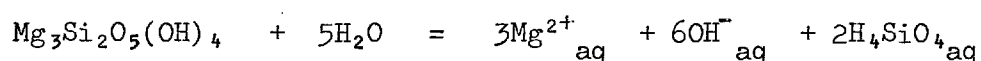
II.9 Discussion

In the experiments outlined above a number of points need further explanation.

(i) The pH of the suspension in static leaching is significantly higher (10.2) than the pH of the fibres initially defibrilated by a Silverson mixer (9.9). The amount of Mg released in the untreated fibres on the first day is higher than the amount released in defibrilated fibres (0.17 mM against 0.12 mM). Furthermore in the dynamic leaching process the amount of Mg released on the first day is much higher than those released on the subsequent days in all the flow rates (24×10^{-2} mM on the first day but steady rate 3×10^{-2} mM). All these points regarding the release of excessive Mg suggest that initially there is a considerable amount of easily leachable Mg present in the fibres. The thin brucite-like outer layer obviously cannot account for the high initial release of Mg (cf leaching of defibrilated fibres). Therefore it must be due to some impurities, which are easily leachable, associated with the chrysotile fibres. Many other workers also reported the presence of magnesium-bearing impurities in chrysotile. Badollet (47) studied the acid decomposition of various asbestoses and reported that most of the chrysotiles are associated with impurities one of which is brucite. Pundsack (48) reported a pH 10.33 for chrysotile and 10.37 for $\text{Mg}(\text{OH})_2$ under the same conditions from which he suggested that the suspension of chrysotile is mainly dominated by dissolution of $\text{Mg}(\text{OH})_2$ layer from the surface of the fibrils. In a later work by Pundsack and Reimschuessel (49), they studied the basicity of chrysotile suspension by acid titration and conductivity measurement. From their results they concluded that Mg^{2+} and OH^- ions are in equilibrium in solution with the chrysotile surface although other anions like Cl^- may be in equilibrium with Mg^{2+} and K^+ present as impurity. On the basis of this assumption they calculated the "solubility product" of $\text{Mg}(\text{OH})_2$ in different chrysotile

suspensions and obtained values ranging from 1.0×10^{-11} to 3×10^{-12} which are quite comparable with the solubility product value of $\text{Mg}(\text{OH})_2$ ($10^{-11.15}$) (46). However, Pundsack and Reimschuessel also reported that most of the chrysotiles examined contained some soluble electrolytes homogeneously distributed over the fibre surface. Examination of our present result shows that, when a steady state is reached, $[\text{Mg}^{2+}] = 2.2 \times 10^{-4}$ moles/l at a pH 10.1, from which the 'solubility product' comes out to be $2.2 \times 10^{-11.8}$ which is again comparable with the 'solubility product' of $\text{Mg}(\text{OH})_2$. Therefore it seems likely that the chrysotile suspension is mainly dominated by $\text{Mg}(\text{OH})_2$. Whether this $\text{Mg}(\text{OH})_2$ comes from the crystal lattice of individual fibril or from the impurities is a point to be ascertained.

Hostetler and Christ (50) in an attempt to determine the activity product constant of chrysotile, studied the dissolution of both synthetic and natural chrysotile at 90°C with time. They initially assumed that chrysotile dissolves congruently in water according to the equation



However, they found the Mg/SiO_2 ratio much higher than the expected value from the above equation. They explained this as due to the presence of relatively soluble magnesium-bearing impurities, mainly MgCO_3 . Nevertheless, they arrived at a solubility product value on the assumption that a reversible equilibrium was reached at 90°C . They plotted the activity-product value against inverse of time to obtain a value for activity product at infinite time. Their value for

$$K_{\text{chr}} = [\text{Mg}^{2+}]^3 [\text{OH}^{-}]^6 [\text{H}_4\text{SiO}_4]^2 = 10^{-49.1 \pm 10^{0.5}}$$

These authors have also done some calculations for K_{chr} from thermodynamic data and plotted them against temperature. From their curve K_{chr} at 37°C

is 10^{-51} (approximately).

In our static leaching at "equilibrium" $[Mg^{2+}]$ was 2.2×10^{-4} moles/l and $[H_4SiO_4]$ was 1.7×10^{-5} moles/l at pH 10.1. Hence, if chrysotile came to equilibrium at $37^\circ C$ - which appears very unlikely, as weeks were required in the work of Hostetler and Christ - the value of K_{chr} will be 3×10^{-46} which is more than the theoretical value by a factor of 10^5 . (In the above calculation activity coefficients were ignored). This obviously means that the reversible equilibrium was not established in the specified time.

Recently Choi and Smith (51) have studied the kinetics of dissolution of chrysotile in water at temperatures ranging from 5 to $45^\circ C$. They observed that the initial rate of Mg^{2+} dissolution was higher and it slowed down with time. The pH of the suspension also decreased with time which they explained as due to the formation of $MgOH^+$ or readsorption of $Mg(H_2O)_6^{2+}$ and $MgOH^+$ ions on the negative sites of silica surface exposed as chrysotile dissolved. However, from their experimental details it did not appear that the above authors took any precaution to avoid the dissolution of atmospheric CO_2 which obviously dissolves slowly and reduces the pH of chrysotile suspension. From the calculation of activation enthalpy (5.5 and 6.5 kcal/mole for Mg^{2+} and OH^- respectively) these authors suggested that the rate-controlling mechanism for both magnesium and hydroxyl ion dissolution is diffusion from the surface into water.

Atkinson and Rickards (52) studied the acid decomposition of highly opened chrysotile and observed that the acid decomposition of chrysotile proceeds by a rate-controlling diffusion process through a layer of siliceous residue. The rate of reaction is directly proportional to the normality of

the acid within the range 1-12 N, and the reaction rate increases with temperature according to Arrhenius equation. Monkman (53) also studied leaching of chrysotile with acids and observed that the rate of reaction at any particular pH depends on the wettable surface area of the fibre and is greatest for the fibres which received the most mechanical treatment.

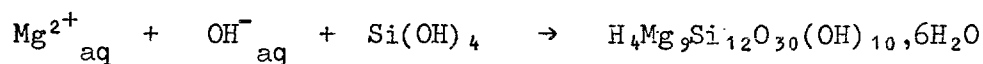
The observation made by the above workers suggests that the release of Mg^{2+} from the actual crystal lattice of chrysotile must be a very slow process in water. In the present experimental results initial high pH and high dissolution of magnesia cannot be attributed simply to the dissolution of outer brucite-like layer of chrysotile fibrils. Therefore it must be associated with some magnesium-bearing impurities. The possibility of $MgCO_3$ being present was considered although it would not give a pH as high as 10.2. Examination of the fibres under microscope with a drop of HCl did not produce any effervescence which ruled out the possibility of appreciable amounts of $MgCO_3$ being present. Therefore the only other impurity that can be present and will probably be able to explain many of the anomalies observed by other workers is brucite ($Mg(OH)_2$). Moreover, in our present experimental sample (chrysotile, Bells) the presence of brucite to the extent of 5% has since been proved by thermogravimetry and X-ray analysis. (These investigations will be discussed in the next chapter.)

(ii) The amount of silica released in the static leaching process is exceedingly low compared to the amount of Mg^{2+} . Considering the formula of chrysotile as $Mg_3Si_2O_5(OH)_4$, the ratio of $[Mg^{2+}] : [SiO_2]$ should be 1.5 : 1. But the experimental values are far lower than the theoretical values. The amount of silica released in static leaching is 1.2×10^{-2} millimoles as against 2.2×10^{-1} millimoles of Mg^{2+} .

Other workers also found the same anomalies regarding the release of silica. Clark and Holt (39) found at 25°C in water the ratio of MgO/SiO₂ released was about 10 : 1. But on heating the extract to 90°C the amount of silica released increased. They tried to explain this anomaly by considering that either colloidal Mg-silicate is formed during leaching or colloidal silica is released from the surface of chrysotile. These colloidal particles easily pass through the filter paper. At 25°C colloidal silica, Mg-silicate or polysilicic acid are unreactive to molybdate. But when the extract is heated to 90°C, Mg-silicate may hydrolyse to orthosilicic acid or the colloidal silica may produce orthosilicic acid to react with molybdate, thus showing an increased amount of silica released.

Hostetler and Christ (50) also found the anomaly in the ratio of MgO/SiO₂ released. But they explained the excess Mg release as due to the presence of impurity like Mg-carbonate. None of the above authors did consider the solubility of silica in presence of excess of Mg. In the experiment on solubility of silica in presence of excess of Mg (cf II.8) it was shown that pptd. silica is soluble to the extent of 55.2 p.p.m. in excess of Mg as against 490 p.p.m. at pH 10.2. That is, the solubility of silica is decreased almost ten times due to the presence of excess Mg²⁺ ions. Wey and Siffert (54) showed that the solubility of both monomeric silica and Mg decrease in presence of each other around pH 10-12. The solubility of silica decreases from 150 to 50 p.p.m. in presence of 78 p.p.m. of Mg²⁺ ions.

Way and Siffert further showed (55) that sepiolite, a Mg-silicate can be synthesised at ordinary temperature above pH 7.8 from MgCl₂ and Si(OH)₄



This work probably explains the low solubility of silica at relatively high pH even at ordinary temperature.

The other point in the leaching process requiring explanation is the release of increasing amounts of silica with time in the dynamic leaching process. It has already been shown that some small fragments of chrysotile itself come out during the flow of water. But that was not enough to account for the high release of silica in successive periods. This may probably be explained as follows. Chrysotile has a layered structure, Mg atoms being between two siloxane layers (Si-O). The sheets are rolled. When water passes through these layered sheets, it first washes out Mg as hydroxide, leaving the skeleton of Si-O-units. These units being very small and fragile break away and are not retained by the filter and pass with the flow of water. As more and more of Mg is washed out more of these Si-O-units are formed which pass with water. These remain in colloidal state but on boiling with NaOH and subsequent acidification form molybdate-reactive orthosilicic acid. It is clear from the experimental results that at first Mg comes out as hydroxide, giving a high release of Mg; this is then followed by the washing out of Si-O-units which obviously increases the amount of total silica released.

CHAPTER III

DETERMINATION OF BRUCITE IN CHRYSOTILE

III.1 Presence of brucite in chrysotile

It has been mentioned in chapter II that the excessive release of Mg and high pH shown by a suspension of chrysotile must be due to the presence of some Mg impurity. The presence of carbonate (alone) has been ruled out. (see Chapter II). It has been assumed that the most likely impurity present is brucite (Mg-hydroxide). The following tests were performed in order to establish the presence or absence of brucite.

III.2 Density test

A heavy liquid mixture of density 2.45 was made by mixing bromoform ($\rho = 2.9$) and carbon tetrachloride ($\rho = 1.6$) in appropriate proportions. Samples of chrysotile fibres were carefully teased apart and suspended in the heavy liquid mixture. The density of brucite is given as 2.39 and that of chrysotile as 2.55. Therefore, in the heavy liquid mixture of $\rho = 2.45$ any chrysotile particle should sink, leaving the brucite particles floating. However, no sign of any separation into fractions of different density was observable.

III.3 Acid-test under the microscope

A distinguishing feature between brucite and chrysotile is that brucite is completely soluble in dilute acid whereas chrysotile leaves a pseudomorph of silica. On a microscope slide, teased fibres were treated with dilute acid and examined under the microscope; but no evidence of completely

acid-soluble fibre was found.

Although the above two tests did not prove the presence of brucite, the possibility of its presence was not completely ruled out since it might still have been present in sub-microscopic form. Further tests were therefore carried out.

III.4 Gravimetric test

This was done by conventional thermogravimetric method, taking advantage of the difference in the decomposition temperature of brucite and chrysotile. Brucite decomposes (by dehydroxylation) at a temperature $350 - 450^{\circ}\text{C}$ into MgO and water (56) whereas the dehydroxylation of chrysotile takes place in the range $600-780^{\circ}\text{C}$. A weighed amount of chrysotile (Bells) in a fused silica crucible was first heated in an oven at 120°C , to remove moisture, cooled in a desiccator and weighed; this procedure was repeated several times till it came to a constant weight. The crucible with chrysotile was then heated in a muffle furnace at a temperature $400-420^{\circ}\text{C}$. After every 24 h the crucible was taken out, cooled in a desiccator and weighed again; this was repeated several times until it came to a constant weight (when the decomposition of any brucite was complete).

Results of this experiment performed in duplicate gave 5.0 and 5.0% brucite in good agreement with some data reported by Turner Brothers Asbestos Co. (56).

A private communication from Turner Brothers Asbestos Co., giving the brucite content of different types of chrysotile asbestos is reproduced below. These results indicate that the apparent brucite content ranges from

0-14.6%. The figure 0 confirms that "pure" chrysotile does exist (exceptionally) and does not decompose at 400-420 °C, but other samples of chrysotile from the same deposits may contain several percent of brucite.

TABLE 9

Percentage of brucite content in different
types of chrysotile

Fibre source	Lowest	Highest	Average
Black lake (Quebec)	1.9	8.5	4.5
King beaver	0.2	5.0	3.0
Normandie	0.0	2.6	1.5
J.M. Jeffery	1.3	6.0	3.0
Bells	0.0	4.9	2.3
Carey	2.6	14.6	10.6
Cassiar (British Columbia)	0.0	0.8	0.2
Shabanie (C&G) Rhodesia	0.0	2.4	1.0
King mine (VRAK)	0.3	5.6	3.4
Faths mine (VRAG)	2.1	3.1	2.4
Havelock	0.1	2.4	1.0

III.5 D.T.A. and T.G.A. of chrysotile as a further proof of the presence
of brucite

III.5(a) D.T.A.

A sample of chrysotile (Bells) was run in a D.T.A. apparatus at Cape Asbestos Research Laboratory by courtesy of Dr. A.A. Hodgson. The D.T.A. curve obtained at a heating rate of $10^{\circ}\text{C}/\text{min.}$ is reproduced in fig. 5 and shows the following features

- (a) Dehydration starts at a temperature lower than 100°C and proceeds up to above 250°C .
- (b) At 410°C there is an endothermic peak which could well be due to the decomposition of brucite.
- (c) Another sharp endothermic peak occurs at 690°C , which is due to the decomposition of chrysotile.
- (d) A sharp exothermic peak occurring at 810°C shows the recrystallisation to forsterite and silica.
- (e) Before the sharp endothermic peak at 690°C , the curve shows a broad but well defined endothermic region at about 570°C , the cause of which is obscure.

III.5(b) T.G.A.

In the previous direct gravimetric experiment (Ch. III.4) it was shown that Bells chrysotile apparently contains about 5% brucite. The D.T.A. run on chrysotile showed an endothermic peak at about 410°C , which was postulated to be due to the dehydroxylation of brucite. In order to obtain a quantitative estimate of the weight loss in the region of 400°C and also to separate the dehydration of brucite from the changes in chrysotile, the following T.G.A. experiments were carried out. Three different runs were carried out with chrysotile (Bells) in a "Stanton" thermogravimetric balance at a heating rate of $6^{\circ}\text{C}/\text{min.}$

- (a) With original chrysotile fibres a straight run (fig. 6)
- (b) With original chrysotile fibres but keeping the temperature constant

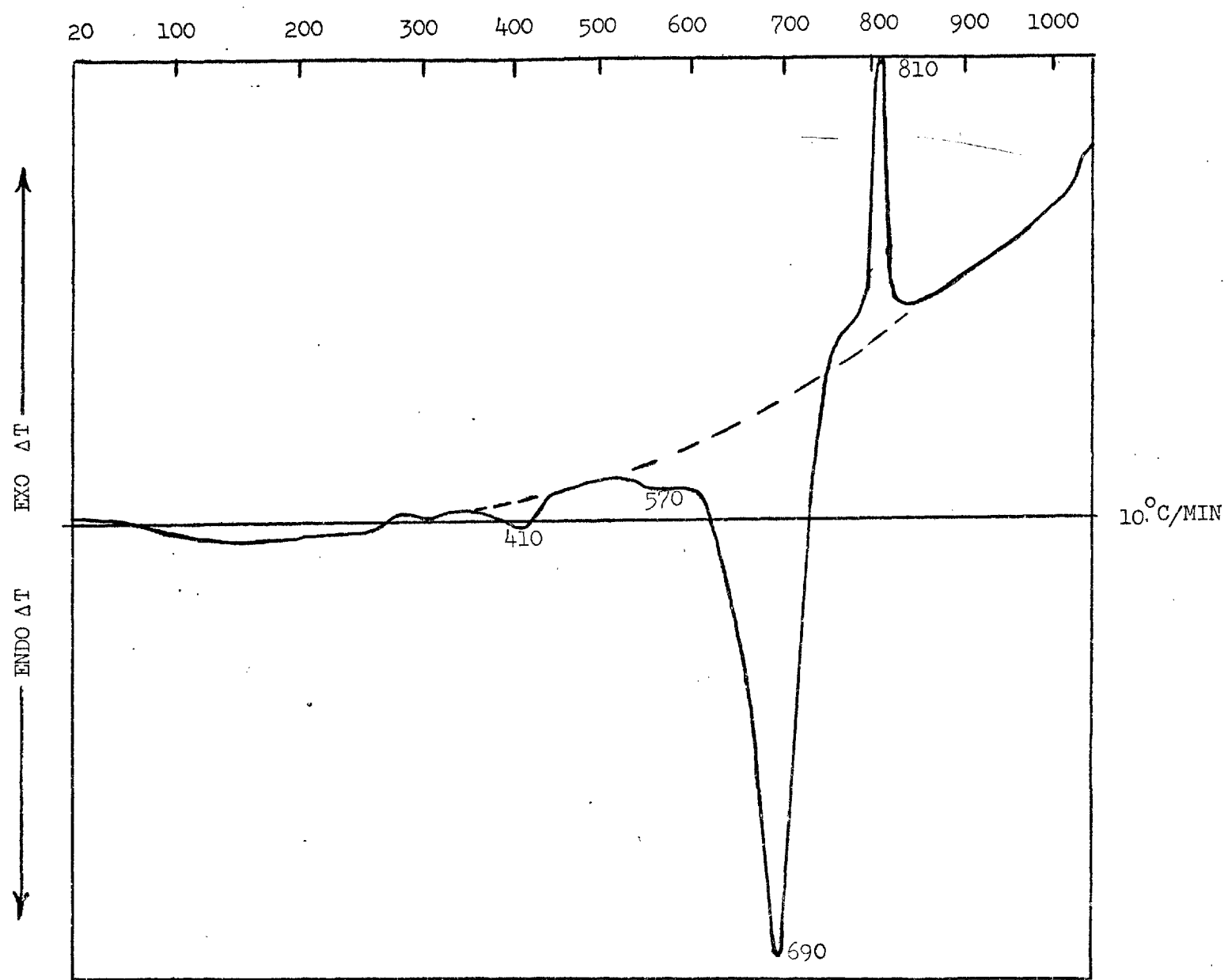


Fig. 5. D.T.A. CURVE FOR CHRYSOTILE (BELLS)

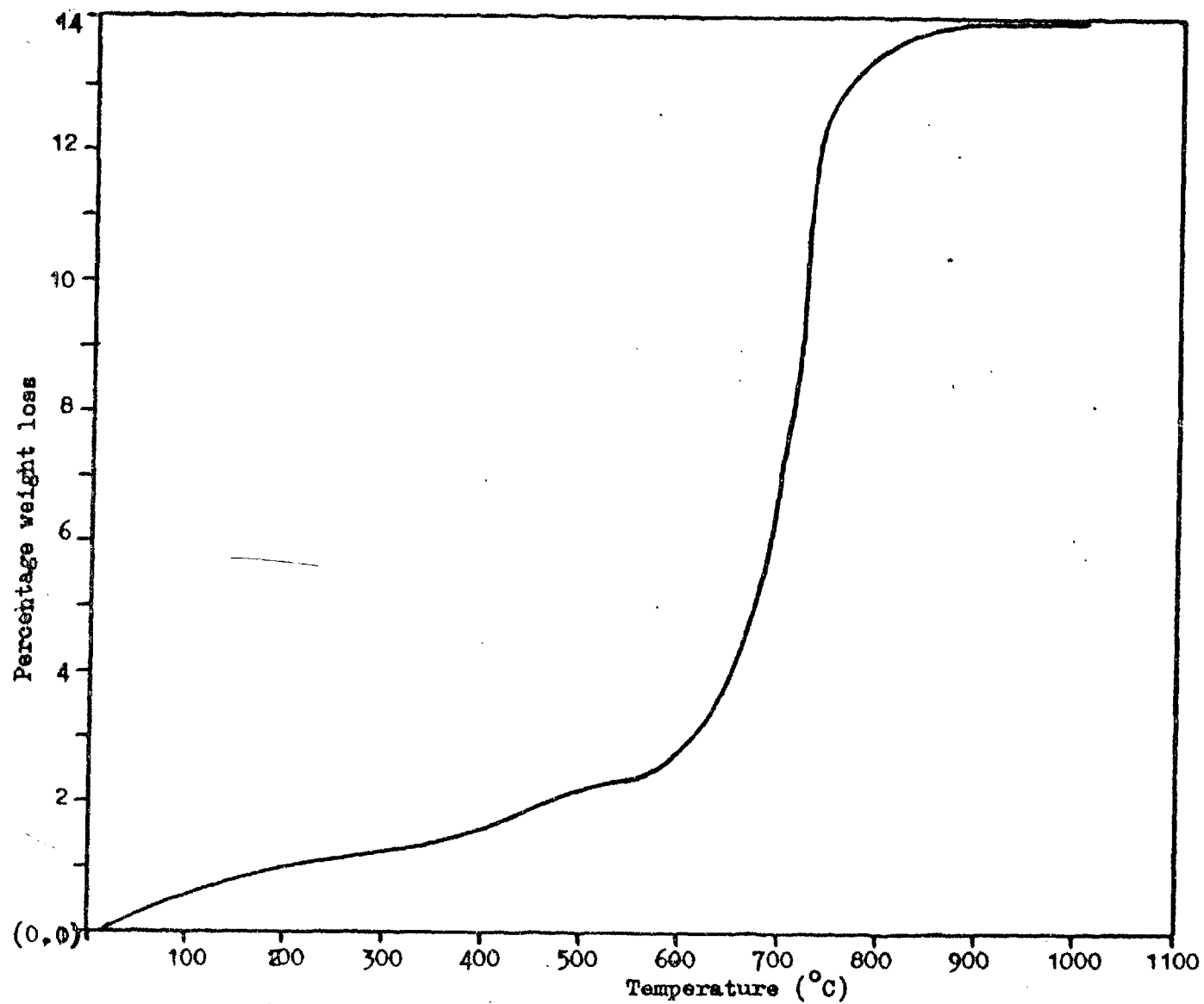


Fig. 6. T.G.A. of chrysotile
weight : 0.6180g, rate of heating - 6°C/min.

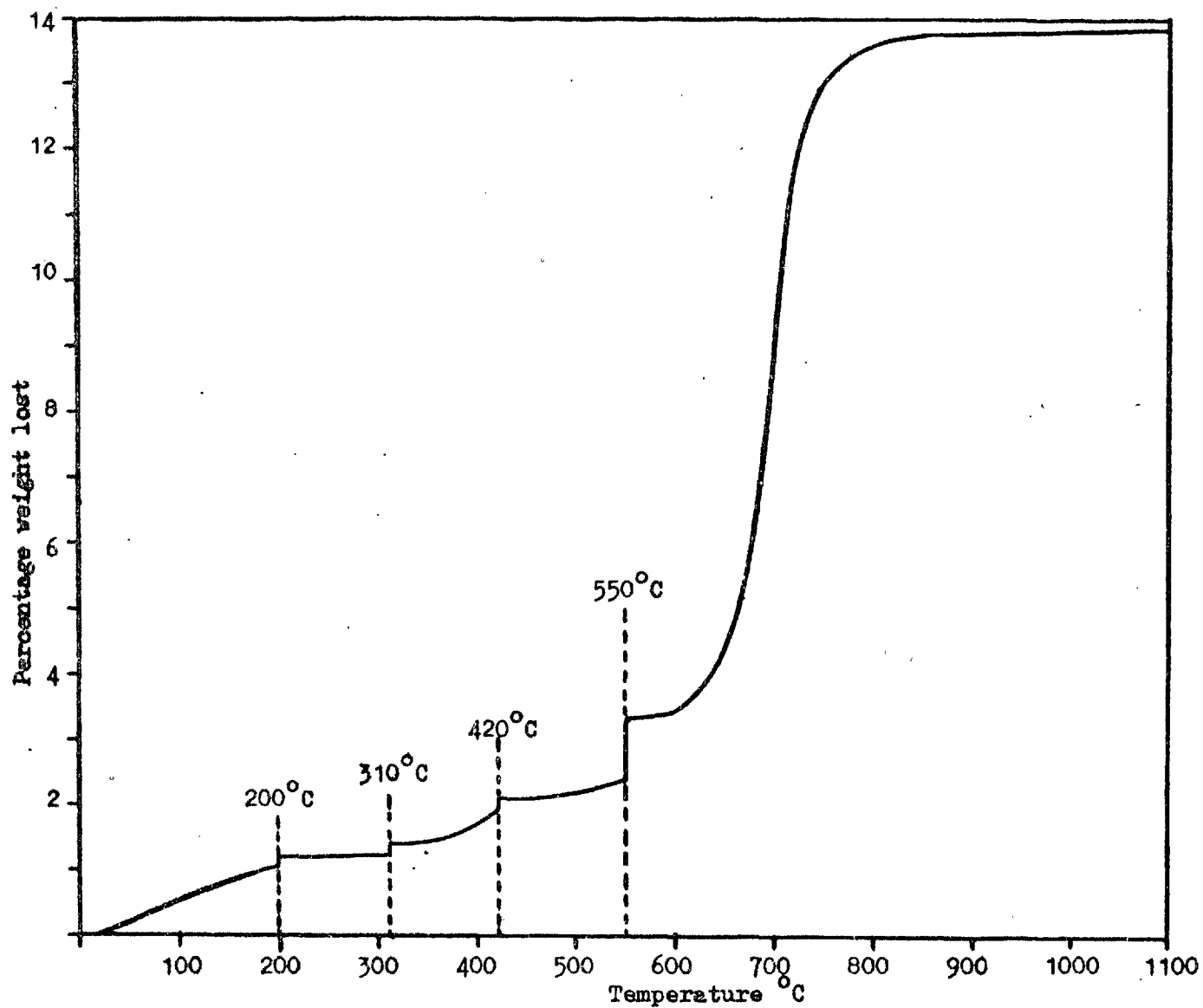


Fig. 7. T.G.A. Chrysotile (Temp. held constant at 200, 310, 420 and 550°C
weight : 0.6180 g rate of heating: 6°C/min.)

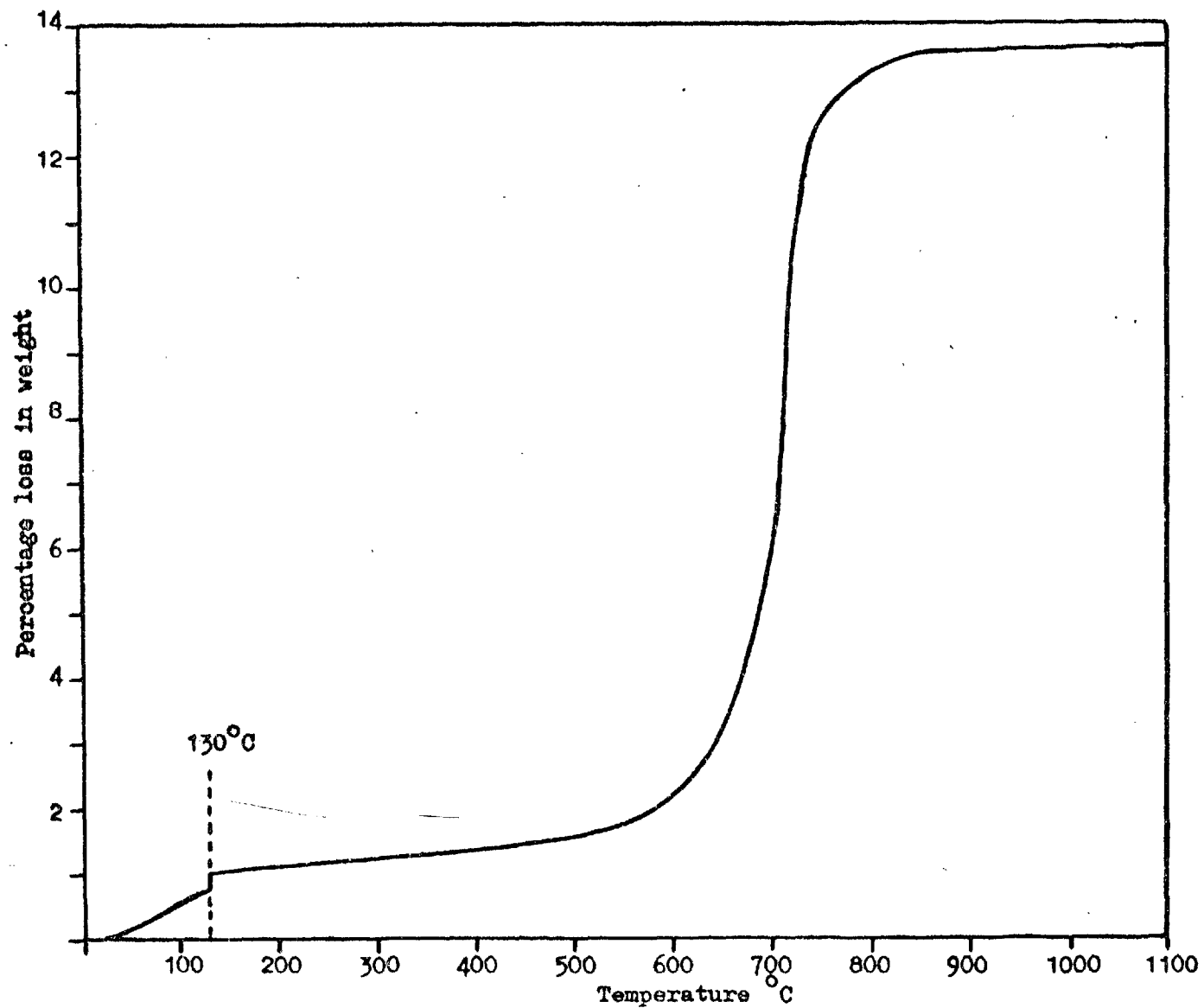


Fig. 8. T.G.A. of chrysotile leached with acetic acid
weight : 0.7443g., Rate of Heating - 6°C/min.
pause to constant wt. at 130°C.

at different stages (fig. 7)

- (c) With chrysotile previously leached in dilute acetic acid to get rid of any brucite (fig. 8).

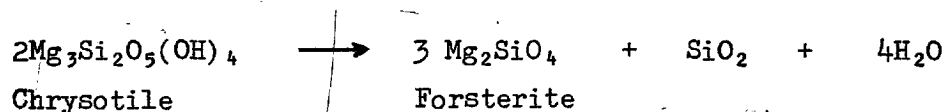
In experiment (a) there is an initial loss in weight due to the loss of physically bound water on the fibre. Above 350°C the curve shows a sudden accelerated weight loss and continues rising rather sharply up to a temperature of about 500°C , where a distinct plateau is seen. This corresponds to the endothermic peak in the D.T.A. curve at 410°C . It is presumed that this loss in weight is due to the dehydroxylation of brucite present with chrysotile.

In experiment (b) the temperature was held constant at different stages in the heating 200° , 310° , 420° and 550°C . At 200° almost all the physically adsorbed water was removed from chrysotile. After this stage no appreciable loss of weight was recorded until up to 310°C , where a slow weight loss was detected. As temperature rose after this stage, the curve showed a definite and sharp loss in weight in the region $350^{\circ} - 420^{\circ}\text{C}$. On keeping the temperature constant at 420°C for some time the decomposition in this region was almost completed. This is evident from the subsequent step where the loss of weight was negligible until the temperature surpassed 500°C : at 550°C there was a considerable rate due to the decomposition of chrysotile itself.

In experiment (c) chrysotile was first treated with dilute acetic acid, washed and dried. In this treatment the fibres lost 10.6% weight (which there must have included some leaching of chrysotile). This sample was then run in the T.G.A. The temperature was kept constant at 120°C for some time to get rid of most of the physically adsorbed water. After this the curve showed a slow rise until up to 550°C . But there is no detectable inflection in the

region 350-450°C, indicating that there is no significant decomposition of anything at this region. The gradual loss of weight over the range 120-500°C is taken to be dehydroxylation of silica gel left after acid treatment.

In all the above three experiments chrysotile itself decomposes mainly in the region 600-800°C:



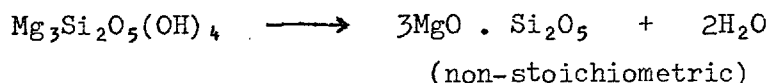
The removal of water is complete at about 800°C after which the curve shows almost constant weight. This result is in agreement with the D.T.A. curve obtained.

From the above observations it can be concluded that this chrysotile does indeed contain small amount of brucite either in the form of needle-shaped crystals or in the form of a layer cementing the thin fibrils. It is this brucite which decomposes at 350-450°C showing a sharp rise in the curve (Fig. 6 and 7). In the third experiment almost the whole of brucite is lost on treatment with acetic acid and the T.G.A. curve did not show any sudden change in the region where brucite decomposes.

It has been suggested (1) that the loss in weight of chrysotile below 600°C is due to the removal of surface hydroxyl groups from the outer layer of chrysotile fibres (which are structurally similar to brucite). The weight loss to be expected from such a reaction can be estimated as follows.

The internal and external diameters of chrysotile fibrils are 110 Å and 260 Å (14) and the distance between the composite layers is 7.3 Å.

It can be calculated that there are on an average 10 layers in a thin individual fibril and of these one is external which is of brucite type. If one layer decomposes the maximum amount of water that could be removed is 2 H₂O per formula weight, i.e.



It follows that 1.3% weight loss should occur if the surface layer of chrysotile decomposes. This 1.3% weight loss (if interpreted as brucite) would correspond to "4.2 % brucite". In other words, any pure chrysotile on heating around 350-450°C should, on this hypothesis, show the loss of 1.3% weight and appear to have "4.2% brucite". It is known, however, that whereas different samples of chrysotile, even from the same ore body, show variations in their weight-loss at 350-450°C; some samples show no significant weight loss, their apparent brucite content being recorded as 0.0%. It follows that the outer layer of chrysotile fibrils does not dehydroxylate at this temperature.

These considerations support the validity of the heating technique as a method of determining the presence of brucite in a sample of chrysotile.

III.6 X-ray diffraction examination of chrysotile (Bells)

Although D.T.A. and T.G.A. of chrysotile have given strong evidences as to the presence of brucite in chrysotile yet the presence of the former as a separate phase needs further confirmation. It is for this purpose that the X-ray diffraction experiment was carried out. Specimens of micro-crystalline Mg(OH)₂, Bells chrysotile (supposed to have 5% brucite), chrysotile + 10% Mg(OH)₂ and chrysotile leached in dilute acetic acid

were examined by X-ray diffraction.

Pure $\text{Mg}(\text{OH})_2$ for this experiment was prepared in the laboratory, based on the method of A. de Schulten (57) which uses a high concentration of caustic alkali in an autoclave. This method when used on a small scale in a platinum crucible, heated in a muffle furnace without any pressure, was found to work well giving crystals of $\text{Mg}(\text{OH})_2$. (2.0g MgCl_2 , $6\text{H}_2\text{O}$ + 56.5 g KOH + 10 ml water was heated in a platinum crucible at 220°C till the whole mass dissolved into a clear liquid. The solid residue was washed with water to remove excess alkali).

The samples for X-ray diffraction were prepared by crushing the chrysotile fibres in a tungsten carbide mill. Powdered samples were then submitted for X-ray diffractometry. The X-ray diffraction was taken in a Phillips PW 1310 X-ray diffractometer, using Ni filter and Cu radiation. The positions of all distinct peaks were noted. (The positions are probably accurate only to $\pm 0.01 \text{ \AA}$). In the following table d-spacings and intensities of four different samples are shown.

As mentioned earlier the object of this experiment was to see whether the supposed 5% of brucite was detectable as a separate phase. The method would not succeed unless the X-ray diffraction spectrum of brucite showed strong lines at a wavelength distinct from those of chrysotile; by good fortune, this proved to be so. Several other weak or very weak lines below $1.313 \text{ \AA}$ appeared with brucite but those are not shown in the table as they are useless for diagnostic purposes. It may be mentioned that most of the lines obtained with chrysotile (Bells) agree with those reported by Whittaker and Zussman (58). An examination of the table shows that the "very strong" lines of brucite at 4.773 and 2.372 appear "weak" and "very weak" in

List of diffractograph lines (d -spacing in Å) recorded with the samples. (Intensities judged visually, ranging from v.w. = very weak to v.s. = very strong.)

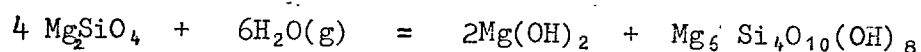
Brucite	Chrysotile	Chrysotile + 10% brucite	Chrysotile leached with acetic acid
11.051 v.w.	11.051 v.w.	-	-
9.509 v.w.	9.509 v.w.	9.509 v.w.	9.560 w.
-	-	-	8.385 v.w.
-	7.406 s.	7.363 s.	-
-	7.344 s.	7.314 s.	7.326 s.
<u>4.773 v.s.</u>	<u>4.783 w.</u>	<u>4.775 m.</u>	-
-	4.552 w.	4.564 w.	4.552 m.
-	3.675 m.	-	-
-	3.663 m.	3.665 m.	3.648 s.
2.730 w.	-	2.979 v.w.	-
-	2.592 v.w.	2.589 v.w.	2.596 w.
-	-	-	2.574 w.
-	2.537 w.	2.534 w.	2.557 w.
-	-	2.525 w.	2.529 m.
-	2.494 w.	-	-
-	2.456 w.	2.451 m.	2.463 m.
-	-	-	2.449 m.
<u>2.372 v.s.</u>	<u>2.374 v.w.</u>	<u>2.374 m.</u>	-
-	2.103 v.w.	-	2.094 v.w.
-	-	1.892 v.w.	-
-	-	1.883 v.w.	-
<u>1.798 s.</u>	-	<u>1.797 v.w.</u>	-
<u>1.576 s.</u>	-	<u>1.576 v.w.</u>	-
-	-	1.574 v.w.	-
-	1.549 v.w.	-	-
-	1.538 v.w.	1.535 v.w.	-
-	1.532 v.w.	1.530 w.	1.533 w.
-	-	-	1.523 w.
1.497 m.	1.496 v.w.	-	-
1.377 m.	-	-	-
1.363 v.w.	-	-	-
1.313 m.	1.315 v.w.	1.307 v.w.	1.312 v.w.

chrysotile (Bells) but they intensify in the sample to which 10% brucite has been added and disappear in the chrysotile which has been leached with acetic acid with loss of 10% wt. The two "strong" lines do not appear in chrysotile but appear very weak in the sample mixed with brucite and are, of course, also absent in case of leached sample. They are, therefore, not required, as the 4.77 and 2.37 lines provide the required evidence.

It is clear that (a) the acid-treated chrysotile is still well-crystalline and substantially unchanged in structure (note, for example, the 7.34, 5.44, 3.66, 2.55, 2.45 and 1.53 lines which are well clear of any brucite lines). Therefore the 4.77 and 2.37 lines do not occur in the chrysotile spectrum; (b) adding 10% of brucite to chrysotile (Bells) significantly intensifies the 4.77 and 2.37 lines and (c) both lines are detectable in chrysotile (Bells). These results are therefore completely consistent with the presence of $\text{Mg}(\text{OH})_2$ to the extent of about 5% in this sample.

III.7 Discussion

There are several reasons for doubting whether the brucite determined by 400°C heating really represents separate brucite crystallites. It is true that serpentines are believed to have been formed by hydrothermal alteration of ultra-basic silicate rocks, and most chrysotile show 0.1 - 7 percent brucite. For example action of water on olivine mineral forsterite (Mg_2SiO_4) could lead to serpentine (e.g. chrysotile) + brucite, by the well established reaction



This reaction is known to come to a reversible equilibrium at 400°C ; which according to Deer, Howie and Zussman (59) "experimental studies on the system $\text{MgO-SiO}_2\text{-H}_2\text{O}$ have indicated that serpentines can not form at temperatures above 500°C , and that formation of serpentine can occur only below 400°C ". This all suggests that some dehydroxylation may be expected from exposed surfaces of fibrils at 400°C . (After all, the outer surface of chrysotile fibrils is virtually identical with the outer surface of brucite layers). This possibility has been noted from D.T.A. curve (private communication from Dr. A.A. Hodgson); in some cases the height of the 700°C peak seems not to account for all the reaction, and there are signs of earlier endothermic recording at lower temperature. Indeed Deer, Howie, and Zussman (59) note "A weak broad, low temperature endothermic peak is shown by some serpentines, corresponding to the expulsion of water which is held on the surface of fine-grained material". But it has been shown earlier (Ch. III.5) that the surface dehydroxylation of chrysotile is improbable.

It is also noteworthy that the earlier microscopic experiments (Ch-II.3) on release of alkali (indicated by pH indicator) never revealed any fibres that were preferentially stained; rather positive indications of alkalinity were always obtained at fractured or creased regions of chrysotile bundles. Thus the "magnesia" could be coming from the surfaces of released chrysotile fibrils or from excess $\text{Mg}(\text{OH})_2$ present as an interfibrillar cement.

X-ray diffraction study has proved beyond doubt that brucite is present as a separate phase with chrysotile. This lends more support to the fact that the weight loss around 400°C is definitely due to the brucite impurity. Since no separate needle or fibrils of brucite could be identified by microscopic examination, this brucite is most probably present as an interfibrillar cement holding the fibrils together.

The relevance of this "impurity" to the present investigation is that in the earlier leaching experiments, Mg^{2+} and OH^- were detected in amounts more than expected from chrysotile. Thus, the impurity entirely dominates the leaching characteristics and the intrinsic leaching of chrysotile is probably obscured.

CHAPTER IV

DISPERSION AND FLOTATION OF CHRYSOTILE

IV Dispersion of chrysotile by surface-active agents and acid; flotation of chrysotile with surface active agents

IV.1 Dispersion by surfactant

Commercially available surfactants are well known dispersing agents and have a remarkable effect on chrysotile. Atkinson and Gettins (60) in determining the fibril length of chrysotile asbestos were able to disperse the fibre bundles into individual fibrils with the aid of a surface-active agent. As details were not, however, published, the following experiments were carried out to ascertain the nature of the process.

"Quix", which is a commercial alkyl-aryl sulphonate solution, was tried as a dispersing agent on chrysotile. A 1% solution was added to 0.1 g of chrysotile in 30 ml water. The suspensions were allowed to stand overnight but no spontaneous dispersion was observed. The bottles were then shaken continuously in a shaker, when the fibres were seen to disperse to a limited extent. In a similar but separate set of bottles, the suspensions were stirred with magnetic stirrers: extensive dispersion of the fibres was observed. A drop of the above suspension when examined under a high power microscope showed a network of thin fibrils. When the concentration of "Quix" was increased (2%) in another set, keeping all other conditions the same, the fibres were dispersed with less stirring. The same effect was observed on increasing the time of standing. In another set, fibres were kept suspended in a 1% suspension for several days when thin fibrils were seen to come off the

surface of bundles; slight stirring with a magnetic stirrer dispersed the bundles immediately.

From the above observations it has been concluded that an anionic surfactant is an efficient dispersing agent for separating the fibrils despite the fact that neutral sodium alkyl aryl sulphonate would not be considered a "solvent" for magnesium hydroxide or magnesium silicate.

Similar tests were tried with a 2% solution of alkaline EDTA (which would be expected to dissolve $Mg(OH)_2$ by sequestration) but this reagent proved practically ineffective.

Finally a 1% solution of Calgon (sodium hexametaphosphate) was also tried. Allowing the suspension to stand overnight and then stirring with a magnetic stirrer produced considerable dispersion. Varying the concentration of Calgon, time of standing; the same conclusion was arrived at as in the case of dispersion with "Quix".

The dispersing power of the agents tried lies in the order "Quix" > Clagon > EDTA.

IV.2 Dispersion by acid

Dr. R.J. Atkinson (private communication) in course of studies of surface chemistry of asbestos observed that when 0.25 g of "Paperbestos No. 5" was suspended in 50 ml 0.01 M HCl for 6 h and then centrifuged at 5000 g for 5 mins. the supernatant liquid appeared faintly turbid (61). No such

turbidity was found with much shorter or much longer treatment.

Repetition of this experiment confirmed these observations. Further investigation showed the following

- (i) Under the same conditions of suspension concentration, acid strength, time of centrifugation and speed, turbidity was checked with time of standing. It was found that a faint turbidity appeared in the suspension allowed to stand for 1 h. Maximum turbidity was observed in case of the suspension allowed to stand for 3-4 hours. Faint turbidity was observed with the suspension after overnight standing. But the suspension which was kept standing for more than a day did not show any turbidity.
- (ii) Increasing the acid strength (0.05 M) and keeping other conditions the same, no turbidity was observed. Increasing the suspension concentration (1%) and keeping the other conditions the same, no turbidity was observed.
- (iii) With the same suspension concentration (0.5%) in only water turbidity of the same order was observed; faint turbidity in case of the suspension allowed to stand for 1 h and maximum turbidity with suspension standing for 3-4 hours. Increase of suspension concentration did not produce any greater turbidity.
- (iv) The turbid suspension obtained above when centrifuged another 10 mins. at 600 g, became completely clear, with bigger particles collecting at the bottom of the tube.
- (v) The turbid suspension when filtered through Whatman 542 filter paper (mean pore size 0.4-1.1 μm), became completely clear but when filtered through Whatman 541 (mean pore size 3.4-5 μm), the turbidity still persisted but with slightly less intensity. This shows that the majority of the particles causing the turbidity are within the range of 1-5 μm .
- (vi) When two samples of turbid suspensions from acid and water extract were

allowed to stand, it was observed that particles grew in size in the water extract making the turbidity less and less. The acid extract formed a relatively stable turbid suspension. This shows that the H^+ ions might be responsible in making the suspension stable.

(vii) The turbid suspension obtained from acid extract showed pH 2.5; with the addition of ammonia drop by drop, a brown precipitate appeared around pH 6.8. The brown precipitate on analysis was found to be $Fe(OH)_3$. This shows that "Paperbestos No. 5" is contaminated with a considerable amount of Fe. The water extract showed a pH 9.0 and addition of ammonia drop by drop increased the turbidity around pH 10.5 when $Mg(OH)_2$ was precipitated.

(viii) The same experiments were performed with Bells in original fibre state and with ground fibres but no detectable turbidity appeared in any case.

Attempts were made to detect the material causing the turbidity in the photomicroscope but without any success. Electron micrographs obtained with the turbid suspension did, however, show the presence of very thin fibrils of chrysotile. The electron micrograph is shown in fig. 9. This confirms the conclusion that the turbidity was due to the very thin, short, fibrils coming off the bundles of fibres.

The relevance of these thin fibrils to asbestosis is doubtful. Such particles are indeed found in the lungs of affected persons, but are presumed to have arrived there as air-borne particles, not to have been formed by disintegration of bundles by leaching.

The colloidal stability of particles of chrysotile is considered later in connection with zeta-potential measurements.

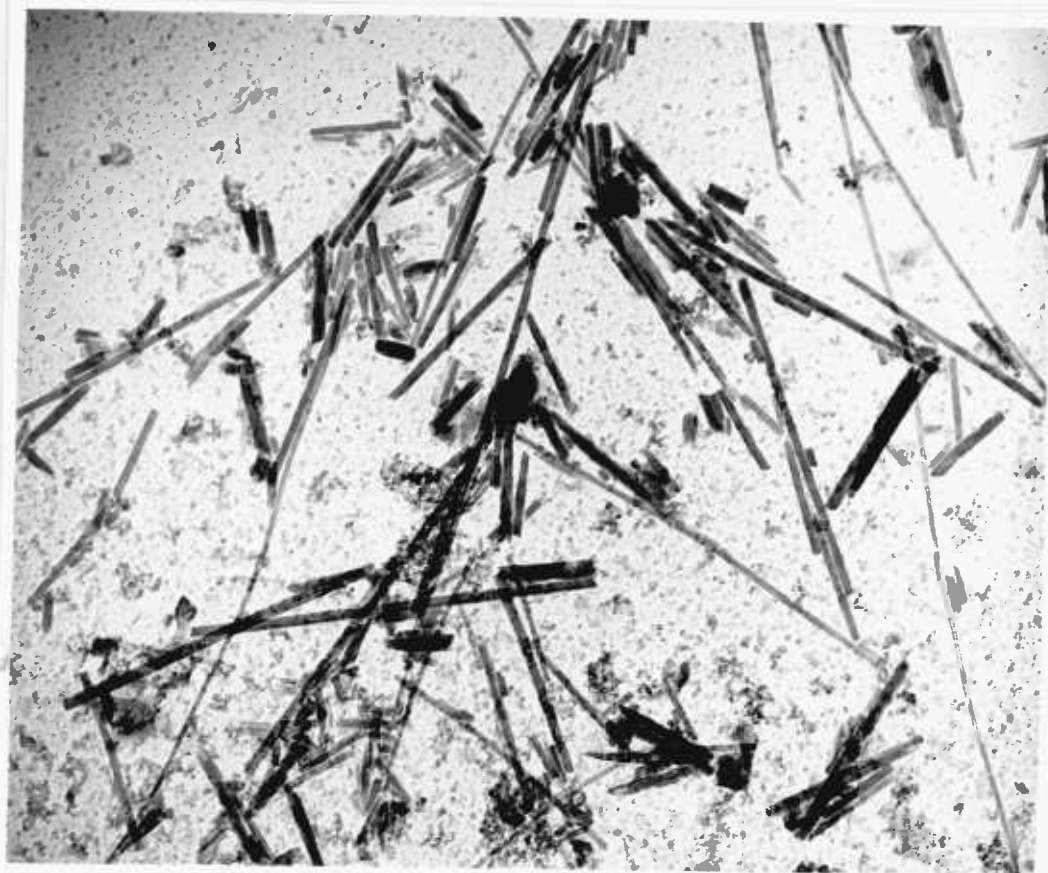


Fig. 9 Électron micrograph of 'Paperbestos No. 5'
dispersed with acid (magnification : 34500 X)

IV.3 Flotation of chrysotile with surface-active agents

Gettins and Mallon (62) studied the adsorption of surface-active agents such as DBS (Na-dodecyl benzene sulphonate) and Na-laurate on chrysotile. They observed that as the surface-active agent is added to the fibres they pass from a flocculated state to a dispersed state when the maximum coverage of the fibre surface is attained. They studied the adsorption isotherm of surfactant on chrysotile and suggested that the adsorption of the majority of the surface-active molecules is non-specific and the adsorbed molecules are oriented with their polar heads facing the solution.

Novak (63) from his experiment concluded that a significant proportion of surfactant molecules were directly chemisorbed on to the magnesium ions on the fibril surfaces and that the remainder were oriented in the reverse directions with the polar heads of the surfactant molecules facing away from the fibre surface.

On the basis of these two works, a simple experiment was carried out in order to study the flotability of chrysotile with surface-active agents. DBS and Aerosol OT (Na-diethyl hexyl sulpho succinate) were chosen as the surface-active agents.

Experimental - In 0.2% suspension of chrysotile different concentrations of DBS and Aerosol OT were added separately. The fibres were then subjected to a flotation test by passing air through the suspension.

It was observed that with DBS the fibres floated with a minimum DBS concentration of 0.0025% and flotation continued over a wide range of surfactant concentration up to 0.05%. But the best flotation was attained with a

concentration of 0.005% DBS. With Aerosol OT flotation of the fibres was obtained within a concentration range of 0.1 - 5% . Best flotation was obtained with surfactant concentration 1%.

The fibres which floated were taken out and washed in water several times and then subjected to flotation tests but these fibres did not then float. However, some air bubbles were found to stick on the surface of the fibres. This shows that only a very few molecules of surfactant were strongly chemisorbed.

IV-4 Discussion

The action of surfactant in dispersing the fibres seems to be a genuine example of "Rehbinder effect", the weakening of polycrystalline solids by adsorbed substances. The reagent slowly creeps along the grain boundaries and gets adsorbed thus weakening the particle/particle adhesion (64, 65). These fibres when slowly stirred are readily dispersed.

In the flotation experiment it has been shown that some molecules of the surfactant are chemisorbed on the surface of asbestos. Gettins and Mellon have suggested that the majority of the surfactant molecules attach themselves on the fibre with the polar heads away from the surface. However, they did not study the flotation of the fibres which occurs at low concentrations. In order that the fibres should float the hydrophilic heads of the surfactant molecules should be attached to the surface with the non-polar "tails" exposed to the surface. On the basis of the above results it is suggested that after a few molecules of the surfactant are chemisorbed on the surface, others are attached by "hydrophobic association" with polar

groups free and exposed. This is the currently accepted theory of adsorption of anionic flotation "collectors" on minerals carrying basic groups.

CHAPTER V
ADSORPTION OF INORGANIC
IONS ON CHRYSOTILE SURFACE.

This project started with the hypothesis that asbestos fibres entering the lungs may be involved in some chemical reactions with the surrounding substances. Therefore one of the important steps would be to study the adsorption of some of the inorganic ions which are present in human blood and lung fluid. Some experiments have, therefore, been carried out on the adsorption of the most important ions namely Ca^{2+} , Na^+ . These adsorption studies were made with special reference to their concentration in human blood. Calcium is present in human blood to the extent of 10 mg/100 ml and the Na content is 316 mg/100 ml (66).

V.1 Estimation of calcium

Calcium was determined by atomic absorption spectrophotometry. In the present experiment Ca estimation was expected to be subject to some interference from silica and Mg as these two materials would come from the chrysotile fibres. A check was therefore made on the interferences. It was observed that Mg alone does not interfere with the Ca determination; but silica causes serious interference. Silica concentration as low as 0.2 p.p.m. was found to suppress the absorbance of Ca. Both La^{3+} (1%) and Sr^{2+} (1500 p.p.m.) (41) were tried as the agents for removing interference and it was found that both worked satisfactorily. But when La^{3+} was used to the extent of 1% the absorbance was more enhanced. Therefore, La^{3+} has been chosen as the reagent to remove the interference due to silica

in Ca estimation.

In atomic absorption Ca can be estimated within the range 1-10 p.p.m. in presence of 1% La^{3+} solution. La^{3+} was used in the form of its chloride which, in turn, was obtained by dissolving La_2O_3 .

For preparing a 5% La^{3+} solution 58.65 g of La_2O_3 is first wetted with distilled water and 250 ml of conc. HCl is added very slowly with constant stirring. The solution appears at first slightly turbid but when slightly heated becomes clear. This is then cooled and diluted to 1000 ml.

The addition of La^{3+} to Ca solution was found to be very critical; exactly the same amount of La^{3+} solution has to be added to all the standard and the test-solutions.

V.2 Adsorption of Ca^{2+} on chrysotile surfaces with different Ca^{2+} ion concentration

Experimental In each of several separate polypropylene tubes 0.2 g of chrysotile was kept suspended in 40 ml Ca^{2+} solution of different concentration. The polypropylene tubes were continuously shaken at 37°C . After 96 hours the tubes were taken out, the pH of the suspension was measured, it was centrifuged and unadsorbed Ca^{2+} was measured in the supernatant according to the above procedure. The Ca^{2+} solution used in this experiment was made by dissolving "Analar" CaCl_2 which was also standardised by atomic absorption.

Mg and silica released were measured by atomic absorption and colorimetry

according to the method described in chapter II. The results of this experiment are given in tabular form. This experiment was performed in duplicate and results correspond to the mean of two readings.

TABLE 11

Adsorption of Ca^{2+} on chrysotile with concentration

The following figures correspond to 40 ml of the suspension containing 0.2 g of chrysotile : results are presented in μmoles .

Ca^{2+} added	Ca^{2+} adsorbed	Mg^{2+} released	silica released
0	0	6.1	10.2
17	1.8	6.5	9.5
35	3.0	8.9	7.6
53	3.9	9.2	6.1
72	5.5	9.2	4.2
81	8.0	9.2	4.0
90	10.0	10.5	4.2
99	10.9	9.0	4.6
107	10.9	9.5	4.6
126	11.9	8.6	3.5
144	12.9	9.8	2.8
180	11.9	8.7	2.8
200	14.9	10.3	2.4

The above results show that at all concentrations of added Ca^{2+} ion at least

one tenth of the amount is adsorbed on the chrysotile surface. But the extra Mg^{2+} ions released are not equivalent to the number of Ca^{2+} ions adsorbed. For example, 6.10 micromoles of Mg^{2+} is released in normal leaching process and the Mg^{2+} released after adsorption of 2-14 micromoles of Ca^{2+} is only 9-10 micromoles. On the other hand as the Ca^{2+} adsorption increases the amount of silica released decreases. It is quite evident that with the adsorption of Ca^{2+} ions the amount of Mg^{2+} released is slightly increased which suggests that a process of cation exchange is going on. But the major amount of Ca^{2+} adsorbed is presumably on the surface of silica exposed after the release of Mg^{2+} and as the Ca^{2+} adsorbed increased the silica released is more and more decreased. This fact is more evident from the next experiment.

V.3 Influence of pH on the adsorption of Ca^{2+} ions on chrysotile surface

In the previous experiment it was not quite clear whether Ca^{2+} adsorption is a simple case of ion exchange or a process of adsorption on the silica surface. To obtain more information as to the nature of adsorption this experiment was performed.

Experimental In a series of separate polypropylene tubes 0.2 g of chrysotile was kept suspended in 40 ml of Ca^{2+} solution of the same concentration but with different amounts of HCl and NaOH added. The initial pH of the suspensions were measured. These tubes were kept continuously shaken at $37^{\circ}C$ for 96 h and final pH recorded. The amount of Ca^{2+} adsorbed and the amount of Mg^{2+} released were measured. The results are given below.

TABLE 12

Adsorption of Ca^{2+} on chrysotile with
change of pH

The figures correspond to 0.2 g chrysotile in 40 ml Ca^{2+} solution.

Ca^{2+} added (μmoles)	HCl added (μmoles)	NaOH added (μmoles)	Initial pH at 37°C	Final pH at 37°C	Ca^{2+} adsorbed ($\mu\text{ moles}$)	$^{2+}$ Mg released ($\mu\text{ moles}$)
0	7530	0	1.2	1.7	0	1210
114	7530	0	1.2	1.7	0	1210
"	2510	0	1.7	3.1	1.9	516
"	1750	0	1.8	3.6	2.9	370
"	1255	0	2.1	4.1	2.9	269
"	502	0	2.5	7.0	4.9	116
"	251	0	2.7	7.6	6.0	59
"	125	0	3.4	7.9	7.0	38.6
"	87	0	7.2	8.6	9.0	
"	62	0	8.3	8.8	14.0	24
"	0	0	9.0	9.2	10.9	9.8
"	12	0	8.9	9.1	14.9	13.0
"	6	0	8.8	9.2	13.9	13.0
"	1	0	8.8	9.2	11.9	
"	0	448	11.2	11.3	34.9	0.5
"	0	1120	11.5	11.6	38.9	0.2
"	0	2240	12.0	12.0	38.9	-
"	0	4480	12.2	12.2	47.9	-

From the above results it is clear that the amount of Ca^{2+} adsorbed is not very significant at lower pH. It shows a slight increase up to pH 9.2; but over pH 9 the amount of Ca^{2+} adsorbed sharply increases and then follows an increase with the rise of pH. These results seem to be comparable to the adsorption of Ca^{2+} on quartz surfaces (68).

V.4 Release of Mg^{2+} from chrysotile in presence of Ca^{2+}

The fact that cation exchange of Ca^{2+} for Mg^{2+} is not very marked is particularly evident from the following short selection of results in which the Mg^{2+} release in presence or absence of added Ca^{2+} is compared at $\text{pH} < 9.1$.

TABLE 13

Release of Mg^{2+} from chrysotile
in presence of Ca^{2+} .

(The figures correspond to 0.2 g chrysotile in 40 ml solution)

HCl added (μ moles)	Final pH	Mg^{2+} released in presence of Ca^{2+} (μ moles)	Mg^{2+} released in absence of Ca^{2+} (μ moles)
7530	1.7	1210	1200
2510	3.1	516	490
1250	4.1	269	279
502	7.0	116	115
251	7.6	59	60
12.5	9.1	13	14

The above results show that in presence of HCl the amount of Mg^{2+}

released is not enhanced by the presence of Ca^{2+} in solution. Thus the leaching in dilute acid is a straight forward dissolution with negligible reversibility.

V.5 Adsorption of Ca^{2+} on acid-leached chrysotile

In the two previous experiments it appeared that the process of Ca^{2+} adsorption is not a direct ion-exchange taking place on the surface of chrysotile lattice but is a direct case of adsorption on exposed silica surface. In those experiments it was not possible to show quantitatively that the amount of silica surface exposed is enough to account for the adsorbed Ca^{2+} . In order to establish this, the present experiment was carried out.

Experimental - Equal amounts of chrysotile (1 g) were kept suspended in the same volume of 0.1N HCl in different polypropylene bottles at room temperature. Each of the bottles was taken out at different time intervals; the fibres were filtered, washed with water and dried at 120°C . 0.2 g of each of the samples was suspended in 40 ml of Ca^{2+} solution of the same concentration in different polypropylene tubes at 37°C . After 96 h the amount of Ca^{2+} unadsorbed in each case was measured. The results are shown in the following table.

TABLE 14

Adsorption of Ca^{2+} on acid-leached
chrysotile

The results correspond to 0.2 g of acid-leached fibres in 40 ml Ca^{2+} solution

Time of leaching in acid (hours)	Amount of Ca^{2+} added (μ moles)	Amount of Ca^{2+} adsorbed (μ moles)	pH of the solution
2	93.8	6.9	7.1
24	"	7.9	7.0
48	"	8.8	7.0
120	"	11.9	7.0

The above results show that the amount of Ca^{2+} adsorbed increases with the increase of leaching time; the pH of the suspension in Ca^{2+} solution remains constant. Therefore this increase in Ca^{2+} adsorbed cannot be due to a pH effect (cf. ch. V-3). The most probable explanation is that as the time of leaching in acid increases more and more of the Mg is leached out off the surface of the fibres exposing additional active silica surface which adsorbs Ca^{2+} .

V.6 Adsorption of Na^+ ions on chrysotile

As in human blood Na is present to the extent of 316 mg/100 ml (i.e. 3160 p.p.m.) (66), adsorption experiments should be carried out around that concentration.

V.6(a) Determination of Na by atomic absorption spectrophotometry

Willis, J.B. (69) showed that Na can be estimated in absence of other material within certain ranges by atomic absorption. But in our present experiment Mg and silica released from chrysotile were expected to interfere with Na estimation. However, Mg alone was found not to interfere. But when silica is present with Na to the extent of 1 p.p.m. the absorbance due to Na is slightly increased.

Attempts were made to remove the interference by addition of reagents such as NH_4Cl , LaCl_3 , etc., but without success. It was supposed that the silica present might be in the form of colloidal silica which causes the absorbance increase. In order to test it, to the solution HF (1%) was added to dissolve colloidal silica and excess HF was then complexed by adding boric acid (4%) and ultimately LaCl_3 was added to remove the effects due to boric acid and others. But this also met with failure. Next, an attempt was made to find the minimum amount of silica which when present with Na will interfere in its estimation. The following results were obtained.

TABLE 15

Interference of silica on sodium estimation by atomic absorption spectroscopy

p.p.m. of Na	p.p.m. of SiO_2	Absorbance (1x20 scale)
4	0	5.1
"	0.1	5.1
"	0.2	5.1
"	0.5	5.1
"	1.0	5.2
"	5.0	5.5
"	10.0	6.0

It is evident from the above table that Na estimation can be carried out in presence of silica quite safely when the silica concentration is less than 1 p.p.m. and then Na can be estimated within the range 1-10 p.p.m..

V.6(b) Na⁺ adsorption on chrysotile - experimental

In a series of separate polypropylene tubes 0.2 g of chrysotile was kept suspended in 40 ml of Na⁺ solution of different concentration. These were kept shaken for 96 h in a water-bath at 37°C. The tubes were then taken out, the suspension centrifuged and the amount of unadsorbed Na⁺ in the supernatant was measured by the above method. The amount of Mg²⁺ released was also measured as usual by atomic absorption. The experiment was performed in duplicate and the results are shown in the table.

TABLE 16
Adsorption of Na⁺ on chrysotile with concentration.

(The following figures correspond to 0.2 g of chrysotile in 40 ml of the suspension)

Na ⁺ added (μ moles)	Na ⁺ adsorbed (μ moles)	Mg ²⁺ released (μ moles)
0	0	6.1
2600	52	7.7.
3470	69	7.8
4340	86	8.1
5210	86	7.9
5650	95	8.1
6080	120	8.2
6520	100	8.1
6950	130	7.5
7820	170	8.0

From the above results it is evident that the amount of Na^+ adsorbed on the chrysotile surface is not very significant. The amount of Mg^{2+} released is only slightly increased and there is no stoichiometric relation between the two. The small amount of Na^+ adsorbed might have been on the silica surface; it was clearly not taken up by cation exchange in the chrysotile lattice.

V.7 Discussion

Consideration of the results of all the above experiments suggests that the adsorption of Ca^{2+} ions on the surface of chrysotile is not an easy process of ion-exchange; rather it seems more plausible to think that the adsorption is on the silica surface exposed due to leaching of the uppermost brucite layer of chrysotile. Indeed, it is not to be expected that Ca^{2+} (radius 0.99 Å) could replace Mg^{2+} (0.65 Å) in the chrysotile lattice because the size of the octahedral sites (6-co-ordination of O^{2-} ions of 1.40 Å) is approximately 0.58 Å in the unstrained state. Furthermore it is well known that the natural serpentine minerals (including chrysotile) invariably contain only traces of Ca, despite the approximately equal abundance of Ca and Mg in the earth's crust. It is clear that Ca^{2+} is effectively excluded from Mg^{2+} sites in geochemistry.

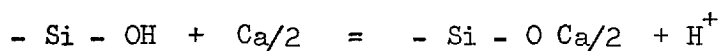
There is a considerable volume of information available on the adsorption of inorganic ions on silica surfaces. Clarke and Cooke (68) studied the adsorption of Ca^{2+} ions on quartz surfaces. They found that the Ca^{2+} adsorption is constant over the pH range 4-10. After pH 10.5 it sharply increases, but there is again considerable desorption at pH 13.

As to the mechanism of adsorption Clark and Cooke considered that a negative charge is acquired by quartz in alkaline solutions when the surface silicic acid dissociates. Cations are attracted to the negative surface to balance the surface charge. Divalent cations such as Ca^{2+} , Ba^{2+} , Mg^{2+} are specifically adsorbed.

French and Howard (70) studied the adsorption of different inorganic salts on silica gel. They found that the number of gram equivalents of cation adsorbed was equal to the number of gram equivalents of hydrogen ion liberated. They postulated the adsorption to be a strictly replacement process.

Churms, S.C. (71) published a review of the works of different workers on the adsorption of different cations on silica gel. Strazhesko and Yankovskaya (72) studied the sequence of affinity of different cations to silica gel. They reported that for ions Sr^{2+} , Ca^{2+} , Ag^+ and Na^+ the affinity sequence was $\text{Na} < \text{Ag} < \text{Ca} < \text{Sr}$; and the bivalent ions are preferred to the monovalent.

In chrysotile, after the upper brucite layer is leached out, active silica surface with the group $-\text{Si}-\text{OH}$ is exposed. The H^+ in $-\text{Si}-\text{OH}$ is replaceable by any cation. Therefore with Ca^{2+} most probably the following reaction takes place



As has been mentioned by Clarke and Cooke and others, the bivalent ions are more preferred for this reaction to the monovalent ions. This is more evident from the experimental results shown above that Ca^{2+} is adsorbed

more than Na^+ (10% of added Ca^{2+} was adsorbed against about 2% of Na^+ under normal conditions). Therefore, it can be concluded that the adsorption of inorganic ions on chrysotile surface is replacement process taking place on the active silica sites.

Finally there seems no reason to attach any special biological significance to the small adsorption of Ca^{2+} on leached chrysotile. The quantity is utterly negligible compared with the reserves in the body fluids, and its effect on the surface properties of chrysotile would simply be to reduce somewhat the zeta-potential. The possibility that Ca^{2+} ions in ambient medium activate adsorption of carboxylic or other anionic substances is a separate consideration from the simple adsorption.

CHAPTER VI

SURFACE AREA OF DIFFERENT ASBESTOSES

ADSORPTION OF WATER VAPOUR AND BENZENE VAPOUR ON CHRYSOTILE.

VI.1 Surface area of different forms of asbestos

The surface area of the asbestos were determined by B.E.T. krypton adsorption, the molecular area of Kr being taken as $18 \text{ \AA}^2/\text{molecule}$. The surface areas obtained for different samples are shown below.

TABLE 17

Surface area of different asbestos

Samples	Specific surface area (m^2/g)
chrysotile (Bells) commercial "opened"	12.2
chrysotile (Bells) mechanically ground and dried	17.7
chrysotile hand extracted from solid rock and gently teased	4.59
chrysotile (Bells) collected from air-borne dusts (length of fibrils, 1 - 5 μm)	14.9
chrysotile (Cassiar) collected from air-borne dusts (length of fibrils, 1 - 5 μm)	21.1
amosite, teased	0.72
crocidolite, teased	1.28

A sample of chrysotile directly obtained from the solid rocks in the form of small sticks was subjected to surface area determination. It was observed that in 6 h time the adsorption of krypton did not reach equilibrium; more and more of the gas continued to penetrate. However, an approximate calculation gave a surface area of $0.4 \text{ m}^2/\text{g}$. This shows that although the sample is in a compact form krypton molecules can slowly enter. This indicates a form of micro-porosity. From the above results it is further evident that chrysotile (Bells) commercial sample and the sample collected from air-borne dusts have almost the same surface area ($12.2 \text{ m}^2/\text{g}$ and $14.9 \text{ m}^2/\text{g}$). This shows the accessibility to krypton molecules through the bundles of chrysotile fibrils; "opened" asbestos shows almost as large an area as the most finely-divided dusts prepared from the same material. Even the gently teased rock shows as high a specific surface area as finely divided powders. An order of magnitude calculation indicates that if the fibrils were of diameter $400 \text{ \AA}$ and fully separated, the specific surface area would amount to about $40 \text{ m}^2/\text{g}$.

It can therefore be concluded that the fibrils in chrysotile are only weakly stuck together, and are easily separated when the material is deformed, exposing much of the fibre surface. The amphiboles do not show quite such large areas.

VI.2 Adsorption of water vapour on chrysotile

This, approximate, measurement was performed in order to check whether there is any capillary condensation in chrysotile. In a number of separate desiccator jars, saturated solutions of different salts to give different relative humidity were set up. The samples of chrysotile taken in small

petri dishes were first dried in an oven at 120°C and then kept overnight over P_2O_5 before weighing. (Dried chrysotile takes up water vapour avidly). After weighing, the samples were kept standing in the first desiccator with the lowest humidity. They were allowed to stand 24 h after which they were weighed again. Subsequently the samples were transferred from one desiccator to another, allowed to stand 24 h in each desiccator and weighed after every 24 h. In this way samples were taken from the lowest to the highest humidity and then brought back from the highest to the lowest, repeating the same procedure.

The increases of weight (per gram of the asbestos) at different humidities while going up and coming down were recorded. The graph of weight increase per gram against relative humidity is shown in fig. 10. From the S-shape of the isotherm, it is evident that a monolayer is formed over the chrysotile surface at relative humidities of around 0.2. Over the relative humidity of 0.33 multilayers build up.

At a relative humidity 0.2 where chrysotile surface becomes covered with a monolayer of water vapour, the amount of water vapour adsorbed is about 4 mg/g chrysotile. The cross-sectional area per molecule of water calculated from this result is $9 \text{ \AA}^2$ which can be compared with the theoretical value $10.5 \text{ \AA}^2$ /molecule. (73), confirming the equal availability of surface to Kr and H_2O .

The desorption isotherm does not exactly follow the adsorption and hysteresis occurs. The presence of a hysteresis loop suggests that capillary condensation of the adsorbate occurs in chrysotile (73). The water vapour condenses inside the pores which does not desorb unless the relative vapour pressure falls below the value at which the water was adsorbed. The fact

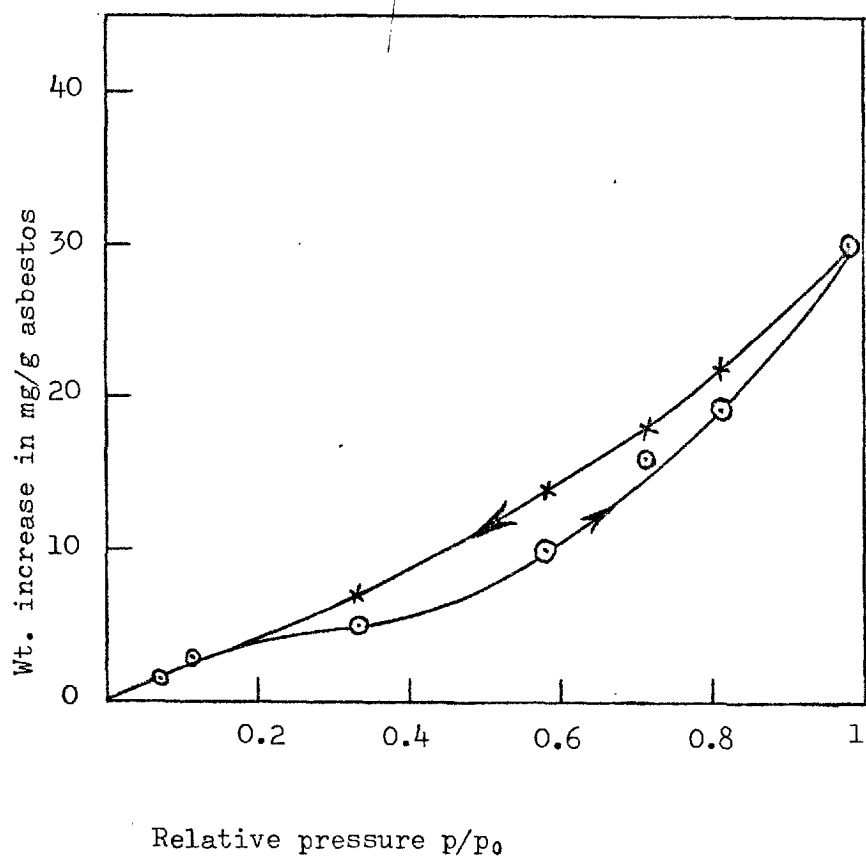


Fig. 10. Adsorption of water vapour on
chrysotile (Bells)

that the capillary condensation hysteresis loop does not close until a p/p_0 value of about 0.2 is reached indicates that some of the capillaries are of very small radius. On the basis of the Kelvin equation, condensation of water at $r.h. = 0.2$ would require capillaries of radius $\sim 7\text{\AA}$. At $r.h. \approx 0.98$ the amount of water vapour adsorbed was 30 mg/g.

Young and Healey (74, 75) studied the adsorption isotherm of nitrogen and water vapour on chrysotile (Johns Manville grade 7-R). But they did not observe any hysteresis in the isotherms; instead they found that the area available to water vapour was twice that available to nitrogen; on activation of chrysotile up to about 425°C , water and nitrogen areas agreed. Depending upon these experimental results and adsorption of other gases, they derived the conclusion that "chrysotile has an internal capillary structure, the capillaries appear to be within the individual fibres, the capillaries appear to be blocked in some manner with strongly sorbed water plugs, the water plugs are removed by activation at 425°C ".

However, the conclusion derived by Young and Healey from activation of chrysotile at 425°C may not be correct. Most naturally-occurring chrysotiles are contaminated with brucite and this substance decomposes at $350 - 400^\circ\text{C}$ to MgO and H_2O . Therefore the increase of available surface for water adsorption at 425° may be due to the formation of MgO which will provide more surface for adsorption of water vapour.

VI.3 Adsorption of benzene vapour on chrysotile

In order to make approximate measurements of the adsorption of benzene vapour (without the need to set up an elaborate vacuum apparatus) advantage

was taken of the characteristic u.v. absorption spectrum. Benzene in solution in iso-octane has a strong absorbance in the ultra-violet region.

Chrysotile (Bells) dried at 120°C and cooled in a desiccator was packed in a tube having openings at both the ends; nitrogen gas was bubbled through a mixture of 90% benzene and 10% liquid paraffin to avoid the distillation of benzene at saturated vapour pressure and to pick up a definite partial pressure of benzene vapour and was then passed through the bed of chrysotile for 2 hours at 22°C . After 2 h the chrysotile was shaken with 10 ml iso-octane to extract the adsorbed benzene. The clear liquid was separated off and the absorbance measured at 255 nm with pure iso-octane in the reference cell. The amount of benzene adsorbed on dry chrysotile was found to be 8.7 mg/g chrysotile at 22°C .

In another experiment the same amount of chrysotile was first saturated with water vapour by keeping it over a solution of 98% relative humidity for a few days. The chrysotile was then packed into the tube having openings at the both ends. Nitrogen was bubbled through a mixture of 90% benzene + 10% liquid paraffin having a drop of water to maintain the water vapour pressure and the gas was led into the bed of chrysotile for 2 h. The adsorbed benzene was then extracted with iso-octane and the absorbance measured as before. It was found that the amount of benzene adsorbed on the chrysotile already saturated with water was 3.5 mg/g chrysotile.

From the above experiments it is observed that the amount of benzene adsorbed on dry chrysotile was 8.7 mg/g chrysotile. This value corresponds to 2-3 monolayers of benzene over the available B.E.T. (Kr) surface area. This can be compared with the amount of water (near saturation) of 30 mg/g chrysotile. Relatively higher amount of water vapour adsorption must be

associated with the capillary condensation of water vapour on chrysotile.

The results of this experiment show that the presence of water vapour which has been shown to undergo capillary condensation on chrysotile, a hydrophilic solid, has some effect on the physical adsorption of benzene. Adsorption of benzene is reduced by 60% due to prior adsorption of water vapour on chrysotile. These results are comparable with the observations made in wetting experiment (cf. Ch X) which showed that clean chrysotile has a stronger work of adhesion to water than to benzene (since a drop of benzene does not make 'contact' with chrysotile in water).

CHAPTER VII

SYNTHESIS OF CHRYSOTILE

Various attempts have been made since the 1920's by different workers to synthesise chrysotile. The processes are mainly of academic interest, since the world's reserves of chrysotile are extensive; consequently intensive research into the production of chrysotile on a large scale has not been seriously taken up. The processes so far available produce fibres of very short length, some of which can only be seen with the aid of the electron microscope. Synthetic chrysotile when observed under high resolution electron microscope is found to have cone-in-cone shape structure (67,76). The various reported syntheses are summarised below in tabular form (table 18).

The diagram showing composition (in moles) of several phases in the system $\text{MgO} - \text{SiO}_2 - \text{H}_2\text{O}$ at $350-400^\circ\text{C}$ according to Bowen and Tuttle (5) is shown in the fig. 11. Sepiolite ($2 \text{MgO} \cdot 3\text{SiO}_2, 2 \text{H}_2\text{O}$) and palygorskite ($5\text{MgO}, 8 \text{SiO}_2, 9 \text{H}_2\text{O}$) do not form at this temperature. Wey and Siffert (55) have proved that the product of reaction of silicic acid (saturated solution) and $\text{Mg}(\text{OH})_2$ (saturated solution) at ordinary temperature is sepiolite. They could not detect any serpentine at ordinary temperature. Palygorskite which is a fibrous form of Mg-silicate is reported by some to be formed by alteration of amphiboles and pyroxenes in sediments; others believe it to be formed as a direct precipitate from highly concentrated solutions of magnesium, calcium and silicon in nature (81).

The "Bells" chrysotile used for most of the present project was proved to contain 5% free brucite as impurity. In order to obtain a pure sample of chrysotile for surface-chemical study, it was necessary to convert the excess brucite to chrysotile. For this purpose the method described by Bowen and

TABLE 18
Synthesis of chrysotile as obtained from
literature

Authors	Year	Starting materials	Conditions	Products	Remarks
Wells, F.G.(77)	1929	Magnesium carbonate rock or magnesium solutions with silicifying agent like Na-silicate and water	Temperature : 375°C Pressure : 219 atm Few days of heating	Serpentine (chrysotile)	No information about the size of the fibres
Syromyatnikov, F.V. (78)	1935	Magnesium hydroxide + silica + super heated water vapour	Temperature : 400°C Pressure : 260Kg/cm ² Heated in autoclave	Serpentine (chrysotile)	No information about the size of the fibres
Jander, W. and Wührer, J. (79)	1938	Magnesium oxide (heavy) + alkali free SiO ₂ (prepared by hydrolysis of SiCl ₄ and heated to 1200°C) + water Oxide mixture (MgO : SiO ₂) ratio, 2 : 1 Oxide mixture ratio, 1:1 Oxide mixture ratio, 3:2 Oxide mixture ratio, 3:4	Six-sided steel bomb with 10 mm walls lined with 1 mm silver Temperature : 325°C Time of heating : 85 h " " "	Serpentine (chrysotile) + brucite More talc + less serpentine Talc + serpentine with trace of brucite Talc + little serpentine	Starting with the oxide mixtures it seems impossible to get pure serpentine completely free from brucite

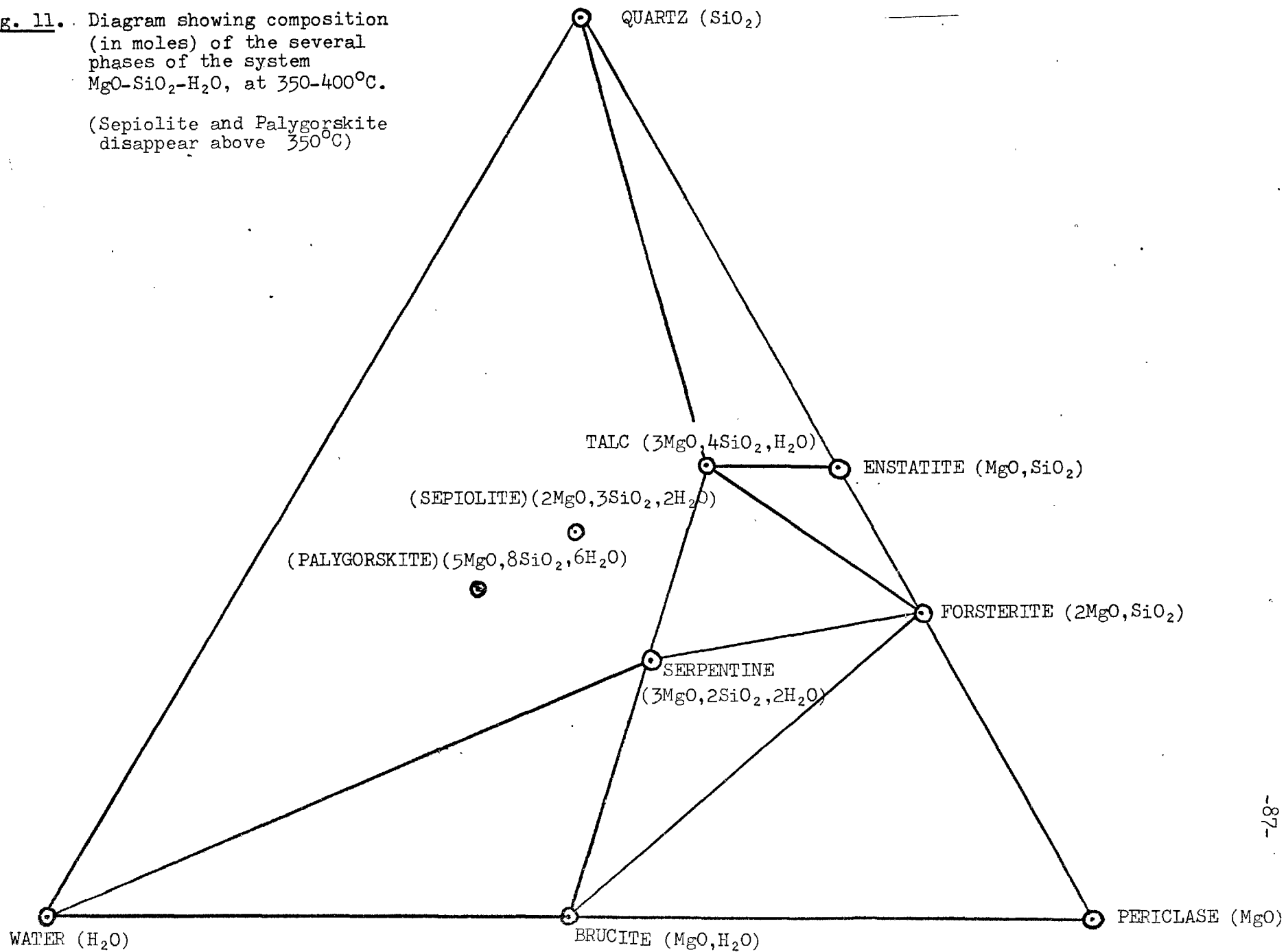
/Continued.....

TABLE 18/Continued.
Synthesis of chrysotile as obtained
from literature

Authors	Year	Starting materials	Conditions	Product	Remarks
Bowen, N.L. and Tuttle, O.F. (5)	1949	MgO ignited + precipitated SiO ₂ + water. Oxide mixture ratio, 3 : 2	Platinum lined pressu- re vessel Temperature : 500°+10 Pressure : 2000- 4000 lb/in ²	Serpentine (chrysotile)	Never forms good crystals, always appear as minute fibres
Yang, J.C. (80)	1961	MgO + bulky silicic acid. MgO/SiO ₂ ratio, 1.5, water solid ratio, 10	Temperature : 300 - 500°C Pressure : 1230 - 1800 psi Time : 5-7 days pH : 10.3 - 10.7 Mineralizer : 1-2% of F ⁻ as NH ₄ F	Serpentine (chrysotile)	Fibres fairly large (50 μm), but chrysotile produced always have some F ⁻ ions adsorbed on the surface.

Fig. 11. Diagram showing composition
(in moles) of the several
phases of the system
MgO-SiO₂-H₂O, at 350-400°C.

(Sepiolite and Palygorskite
disappear above 350°C)



Tuttle (5) was thought to be most suitable. As it is not certain that conversion would be 100% with exactly stoichiometric proportions, three samples were carefully prepared by mixing "Aerosil" silica with finely powdered chrysotile.

- (a) 2.0 g chrysotile with 0.072 g "Aerosil" which is in just stoichiometric proportion to convert the excess of brucite to chrysotile
- (b) 2.0 g chrysotile with 0.1 g "Aerosil" which will contain slightly excess of silica than the stoichiometric proportion for chrysotile
- (c) 2.0 g chrysotile with 0.144 g of "Aerosil" which is in stoichiometric proportion to convert the excess of brucite to talc.

All the above three mixtures were intimately mixed separately in a vibratory mixer with tungsten capsule. These samples were then separately heat-treated in gold-coated tubes in an autoclave at 390°C and 6000p.s.i. for 18 h. This operation of autoclaving was kindly carried out in the "Crystal Growth Laboratory" of the Department of Electrical Engineering at Imperial College, under the supervision of Dr. E.A.D. White.

The electrokinetic properties of these samples were determined to compare the results with those of the original chrysotile and of talc.

CHAPTER VIII
SURFACE CHARGE AND ELECTROKINETIC
POTENTIAL OF CHRYSOTILES

VIII.1 Surface charge

The sign of the surface charge of chrysotile was examined first in a Leeds-Northrup "Hydroscan Streaming Current Detector". This is a direct reading instrument, which is supposed to give the average surface charge of a suspension. A 0.5% suspension of the powdered sample was used. With chrysotile the "Hydroscan" reading was positive.

VIII.2 Electrokinetic potential (zeta-potential) of chrysotiles from different sources

The zeta-potentials of the different chrysotile samples were measured mainly by microelectrophoresis; for comparison an electro-osmotic measurement was also made on one sample.

VIII.2(a) Microelectrophoresis

The microelectrophoresis apparatus used in the experiment was the MK.II apparatus manufactured by Rank Bros., Bottisham, Cambridge. The particles in the suspension were observed by a microscope situated at the side of the apparatus in the same plane as the light source. The cell used was a flat one with a thin viewing window. Two palladium electrodes were immersed in the suspension at the two ends of the cell. A stabilised current circuit provided the potential gradient, and the cell was clamped in a thermostatic

bath. The correct alignment of the cell relative to the microscope was made so that the flat plane of the cell was positioned horizontally and perpendicular to the optical path of the microscope by adjustment made to screw clamps. Minute scratches on the inside and outside walls of the cell were used as focussing points of the microscope which was done by rotating the vernier adjustment on the microscope.

The position of the stationary level as obtained from Komagata's equation is given by $X = 0.194 D$ (for a cell whose length : thickness = 10), where X is the distance from the inner wall to the stationary level and D is the thickness of the cell, which was determined from a plot of the velocities of particles across the tube. The plot of velocity against the distance gave a parabola, as required by theory. Before the experiment the cell was cleaned with chromic acid and then with NaOH. It was then well washed with a continuous flow of distilled water. The suspension was run through the cell 2-3 times before finally filling up the cell for the experiment. The cell was allowed to stand in the thermostat until it attained a steady temperature (25°C) then the electric current was switched on. By alternating the direction of the current after each measurement the polarisation effect was minimised. The electrophoretic measurements were done on relatively large particles ($\sim 2 \mu\text{m}$ diameter). The time required to traverse one square in the eyepiece gaticule was recorded. Each mobility value used for zeta-potential calculation was the mean of 20 particle mobilities (10 in each direction) yielding a standard deviation of 5%.

VIII.2(b) Calculation of zeta-potential from mobility

The relationship between the electrophoretic mobility, defined as the

velocity of migration of the particle under unit potential gradient, and the zeta-potential which is the potential at the surface of shear between the charged surface and the electrolyte solution depends on the ionic strength, size and shape of the particles, viscosity and the dielectric constant of the liquid phase. Two equations have been derived to relate electrophoretic mobility to zeta-potential. The first of these, the Debye-Hückel equation, is known to be valid when the particle is small in size compared to the thickness of the electrical double layer. The Debye-Hückel equation may be expressed by:

$$U = \frac{\epsilon \zeta E}{6 \pi \eta}$$

where U is the electrophoretic mobility and η is the viscosity, E the potential gradient, ϵ the permittivity. The derivation of this equation involves Stokes's law for flow in a viscous medium and the application of the spherical condenser theory.

The second equation, derived by Smoluchowski, is applicable to a suspension containing particles large relative to the size of the double layer. This may be expressed by

$$U = \frac{\epsilon \zeta E}{4 \pi \eta}$$

Henry' (82) later formulated a more general equation applicable over a range of κa , (where κa is the ratio of radius of curvature to double layer thickness) which converges to the Smoluchowski and Hückel equations at high and low value of κa respectively. The derivation of the equation based on similar assumptions to Smoluchowski in that :

- (1) The hydrodynamic equations of motion in the viscous bulk medium were applicable in double layer .
- (2) The applied field was considered to be simply superimposed on the double layer force field.
- (3) A velocity gradient surrounds the particle such that the velocity of the fluid at the particle surface is equal to that of the particle.

Henry expressed his equation in the form of

$$U = \frac{\epsilon E \zeta}{6 \pi \eta} \left[1 + \frac{(\kappa a)^2}{16} - \frac{5(\kappa a)^3}{48} - \frac{(\kappa a)^4}{96} + \frac{(\kappa a)^5}{96} \right]$$

This expression reduces to:

$$U = \frac{\epsilon E \zeta}{6 \pi \eta} f(\kappa a)$$

where values of $f(\kappa a)$ have been tabulated for a wide range of κa values.

For large values of κa , $f(\kappa a)$ becomes 1.5 and the equation reduces to the Smoluchowski form. For small values of κa , $f(\kappa a)$ becomes 1 and the equation approximates to Hückel form.

From theoretical studies it has been shown that the Smoluchowski and Hückel equations are invalid at intermediate values of κa ($0.2 < \kappa a < 50$). A more sophisticated model has been proposed independently by Overbeek (83) and Booth (84). They applied corrections due to retardation and relaxation effect which can occur due to internal forces which develop during the particle motion in the applied external field. The equation arrived at is given by:

$$U = \frac{E \zeta}{6 \pi \eta} \left[f(\kappa a) - \frac{Z^2 e \zeta}{kT} f_3(\kappa a) - \frac{P_+ + P_-}{2e} \cdot \frac{e kT}{6 \pi \eta e} \left(\frac{e \zeta}{kT} \right)^2 f_4(\kappa a) \right]$$

The first term is Henry's term but the subsequent terms account for relaxation forces and involve the frictional constants of the anion and cation represented by P_+ and P_- respectively.

The correction term is small for low values of zeta-potential (<25 mV) and is considered to be unimportant in the region where κa has very high values. Unfortunately, the more sophisticated theories of electrophoresis apply only to insulating, spherical particles. Chrysotile particles are rod-shaped and may have appreciable surface conductivity (see below). Consequently zeta cannot be obtained accurately from the mobility except in the limit $\kappa a \gg 1$, when the shape of the particle becomes unimportant. Therefore for the present experimental purpose nominal zeta-potential values were calculated from Smoluchowski's equation which for water at 25°C reduces to

$$\zeta = 12.83 U$$

U being equal to v/E , where v is the particle velocity in μm per sec. and E is the applied field strength in volt per cm.

VIII.3 The zeta-potentials of chrysotiles from different sources as measured by microelectrophoresis

Electrophoretic measurement was done on chrysotile (Bells) with various

electrolytes. The results are shown below.

Results

1. Chrysotile (Bells) suspended freshly in water, $\zeta = +44.8$ mV
2. Leached in water (5 days, final pH = 10.2), $\zeta = +44.9$ mV
3. Leached in 0.1 N HCl for 48 h then washed, $\zeta = -13.4$ mV

The above results show that mild leaching in water (probably in presence of excess brucite) does not alter the surface at all. But drastic leaching by acid changes ζ from positive to negative. This is obviously due to leaching out of not only excess brucite but also the $\text{Mg}(\text{OH})_2$ layer from the surface of the chrysotile rolls thus exposing the silica layer. (Silica always shows a negative zeta-potential in the media of $\text{pH} > 2.0$)

VIII.3(a) Zeta-potential of chrysotile in different electrolytes

The zeta-potential of chrysotile (Bells) was determined in a number of different electrolyte solutions of concentration M/1000. The electrolytes chosen were NaOH, MgCl_2 and Na_2SiO_3 , as OH^- , Mg^{2+} and SiO_4^{4-} may be expected to be the "potential determining" ions for a magnesium silicate.

Chrysotile in :

- 1 mM NaOH, $\zeta = +16.8$ mV
- 1 mM MgCl_2 , $\zeta = +44.1$ mV
- 1 mM Na_2SiO_3 , $\zeta = -16.0$ mV

The trend of values is as expected on the assumption that Mg^{2+} and SiO_4^{4-} are strongly adsorbed (potential determining). The lack of change on adding

MgCl_2 reflects the fact that the chrysotile sample contains a definite excess of $\text{Mg}(\text{OH})_2$ already corresponding to $\text{pH} \sim 10$. Assuming a solubility product of $\text{Mg}(\text{OH})_2$ as $10^{-11.15}$, $\text{pH} 10$ gives $[\text{Mg}^{2+}] = 10^{-3.15}$. The z.p.c. of $\text{Mg}(\text{OH})_2$ has been given as 12.5 (85). On adding NaOH to $\text{pH} \sim 11$, $[\text{Mg}^{2+}]$ is repressed to $10^{-5.15}$ so ζ is lowered, though not to zero. It is clear that the brucite layer is covered by silicate when sodium silicate is added and thereby shows negative ζ due to the adsorbed silicate ions. It cannot be assumed, however, that a reversible, stoichiometric equilibrium between chrysotile and the aqueous medium is established within practical times at ordinary temperature.

VIII.3(b) Zeta-potentials of different chrysotile

These samples were kindly supplied by Dr. A.A. Hodgson. "Woodsreef" (a) (reported zeta-potential - 0.5 mV by streaming potential). This variety of chrysotile showed variable mobility under the electric field. Most of the particles showed positive zeta-potentials but some showing negative values could also be seen. The highest value of ζ measured was + 17.5 mV for some particles and lowest + 7.8 mV. Particles showing negative ζ gave a value around - 12 mV. From an approximate estimation it was concluded that at least 10% of the particles have negative charge. Woodsreef (b) (reported $\zeta = -1.7$ mV). Electrophoresis of these fibres was practically negligible. Most of the particles settled down without showing any movement at all. Like the previous one, this variety of fibres showed variable mobility under the electric field. The particles which moved with positive zeta-potential had upto +7.6 mV and lowest +6.0 mV. But the particles which had negative values differed very much, the highest negative value -11.4 mV and the smallest measured value -4.0 mV.

From approximate estimation it was judged that the ratio of positive : negative = 1 : 1.

"Zidani chrysotile" (reported $\zeta = 0.85$ mV). This chrysotile also did not show uniformity in the mobility of individual particles, and electrophoresis was slight. Among the moving particles at least 30% had negative sign; the ranges of values actually measured were + 7.5 to +13.6 & -7.8 to -10.9 mV

"Shabani chrysotile" (reported $\zeta = + 8.1$ mV). This chrysotile forms a relatively stable suspension. The particles are all positively charged; no trace of negative particles was observed. They showed no variation of mobility under the electric field, all giving $\zeta = + 22.1$ mV.

"Cassiar". The particles are all positively charged; no variation in their mobility was observed. $\zeta = + 34.3$ mV.

It is assumed that the reason for some of the chrysotile showing both positive and negative charge and also variable mobilities under electric field is associated with the geological history of these chrysotiles. It has been shown that drastic leaching of the chrysotile surface exposes the silica layer, thus converting the surface to negative. These chrysotiles are from sedimentary deposits, having been transported by weathering from the original rocks. They must have undergone leaching whereby the exposed surfaces have become negative but the other fibrils inside the bundles still maintaining their surface "brucite" layer retain a positive charge. Probably many fibrils are partially leached and thus chemically heterogeneous. This state is not revealed by electrophoresis (which gives only an average surface charge). Two micro-techniques are known for investigating heterogeneity of reaction of minerals - (a) the colloidal deposition technique of Thiessen (86), (e.g. with colloidal gold) which reveals small areas of positive or negative charge on crystallites, such as clay platelets of sub-micron size, and (b) autoradiography, after adsorption of reagents

labelled with isotopes such as ^3H or ^{14}C which are weak beta-emitters. For application to chrysotile fibrils either technique would require access to electron microscope.

VIII.3(c) Zeta-potentials of synthetic chrysotile

Pure synthetic chrysotile sample no. 3566-131-4, kindly supplied by Johns-Manville Asbestos Co. (through Dr. S. Holmes, Secretary of the Asbestosis Research Council) was used for this determination of zeta-potential. This particular variety of chrysotile on suspending in pure water of pH 6.0 (0.1 g of solid in 5 ml distilled water) gave pH 8.2 which on standing for a day came to a stable pH 8.5. The zeta-potential of this particular chrysotile was determined at different pH values ranging from 3 to 11 by adjusting the pH with HCl and NaOH. However, owing to the buffering action of chrysotile itself, the pH never remained constant; pH of the same solutions were measured after 1 day and all the tests which started at $\text{pH} < 9.3$ were found to have changed. The zeta-potentials of these samples were determined after 1 day and were found also changed somewhat. The results of pH measurement and zeta-potential are shown in table 19.

It is evident from the table that although the pH changed very much in the acid region (no doubt because of dissolution of $\text{Mg}(\text{OH})_2$ from chrysotile), the change in the value of zeta-potential was virtually negligible. Furthermore, since the pH does not remain constant with time, the study of zeta-potential with time is not simple to interpret.

TABLE 19

Initial		After 1 day	
pH	ζ (mV)	pH	ζ (mV)
11.1	+10.9	11.1	+10.9
10.2	+13.8	10.2	+13.8
9.3	+25.6	9.3	+26
8.2	+25.8	8.5	+25
7.0	+27.2	8.3	+27.3
6.0	+23.6	7.9	+24.3
5.1	+24.7	7.7	+26.2
4.2	+22.0	7.4	+23.2
3.2	+39.0(?)	7.3	+21.6

The first point to be noticed is that none of the high positive values found with Bells chrysotile (+ 44 mV) were observed at any pH with the synthetic chrysotile. It seems possible, therefore, that the Bells fibres are (partly or wholly) coated with brucite. The zeta-potential of a sample of mineral brucite (purity not known) was determined in distilled water adjusted to pH 10 and was found to be + 33 mV.

Secondly, it is clear that if leaching reactions did not take place, zeta of pure chrysotile would increase (in + ve value) as pH was decreased as was indeed, seen for the range 11-7 - because of increasing dissociation of the oxide as a base. But, because chrysotile cannot persist unchanged in even weakly acidic media, the observed value in such suspensions is a transient value which depends on the external leaching which the specimen

has received.

A sample of synthetic chrysotile was leached with 0.1 N HCl for 48 h and then washed carefully with water and the zeta-potential measured. The value was -46.5 mV, which shows that drastic leaching changes the surface from positive to negative just like the Bells chrysotile. The final residue is substantially silica.

The zeta-potential of the chrysotile (Bells) samples which were heat-treated under pressure with definite amounts of "Aerosil" (silica) to convert the excess brucite to chrysotile or talc were also determined in distilled water (pH initially ~ 6).

The sample to which a stoichiometric proportion of silica was added to (ideally) convert excess of brucite just to chrysotile gave a zeta value + 21.15 mV which is to be compared with the ζ of chrysotile, Bells (+ 44.8 mV) and that of pure synthetic chrysotile (+ 25.8). The value is obviously close to that of synthetic chrysotile showing that most of the excess brucite had been converted to chrysotile. This result confirms that the higher ζ value for chrysotile (Bells) must be due to the presence of excess of brucite since the stability data show that no other phase (e.g. talc) could be formed in this experiment.

The sample which had a slight excess of silica above that required for converting the excess brucite to chrysotile gave a ζ value + 28.1 mV, which is perhaps not significantly different from the result for the stoichiometric sample.

The third sample, to which a stoichiometric proportion of silica was added to convert the excess of brucite to talc (so that the product should be chrysotile + 5% talc) gave a ζ value + 20.7 mV. For a comparison, the zeta-potential of "pure" talc was determined. Powdered talc was scraped freshly from a lump of the mineral rock and suspended in water. The zeta value was found to be + 23.1 mV which is not very different from +20.7 mV, the value obtained for a mixture of pure chrysotile and talc.

Huber and Weigh (87) determined the zeta-potential of talc at various pH values and found + 40 mV at pH 3 and about - 30 mV at pH 10.

It is perhaps surprising that talc a layer structure of the type ABA in which the Mg^{2+} is "sandwiched" between the siloxane sheets, should behave more like chrysotile than like silica. The ideal talc structure would be electrostatically uncharged; unlike micas and clays, there would be no net charge on the sandwich and therefore zero zeta-potential (neither should an unbroken siloxane net work present silicic acid groups). However broken edges of talc platelets probably present sites where the brucite layer can ionise, and as seen previously, this is strongly basic (positively charged at all ordinary pH values).

The experiments reported above show that it is very difficult (if not impossible) to study surface properties of chrysotile particles of exactly stoichiometric surface composition. The common mineral forms of chrysotile carry an excess of brucite, which slowly dissolves but bestows a high positive zeta-potential while it is present. At a certain stage of leaching excess $Mg(OH)_2$ may have been dissolved, but then hydrolytic decomposition of the chrysotile follows, eventually leaving hydrated silica gel. The two processes may be going on simultaneously at different places on the same microscopic particle, but the measured zeta-potential is some kind

average value for the whole particle.

It seems possible, however, that since the thermodynamic activity of Mg^{2+} in chrysotile is considerably lower than in $\text{Mg}(\text{OH})_2$ (cf. the work of Way and Siffert (55)), the kinetics of surface leaching might reveal a transition period. In order to check this idea, two experiments were carried out to study the change of ζ with time during leaching in buffer solutions. In the actual experiments very small amounts of powdered chrysotile were suspended in buffer solutions and the zeta-potential measured by electrophoresis, keeping the suspension in the electrophoretic cell. The pH of the suspension was measured before and after the experiment. In one experiment ammonium acetate buffer (10^{-3} M) was used at a pH 6.8 and synthetic chrysotile was suspended in it. The initial zeta value was found to be 29.3 and after 48 h the value changed only to 25.0 and the pH changed to 6.9. This shows that the leaching at pH 6.8 is very slow indeed.

In another experiment, chrysotile was suspended in approximately 10^{-3} M acetic acid at pH 4 and the zeta-potential measured with time. Results of this experiment are shown in fig. 12. It is evident that the zeta values of synthetic chrysotile drop smoothly with time and goes to negative values after about 65 h. when the surface layer has been leached out. But in the case of natural chrysotile (Bells), the value of the zeta-potential drops sharply in the first 10 h and then it follows a smooth decrease finally going to the negative side after about 60 h. The pH of the suspension of synthetic chrysotile went from 4.0 to 4.3 after 72 h and that of Bells went from 4 to 4.5. From the results of these experiments it appears that the surface of Bells chrysotile is more reactive than the surface of synthetic chrysotile. It could be associated with the excess brucite present in Bells chrysotile.

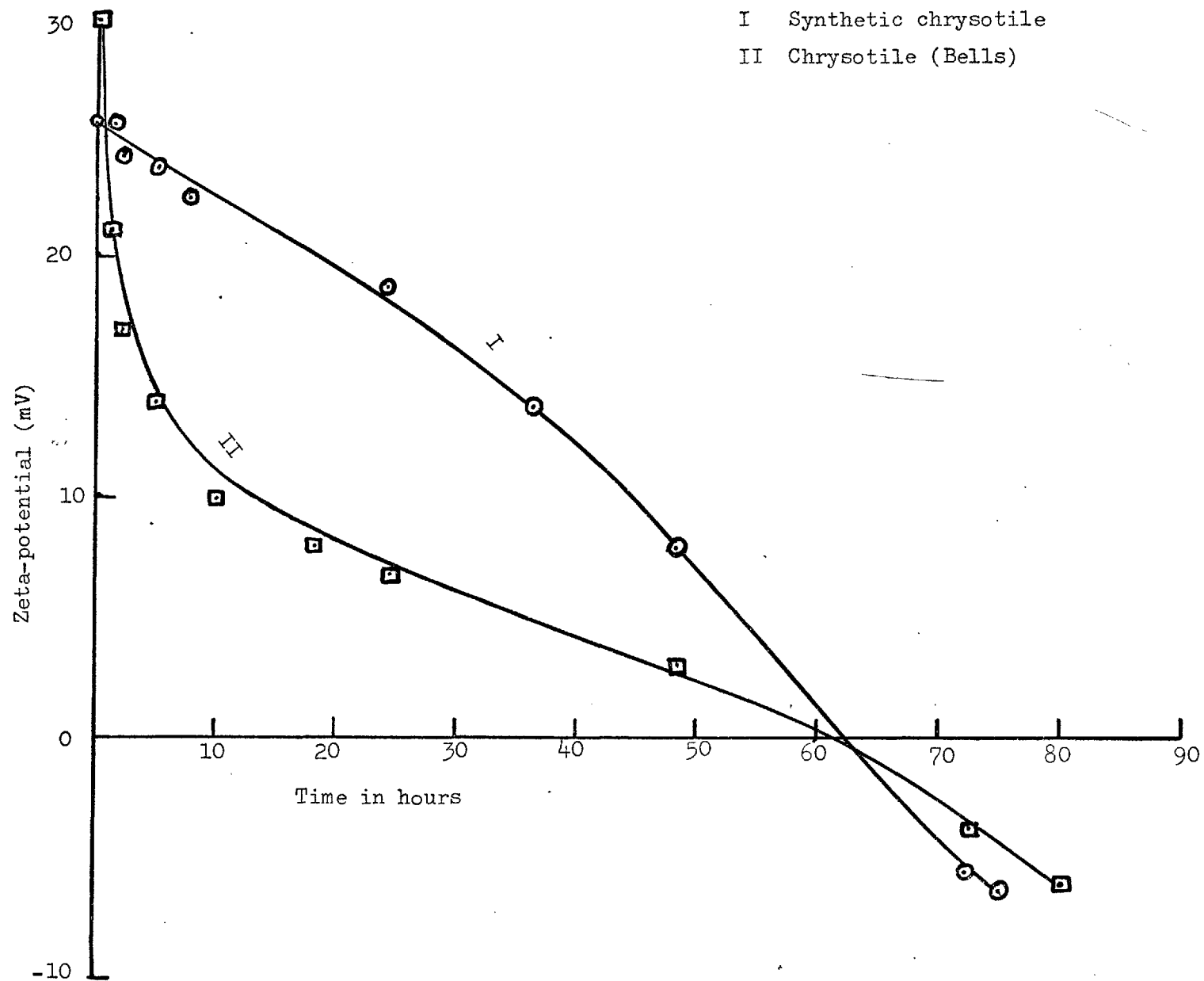


Fig. 12. Zeta-potential of chrysotile with time of leaching in dilute acetic acid (pH 4)

VIII.4 Determination of the zeta-potential of chrysotile by electro-osmosis

Electro-osmosis is perfectly equivalent to streaming potential from the phenomenological point of view. In streaming potential measurements the solution is forced through a packed bed and the steady e.m.f. produced is measured, whereas in electro-osmosis a steady current is passed through a similar cell and the resulting flow of the liquid measured. Current is passed through the cell by applying a relatively high voltage (about 50 V) and the steady current (of order of 1 mA) is measured, together with the rate of flow of the liquid through the plug. The plug is made of mineral powder.

VIII.4(a) Apparatus

The apparatus used in this experiment was that described by Redinha and Kitchener (88). It consists of an U-tube of about 12 mm internal diameter fitted with a coarse sintered glass plate in the stem to support the filter-cake. The two ends of the U-tube are fitted with three-way stop-cocks and small funnels to contain reserve solution for adjustments. The U-tube is connected to the electrode vessel and capillaries on each side through the three-way stop-cock. The electrodes are made of palladium foil. The capillaries are made from approximately 12 cm lengths of precision-bore tubing of 1 mm internal diameter. The capillary arms are attached to a horizontal metal support. The current is provided by a stabilised d.c. power supply capable of providing several different voltages up to 100 V at, say, 10 mA. A good quality multi-range d.c. microammeter giving a full scale of $50 \mu\text{A}$ on its sensitive range was used for measuring the

current. The U-tube containing the mineral powder bed was kept immersed in a water bath of constant temperature.

VIII.4(b) Procedure

The plug was prepared by filtration of a slurry of chrysotile (Bells) in water, avoiding air bubbles. The capillary tubes were properly cleaned to ensure free movement of the liquid, and the electrodes were pre-charged with hydrogen by electrolysis in dilute sulphuric acid.

The final assembly of the apparatus was carried out by fitting together the three sections, each already filled with the solution to be used in the test. Care was taken to avoid any leakage of air through the stop-cock or elsewhere. The cell was then mounted on its stand in the water-bath with the capillaries horizontal. The positions of the menisci were then set near the middle of the scales by manipulating the three-way stop-cocks.

Sufficient time was allowed for the cell to take up the temperature of the bath. The stop-cocks were then opened to the capillaries and levelling adjustment made until the menisci remained stationary. The power supply was then switched on and the movement of the menisci timed - e.g. they were read alternately at 30 sec. intervals for 3 minutes and menisci timed in the opposite direction.

With chrysotile as the bed in the U-tube this experiment was performed with pure water, NaOH (10^{-3} M) and $MgCl_2$ (10^{-3} M).

VIII.4.(c) Calculations

The classical relationship for electro-osmosis through a porous plug is given (in e.s.u.) as

$$V = \frac{I D \zeta}{4 \pi K \eta}$$

where V is the rate of volume flow (from one side of the plug to the other) I is the electric current, D , η and K are the dielectric constant, viscosity and electrical conductivity of the solution respectively, and ζ is the zeta-potential of the solid/liquid interface of the material in the plug.

The above equation is recognised to be subject to a number of assumptions, namely (a) the pores should be large compared to the thickness of double layer, (b) the solid, an insulator, and (c) surface conductivity negligible. In addition D and η are taken as the values for pure water (e.g. for 25°C, 78.5 and 0.89 centipoise respectively). Introducing conversion factors for electrical units gives the working equation in c.g.s. units (for 25°C)

$$v(\text{cm}^3 \text{ per sec.}) = \frac{7.8 \times 10^{-9} I(\text{mA}) \zeta(\text{mV})}{K (\text{ohm}^{-1} \text{ cm}^{-1})}$$

VIII.4(d) Results

The results obtained with chrysotile (Bells) in water and different electrolyte solutions are shown below.

In water , ζ = + 9.0 mV

In NaOH (10^{-3} M), ζ = + 6.6 mV

In MgCl_2 (10^{-3} M), ζ = + 7.9 mV

Comparison of the results obtained by micro electrophoresis and electro-osmosis shows that the values obtained in the electro-osmotic method are much lower than those obtained by micro electrophoresis. Moreover, the results reported by Dr. A.A. Hodgson (89), who used the method of streaming potential, are also much lower than those obtained by micro-electrophoresis. Since the electro-osmotic measurement has only been done on Bells chrysotile it is not possible to compare the values obtained by electro-osmosis and streaming potential. Since electro-osmosis and streaming potential measurements are the same from the phenomenological point of view the results obtained by the two methods should be comparable.

The most plausible explanation for the electro-osmotic values being lower is that the assumptions (a) and (c) listed above may not be valid for a plug of chrysotile. In particular, the surface conductivity may be high. The elementary theory used in packed-bed methods assumes that surface conductivity is negligible; more sophisticated treatments for packed beds have not proved satisfactory (90).

VIII.5 Surface conductivity of chrysotile (Bells)

A test was made to roughly measure the surface conductivity of chrysotile. In a conductivity cell (type CB/01) the conductance of 0.01M KCl solution and distilled water were separately determined. Then two different pastes of chrysotile in the KCl solution and distilled water were prepared

and their 'conductances' determined separately. The conductances obtained are given below.

0.01 M KCl	0.1 milli ohm ⁻¹
" + 10% chrysotile	0.15 "
distilled water	0.3 μ ohm ⁻¹
" + 10% chrysotile	0.8 "

In the case of KCl, the conductance increased by about 50% on adding the chrysotile while with water the increase was more than 100%. These results prove that the surface conductivity of chrysotile is quite high and cannot be neglected. The surface conductance doubtless arises from the dissociation of Mg^{2+} and OH^- ions from the minerals, not merely as a diffuse double layer, but also as an appreciable concentration of dissolved electrolyte, as detected in the leaching experiments. Therefore it can be concluded that because of the high surface conductivity the streaming potential or electro-osmotic methods will give erroneous (too low) results with these minerals. In addition to this source of error, it is known that electrokinetic effects are anomalous in porous bodies (or packed beds) if the effective "thickness" of electrical double layer is comparable with the diameter of the pores. The effects are thereby reduced because of overlapping of the double layers from the adjacent particles. The problems of treating such systems are discussed in a theoretical paper by Churaev and Deryagin (91).

VIII.6 Discussion

Martinez and Zucker (92) studied the zeta-potential of chrysotile by the streaming potential method and reported a value of + 93 mV for chrysotile. This value is much higher than the ones found in the present experiment.

Since it has been shown in the present chapter that the methods of streaming potential and electro-osmosis are subject to errors this value can hardly be considered as reliable, but tend generally to give values lower than the true one. However, in a private communication Dr. Martinez revealed that the values reported in that paper cannot be relied upon. It seems possible that the chrysotile sample used by Martinez and Zucker may have contained other impurities.

Gracheva and Epinateva (93) determined the electrokinetic properties of chrysotile from different U.S.S.R. deposits and found that the chrysotiles differed in their zeta-values. They established a relation between the zeta-potential and filtration capability of the suspension and also discussed the possibility of regulating the filtration capability of asbestos suspension by regulating the electrokinetic properties of asbestos. Filtration aids of asbestos suspensions can be substances which are capable of overcharging the surface of asbestos to zeta-potential zero.

Naumann and Drescher (94), from a study of the surface charge of chrysotile, observed that the electrophoretic mobility of chrysotile suspension is increased by the addition of inorganic salts like aluminium chloride, thorium chloride etc. that aid the dispersion of the fibres. These salts at low pH form positively charged hydrolysis products which adsorb on the surface of chrysotile thereby increasing the effective surface charge.

It is impossible to correlate the zeta-potential value and the complicated surface chemical reactions that may take place inside the lungs leading to asbestosis. All that can be said is that because of the positive surface charge (basic character) free anions, such as Cl^- and CO_3^{2-}

will be attached as counterions and amphoteric materials such as amino acids and proteins are likely to be adsorbed by ionic forces through any anionic groups in their molecular structures. Many biological macromolecules carry a negative charge at physiological pH, and these would tend to be deposited by electrostatic attraction on to chrysotile particles.

CHAPTER IX

AMPHIBOLES

(Leaching, Zeta-potential and Dispersion)

Amphiboles

For the present work, the amphiboles of interest are amosite and crocidolite. As has been mentioned previously, the crystal chemistry of these amphiboles is well established but not much is known about their surface properties and their reactivity in aqueous media. In this part of the work the chemical reactivity of the amphiboles in aqueous media has been studied by both static and dynamic leaching. Furthermore, although Spiel and Leinweber (27) reported that the surface of amphibole is polar, the electrokinetic charge being negative, no definite information is available as to the value of the zeta-potential. The surface charge of amosite and crocidolite and the zeta-potential have been determined by micro electrophoresis.

IX.1 Preparation of samples

Amosite and crocidolite were kindly supplied by Dr. A.A. Hodgson of Cape Asbestos Co. in the form of solid rocks (amosite from Penge and crocidolite from Koegas). Portions of these were first crushed into small pieces in a hydraulic press and fibre bundles were then collected by hand picking. In the case of crocidolite, those small pieces were taken in a big polythene vessel with a lid into which a stirrer, having strong rubber blades, was rotated at high speed. Fluffy fibres came off the hard pieces of fibre bundles. These were then separated by hand picking for experimental purposes. In the case

of amosite this process was less successful. The small pieces of rock were therefore rubbed with a strong brass brush when the fibres came off in fluffy form.

IX.2 Leaching of amosite and crocidolite

Amosite is a silicate of Mg and Fe whereas crocidolite is a Na-ferroso-ferric silicate. A typical variety of amosite has the idealised chemical formula $1.5 \text{ MgO}, 5.5 \text{ FeO}, 8 \text{ SiO}_2, \text{H}_2\text{O}$ and a typical idealised analysis of crocidolite is $\text{Na}_2\text{O}, 3 \text{ FeO}, \text{Fe}_2\text{O}_3, 8 \text{ SiO}_2, \text{H}_2\text{O}$. (Actual specimens depart appreciably from the ideal formula mainly by isomorphous substitution of cations.) From the chemical formulae of the two it is evident that amosite may give out Mg, Fe and SiO_2 into solution whereas crocidolite may release mainly Na, Fe, SiO_2 in solution. Therefore an important step in the study of leaching kinetics will be to establish the method of determination of the different constituents.

It has been found that Mg can be determined by atomic absorption spectrophotometry in presence of 1500 p.p.m. of Sr without any interference from Fe, Na or SiO_2 . Na can be determined in atomic absorption spectrophotometer in presence of less than 1 p.p.m. SiO_2 without any interference from the other constituents. SiO_2 can be determined by colorimetry (blue silico-molybdate method) without any interference from other ions present.

But in the case of the determination of iron by atomic absorption spectroscopy, serious interference was observed on the absorbance of iron due to the presence of silica. However, this interference could be removed by the addition of $50 \mu\text{g/ml}$ Ca. Change of acidity was found to give

erratic results. The same absorbance was observed with iron whether present as ferrous or ferric state. The best working condition was found to be in presence of 1 M HCl and 50 p.p.m. Ca solution and Fe within the range 1 - 10 p.p.m.

IX.2(a) Static leaching of amosite

In each of several separate polypropylene tubes 0.2 g of amosite was kept suspended in 40 ml water. The polypropylene tubes were continuously shaken at 37°C. Two tubes were taken out every day to determine pH of the suspension, the amount of Mg, silica (monomeric and total) and Fe released. The experiment was performed in duplicate and the mean results of the two sets of experiments are shown in the table below.

TABLE 20

Leaching of amosite at 37°C (0.5% suspensions)

Time of leaching (days)	pH	[Mg ²⁺] (μmoles/l)	[Fe ²⁺] (μmoles/l)	Monomeric [SiO ₂] (μmoles/l)	Total [SiO ₂] (μ moles /l)
1	6.7	9.0	<18*	1.8	20
2	6.8	9.0	<18	1.6	20
3	6.8	10.2	18	1.8	21
4	6.7	10.2	18	1.6	17
5	6.8	10.2	18	1.6	17
6	6.8	11.1	18	1.3	18
7	6.8	11.1	18	1.3	20
8	6.8	11.1	18	1.6	20
9	6.8	11.1	18	1.6	20
12	6.8	11.1	18	1.6	20
15	6.8	11.0	18	1.6	20
18	6.8	11.2	18	1.6	20

* i.e. 1 p.p.m.

IX.2(b) Static leaching of crocidolite

0.2 g samples were suspended in 40 ml water in a series of separate polypropylene tubes. The tubes were kept shaken in a waterbath at 37°C. Two tubes were taken out every day and the amount of Na, Mg, Fe and SiO₂ released determined. Results, which represent the mean of the two readings, are shown in the table below.

TABLE 21

Leaching of crocidolite at 37°C.

(The following results correspond to 0.5% suspensions)

Leaching time (days)	pH	[Na ⁺] (μ moles/l)	[Mg ²⁺] (μ moles/l)	[Fe ²⁺] (μ moles/l)	[SiO ₂] (monomeric) (μ moles/l)	Total [SiO ₂] (μ moles/l)
1	8.9	69	7	<18	3.3	43
2	9.0	78	7	"	3.3	43
3	9.0	95	9	"	3.6	39
4	9.1	104	10	"	3.6	38
5	9.1	104	11	"	3.3	45
6	9.1	104	11	"	3.3	43
7	9.0	104	12	"	3.6	43
8	9.1	104	12	"	3.3	40
9	9.1	104	12	"	3.6	38
10	9.0	104	12	"	3.6	43
13	9.0	104	12	"	3.6	40
18	9.0	104	12	"	3.6	40
25	9.0	104	12	"	3.6	40

IX.2(c) Dynamic leaching of amosite and crocidolite

1 g samples of amosite and crocidolite (teased fibres) were kept in separate glass cells fitted with glass filter at one end.

Through the fibres in the cells water was pumped continuously, with the help of a mini-pump (description - Ch.II.6) at a rate of 75 ml/24 h. Water coming through was collected every 24 h and analysed for Na, Mg and Fe. The results are shown in table 22.

TABLE 22

Dynamic leaching of amosite and
crocidolite at 37°C.

Time of leaching (days)	AMOSITE		CROCIDOLITE		
	pH	[Mg ²⁺] (μ moles)	pH	[Na ⁺] (μ moles)	[Mg ²⁺] (μ moles)
1	6.5	0.61	7.5	11.7	1.2
2	6.5	0.50	7.2	1.9	0.7
3	6.6	0.40	7.0	1.9	0.7
4	6.7	0.30	7.0	1.8	0.6
5	6.6	0.23	7.1	1.6	0.6
6	6.2	0.23	6.9	0.9	0.5
7	6.3	0.30	6.6	0.6	0.5
8	6.2	0.23	6.5	0.6	0.4
9	6.1	0.23	6.6	0.6	0.4
10	6.2	0.23	6.6	"	0.4
11	6.2	0.23	6.5	"	0.3
12	6.1	0.23	6.5	"	0.3
13	6.1	0.23	6.6	"	0.3
14	6.1	0.23	6.5	"	0.2
15	6.1	0.15	6.6	"	0.2
16	6.1	0.15	6.6	"	0.2
17	6.1	0.15	6.6	"	0.2
18	6.1	0.15	6.6	"	0.2
19	6.1	0.15	6.6	"	0.2

The results given (amount of Mg²⁺ and Na⁺) correspond to 75 ml of solution. The amount of iron released in both the cases was less than 1 p.p.m. (the

limit detectable in the atomic absorption spectrometer).

IX.2(d) Presence of ankerite in crocidolite

It has been suggested (private communication from Dr. A.A. Hodgson) that crocidolite is sometimes contaminated with ankerite ($\text{Ca}(\text{Mg}, \text{Fe}^{2+}, \text{Mn})(\text{CO}_3)_2$). From the crystal-chemical point of view, ankerite is similar to a dolomite in which Mg^{2+} ions are partly substituted by Fe^{2+} (and sometimes Mn^{2+}). The proportion of Fe^{2+} is variable. Since it is mainly a carbonate of Ca and Mg, simple acid-tests were performed to prove its presence or absence.

(i) In a clean test tube small amount of conc. HCl was taken and a few fibres were introduced into the test-tube. As soon as the fibres came in contact with the acid, effervescence was seen coming off the fibre bundles.

(ii) In a microscopic slide a few fibrils of crocidolite were taken and a drop of conc. HCl was added and the fibres covered with a slide cover and immediately examined under microscope. This test also showed the evolution of effervescence from the fibres.

(iii) In a clean large test tube a few bundles of crocidolite fibres were taken and a smaller test tube containing clear solution of $\text{Ca}(\text{OH})_2$ was inserted. Conc. HCl was added through the side of the large test tube and stoppered immediately. After sometime the smaller test tube was taken out and $\text{Ca}(\text{OH})_2$ solution was found to be milky, confirming the formation of CO_2 .

The above tests showed that crocidolite used in the present experiments is associated with some carbonate impurity which can probably be ankerite. This fact must therefore be taken into account in interpreting the results

of leaching tests.

In the static leaching of crocidolite, distilled water at pH ~ 5.8 was used; the tubes were then sealed and further introduction of CO₂ from the air was avoided. The water initially must have been saturated with CO₂ (which dissociates into HCO₃⁻ and CO₃²⁻ ions). If ankerite (Ca(Mg Fe²⁺, Mn) (CO₃)₂) is present with crocidolite, the system in water will contain Na⁺, Mg²⁺, Ca²⁺, H⁺, OH⁻, HCO₃⁻, CO₃²⁻ (as well as H₄SiO₄ from the silicate). At pH = 9, H₄SiO₄ may be taken as undissociated and a charge balance equation will be

$$[H^+] + [Na^+] + 2[Mg^{2+}] + 2[Ca^{2+}] = [OH^-] + 2[CO_3^{2-}] + [HCO_3^-] \quad (1)$$

From the experimental results at equilibrium, $[H^+] = 10^{-9}$, $[Na^+] = 10.4 \times 10^{-5}$, $[Mg^{2+}] = 1.2 \times 10^{-5}$, $[OH^-] = 10^{-5}$ moles/l. Hence from eqn. (1)

$$2[Ca^{2+}] = 2[CO_3^{2-}] + [HCO_3^-] - 11.8 \times 10^{-5} \quad (2)$$

For the dissociation of the bicarbonate ion

$$\frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = 10^{-10.3} \quad (3)$$

At pH = 9

$$\begin{aligned} [HCO_3^-] &= 10^{1.3} \times [CO_3^{2-}] \\ &= 20 \times [CO_3^{2-}] \end{aligned} \quad (4)$$

From eqn. (2) and (4)

$$[Ca^{2+}] = \frac{22[CO_3^{2-}] - 11.8 \times 10^{-5}}{2}$$

In absence of other information about ankerite, assuming the solubility product of ankerite as that of dolomite ($K_s = 2 \times 10^{-17}$) (34),

$$[Ca^{2+}] = \frac{1.65 \times 10^{-12}}{[CO_3^{2-}]^2} \quad (5)$$

From equations(4) and (5)

$$[CO_3^{2-}] = 5.5 \times 10^{-5}$$

$$[Ca^{2+}] = 5.5 \times 10^{-4}$$

$$[HCO_3^-] = 11 \times 10^{-4}$$

These values, when introduced into charge balance equation (1), exactly satisfy both the sides. However, to give a quantitative estimation of the amount of ankerite dissolved from crocidolite from the above approximate calculations may lead to an erroneous result because the true solubility product of ankerite is not known.

IX.2(e) Discussion

From the above results of static leaching it is evident that both amosite and crocidolite are relatively inert to the action of water at 37°C . The amount of silica released is relatively lower than the total number of cations (Fe^{2+} and Mg^{2+} in case of amosite and Fe^{2+} , Mg^{2+} , Na^+ in case of crocidolite). The amount of silica detected in one case of amosite is $1.6 \mu\text{ moles/l}$ (0.1 p.p.m.) and $3.6 \mu\text{ moles/l}$ (0.22 p.p.m.) which are much lower than the actual solubility of silica (amorphous silica 100 p.p.m. and quartz 10 p.p.m. at 37°C). The very low solubility of silica can be explained as due to the presence of Mg^{2+} . (It has been discussed in Chapter II.8, in presence of Mg^{2+} the solubility of SiO_2 is extremely depressed.) The same explanation probably holds good here in case of the amphiboles - because of the presence of Mg^{2+} and Fe^{2+} ions.

The amount of iron that has been released is probably entirely in the form of Fe^{2+} , because $\text{Fe}(\text{OH})_3$ is exceedingly insoluble at near-neutral pH. Thus for $\text{Fe}(\text{OH})_2$, $K_S = 10^{-15.32}$ and $\text{pH} = 6.8$, therefore $[\text{Fe}^{2+}] = 0.12$ moles/litre. But for $\text{Fe}(\text{OH})_3$, $K_S = 10^{-35.96}$ (95) at $\text{pH} = 6.8$, $[\text{Fe}^{3+}] = 10^{-14.38}$ moles/l. This shows that the $[\text{Fe}^{3+}]$ is so small that there is no chance of getting any detectable Fe^{3+} in solution whereas $[\text{Fe}^{2+}]$ can be quite considerable at this pH without precipitation of ferrous hydroxide. Thus the small amount of iron that has been found in solution is presumed to be entirely in the form of Fe^{2+} .

The observed rise of pH on leaching of crocidolite could be ascribed to the presence of ankerite (or dolomite) in the sample. A saturated solution of dolomite in water ($\text{pH} \approx 5.9$) gives $\text{pH} = 9.9$.

In both the static and dynamic processes it is observed that the amount of Mg released from crocidolite is more than that released from amosite despite the fact that it contains only one fifth as much Mg per Si_8O_{22} unit. The difference could arise from the simultaneous release of Na^+ in crocidolite; in amosite ($\text{Fe}_5\text{Mg}_2\text{Si}_8\text{O}_{22}(\text{OH})_2$) the Fe-cations are not detectably leached by neutral solutions and therefore probably obstruct movement of Mg^{2+} from between the silicate ribbons. (There are no water filled channels in amphiboles, as there are in zeolites.) But in the case of crocidolite the release of Na^+ facilitates the movement of Mg^{2+} between the ribbons and thereby increases the dissolution of Mg^{2+} . But it has been proved that crocidolite is contaminated with some ankerite (or dolomite), therefore, the measured Mg^{2+} found in solution which came from crocidolite is uncertain and only the Na^+ and silica can be unambiguously ascribed to the crocidolite.

In flow-through leaching, the pH of the solution from crocidolite never went above 7.5 whereas in the static leaching process the pH was always 9.0. This is comparable with the difference in pH found in the case of static and dynamic leaching of chrysotile (cf. Ch. II).

In this present dynamic leaching it was not possible to leach out all the Mg and Na from amosite and crocidolite even after 19 days. After a few days both Na and Mg were coming off at a steady low rate. After 10 days in the flowing test, the total amount of Na released was about 5 times that in the static tests and the amount of Mg about 10 times. The observations would be consistent with hydrolytic leaching, in which H^+ displaces Na^+ and Mg^{2+} , with the rate controlled by diffusion through the pseudomorph of silica-gel (or iron silicate in case of amosite).

IX.3 Surface charge and zeta-potential of amosite and crocidolite

The sign of the surface charge on amosite and crocidolite was first examined in a Leeds-Northrup "Hydroscan Streaming Current Detector" (c.f. Chapter VIII for description of "Hydroscan"). A 0.5% suspension of the powdered samples was used. With both amosite and crocidolite the "Hydroscan" reading was negative. This is in agreement with Spiel and Leinweber (27).

The zeta-potentials of amosite and crocidolite were determined in the "Particle Micro electrophoresis Apparatus Mark II". A very dilute suspension of the ground asbestos in distilled water (pH $\sim$ 6.0) was placed in the cell, voltage was applied across two palladium electrodes and the mobility of the particles was measured under the microscope with repeated forward and reverse potentials, care being taken to focus on the "stationary layer". The results obtained with amosite and different varieties of crocidolite are tabulated below

	amosite	crocidolite		
	Penge	Koegas	Cape asbestos (Koegas)	Transvaal
ζ (mV)	-35.3	-31.7	-45.4	-60.6

The differences in the zeta-potential of different samples of crocidolite may be associated with the formation of crocidolite in nature; variations of composition are the rule with such silicates. The negative zeta-potential

arises of course, from release of small quantity of cations (Mg^{2+} or Na^+ + Mg^{2+}) into the solution in the vicinity of the surface of the silicate, forming a diffuse electrical double layer. The surface cannot be regarded as at equilibrium with the medium because as shown by the leaching experiments, the silicates can be continuously hydrolysed by washing. A lower pH would of course, accelerate this process and ultimately the zeta-potential would drift towards the low negative value characteristic of silica (the ionisation of which depends on the dissociation of - SiOH groups, rather than cation release from the interstices of silicate lattice).

IX.4 Dispersion of amosite and crocidolite with surface-active agents (cf. Chapter IV)

"Quix" (alkyl aryl sulphonate), EDTA and "Calgon" (sodium hexametaphosphate) were tried as dispersing agents on both amosite and crocidolite. A 1% solution of "Quix" was added to 0.1 g of each and kept separately in 30 ml water. The suspensions were allowed to stand overnight but no spontaneous dispersion was observed. But when the suspensions were subsequently stirred with magnetic stirrers extensive dispersion of the fibres was observed in both the cases. When the concentration of "Quix" was increased (2%) in another set (keeping all other conditions the same), the fibres were dispersed with less stirring. The same effect was observed on increasing the time of standing.

Similar tests were tried with a 2% solution of alkaline EDTA which would be expected to complex the metal cations but this reagent proved practically ineffective.

Finally a 1% solution of Calgon (sodium hexametaphosphate) was also tried. Allowing the suspensions to stand overnight and then stirring with a magnetic stirrer produced considerable dispersion. Varying the concentration of Calgon, time of standing; the same conclusion was arrived at, as in the case of dispersion with "Quix".

The dispersing power of the agents tried came in the order
Quix > Calgon > EDTA.

As Calgon and EDTA are effective complexing agents for Mg^{2+} etc. (whereas alkyl aryl sulphonate is not) they could be expected to have pronounced solvent action at grain boundaries of the silicate crystallites. Calgon is a well-known dispersant for clay minerals (which are aluminosilicates). Nevertheless, they were markedly less effective in producing dispersion of amphiboles than was the surface-active agent. The action of the surfactant may therefore be ascribed to the "Rehbinder effect" - the reagent creeping along grain boundaries and weakening the particle/particle adhesion by reducing the interfacial energy (64, 65).

CHAPTER XADSORPTION OF ORGANIC MATERIALS (AMINO ACIDS
PROTEINS, LIPIDS) ON THE ASBESTOS SURFACE

This project started with the plausible hypothesis that asbestos particles getting into the lungs may possibly be involved in some surface chemical reactions with the materials present in human blood and body fluid. It is therefore essential that the surface interaction of some of the common organic materials be studied. Some of the typical organic substances present in blood and body fluid such as amino acids, proteins and lipids have been chosen for adsorption studies on the three different asbestos surfaces.

X.1 Adsorption of amino acids

Two amino acids, present in human blood, and having pK in the acid and alkaline ranges, were chosen for this experiment. Glutamic acid, $\text{HOOC} \cdot \text{CH}(\text{NH}_2) \text{CH}_2 \cdot \text{COOH}$, which is acidic, having an iso-electric point at pH 3.22, is present in human blood to the extent of 3.41 mg/100 ml (66). Lysine $\text{HOOC} \cdot \text{CH}(\text{NH}_2)(\text{CH}_2)_3 \cdot \text{CH}_2 \text{NH}_2$ is basic and the iso-electric point is 9.59; it is present in blood to the extent of 2.95 mg/100ml (66).

X.1(a) Estimation of amino acids

The colorimetric method described by Satake and others(119) was used for the estimation of amino acids. In this method 1 ml of the

sample solution was mixed with 1 ml of 4% NaHCO_3 solution and 1 ml of 0.1% 2:4:6-trinitrobenzene sulphonic acid and kept in a dark place at 40° for 2 h. The resulting orange colour solution (3ml) was added with a definite amount of N HCl (1 ml) and the optical density of the acidified solution was measured at 340 nm in a Perkin-Elmer spectrophotometer. Distilled water, instead of sample solution, was used as a blank.

X.1(b) Experimental conditions

A preliminary run was carried out with chrysotile and glutamic acid to determine the time required for the adsorption to come to equilibrium. It was found that 96 h is a quite suitable length of time for the adsorption to come to equilibrium. Therefore in the subsequent adsorption experiments 96 h was allowed as the time for equilibrium adsorption.

0.2 g of asbestos was kept suspended in amino acid solutions (40ml) of different concentration in separate polypropylene tubes. The tubes were kept shaken at 37°C for 96 h; they were then centrifuged and the amount of amino acid left in the supernatant solution was determined. The results are shown in both tabular form and graphical form.

TABLE 23Adsorption of glutamic acid and lysine on chrysotile(specific surface area (Kr) = $12.2 \text{ m}^2 \text{ g}^{-1}$)

GLUTAMIC ACID		LYSINE	
Adsorption ($\mu \text{ moles/m}^2$)	Equilibrium concentration ($\mu \text{ moles/l}$)	Adsorption ($\mu \text{ moles/m}^2$)	Equilibrium concentration ($\mu \text{ moles/l}$)
0.3	20	0.3	25
0.6	50	0.6	60
1.0	125	1.4	110
1.2	175	1.6	170
1.6	200	2.7	182
1.6	250	3.0	245
2.0	300	4.0	280
2.2	400	4.2	400

TABLE 24Adsorption of glutamic acid and lysine on amosite(specific surface area (Kr) = $0.72 \text{ m}^2 \text{ g}^{-1}$)

GLUTAMIC ACID		LYSINE	
Adsorption ($\mu \text{ mole/m}^2$)	Equilibrium concentration ($\mu \text{ mole/l}$)	Adsorption ($\mu \text{ mole/m}^2$)	Equilibrium concentration ($\mu \text{ mole/l}$)
7	50	13	37
14	100	20	95
20	125	45	185
34	200	54	232
41	250	66	280
69	450	77	410

TABLE 25:

Adsorption of glutamic acid and lysine on crocidolite
 (specific surface area (K_r) = $1.28 \text{ m}^2 \text{ g}^{-1}$)

GLUTAMIC ACID		LYSINE	
Adsorption ($\mu \text{ mole/m}^2$)	Equilibrium concentration ($\mu \text{ mole/l}$)	Adsorption ($\mu \text{ mole/m}^2$)	Equilibrium concentration ($\mu \text{ mole/l}$)
7	50	6	50
10	125	12	95
16	200	26	182
19	250	32	225
25	387	35	292
35	550	44	405

The above results are all means of two different series of experiments.

The isotherms obtained by plotting the adsorption of different amino acids on the different asbestoses are shown in the figures 13, 14, 15, 16, 17 and 18. It is evident that the adsorption isotherm of glutamic acid and lysine on chrysotile is approximately of Langmuir type which follows the equation

$$x = \frac{abc}{1 + ac}$$

where x is the amount adsorbed, c is the equilibrium concentration, a is a constant and ' b ' is the limiting saturation value. In order to obtain the value of ' b ' the above equation can be written as

$$\frac{1}{x} = \frac{1}{ab} + \frac{1}{c} + \frac{1}{b}$$

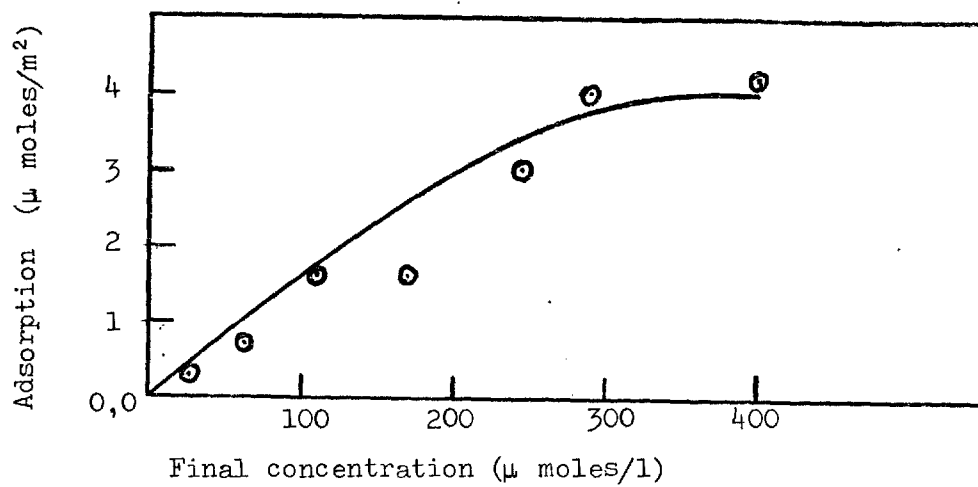


Fig. 13. Adsorption of lysine on chrysotile

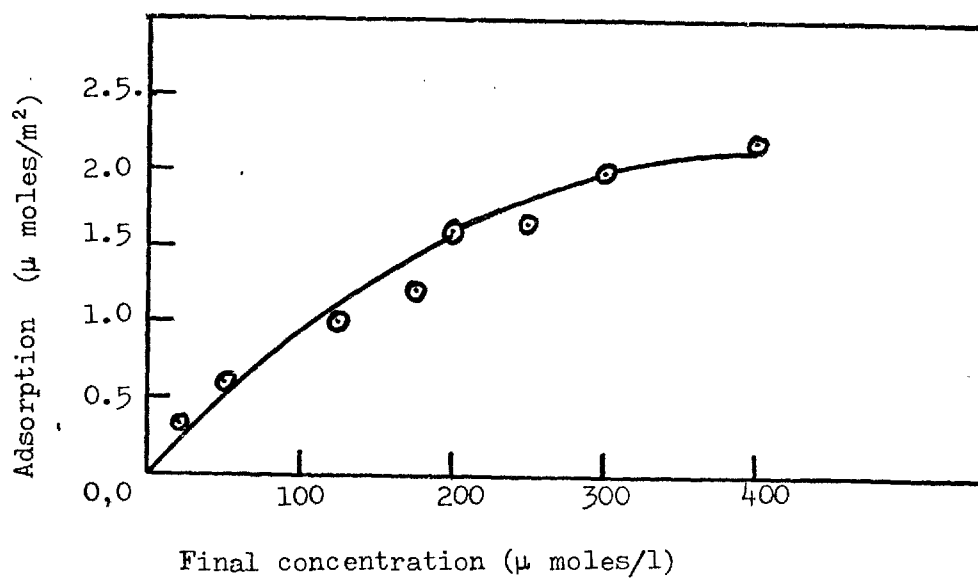


Fig. 14 Adsorption of glutamic acid on chrysotile

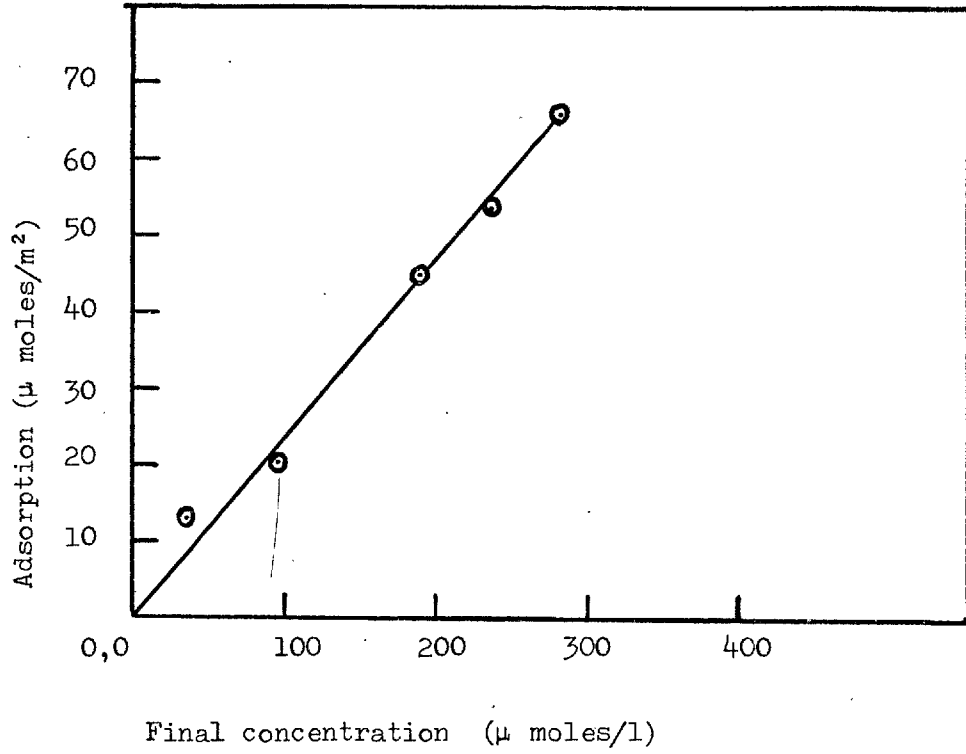


Fig. 15. Adsorption of lysine on amosite

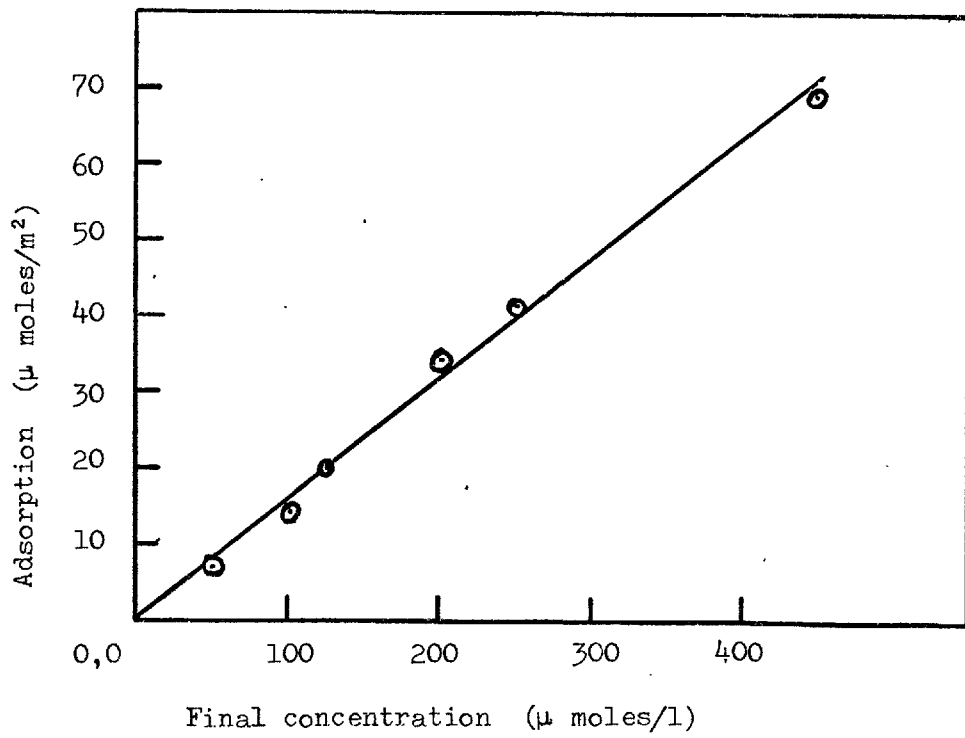


Fig. 16. Adsorption of glutamic acid on amosite

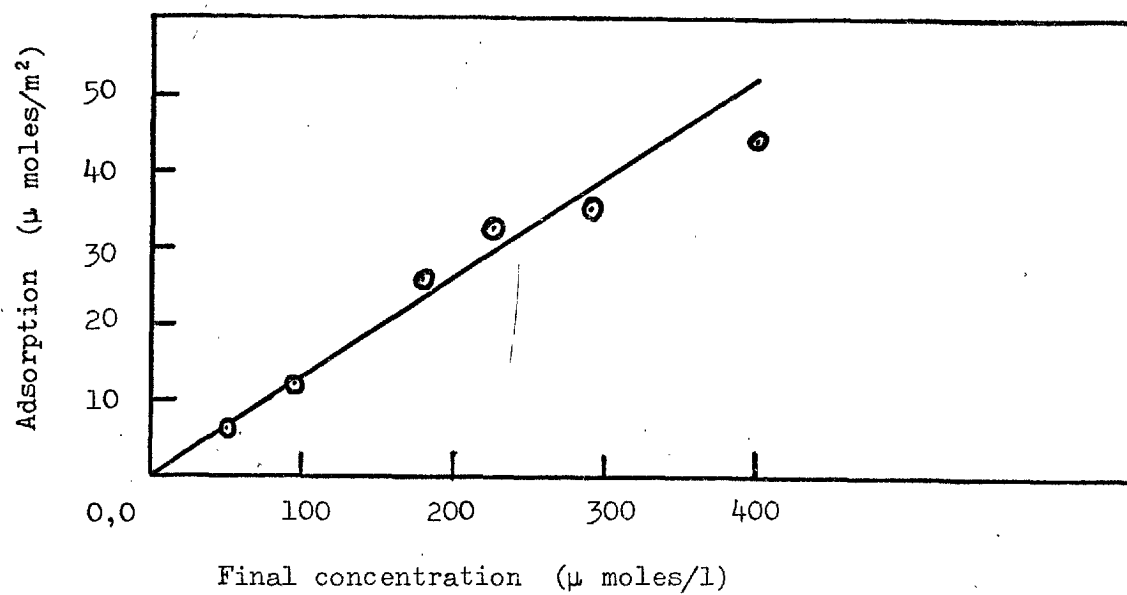


Fig. 17. Adsorption of lysine on crocidolite

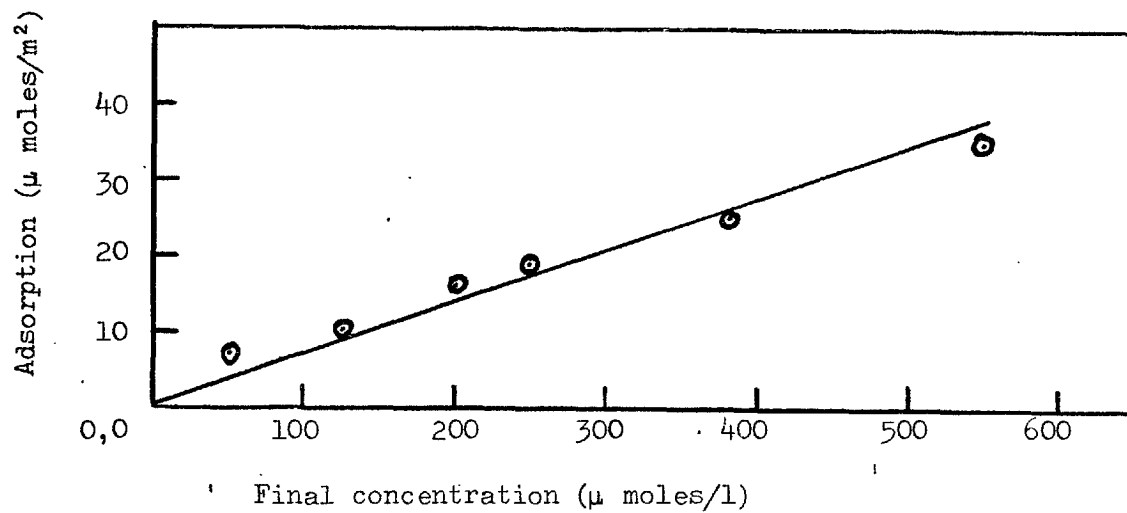


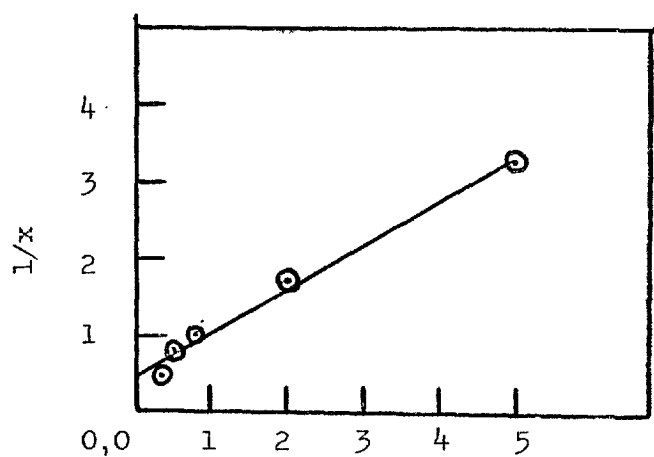
Fig. 18. Adsorption of glutamic acid on crocidolite

Thus plotting $1/x$ against $1/c$ a straight should be obtained, the intercept of which would give the value of $1/b$. However, the plot of $1/x$ against $1/c$ in case of glutamic acid adsorption on chrysotile is shown in figure 19. The value of 'b' obtained from the straight line is 2.2; that is, the saturation limit for this particular adsorption is 2.2.

Considering the cross-section of an amino acid molecule as $35 \text{ \AA}^2$ (obtained from model) for a monolayer coverage the value works out to be $4 \mu \text{ moles/m}^2$. In case of adsorption of glutamic acid on chrysotile the adsorption density is $2.4 \mu \text{ moles/m}^2$ and in case of lysine on chrysotile it is about $4 \mu \text{ moles/m}^2$. The value with glutamic acid seems to be slightly lower than theoretical value but not greatly different. Therefore it can be concluded that the adsorption of glutamic acid and lysine on chrysotile is a case of monlayer formation over the same surface as occupied by Kr atoms.

However, in the case of the amphiboles (both amosite and crocidolite) the isotherms obtained are entirely different. They are more nearly straight lines which means the adsorption never came to saturation in the concentration range studied. To seek an explanation to this anomalous behaviour of the amphiboles the following experiment was performed.

In separate bottles chrysotile, amosite and crocidolite were kept suspended in concentrated solution of glutamic acid and in a separate set of bottles the same amounts of the asbestoses were separately suspended in pure water. The bottles were kept continuously shaken. After a few hours it was observed that both amosite and crocidolite in the amino acid solutions were more dispersed than they were in water. But in the case of chrysotile the dispersion in amino acid solution was not more than that in pure water.



$$\frac{1}{c} \times 10^2$$

x = Amount adsorbed

c = Final concentration

Fig. 19 Adsorption of glutamic acid on chrysotile

The result of this experiment shows that in amino acid solutions amosite and crocidolite are continuously dispersed, exposing more and more of the new surfaces over which further adsorption occurred. Thus adsorption increased linearly and never came to equilibrium in the time allowed. This again explains the higher adsorption density in the case of amosite and crocidolite. The adsorption values shown in the table were calculated assuming the surface areas of amosite and crocidolite as $0.72 \text{ m}^2/\text{g}$ and $1.28 \text{ m}^2/\text{g}$ respectively, these being the values obtained by B.E.T. method with krypton on undispersed fibres. But when the fibres are dispersed in amino acid solution the available surface for adsorption must be much higher than the values obtained by the B.E.T. method and the actual adsorption density should be much lower than the value calculated and may possibly correspond to a monolayer formation.

X.2(a) Infra-red studies of asbestos

These experiments were intended to see if there is any surface interactions between the asbestos and the molecules of amino acids. Infra-red spectra were obtained on a Grubb-Parsons "Spectromaster" double beam infra-red spectrophotometer using the KBr disc method. 1 mg of asbestos was mixed with 1 g of very pure KBr and ground in a tungsten carbide mill. 400 mg of the powdered mixture was made into a disc. The spectra of pure asbestoses were first obtained using pure KBr disc as reference. The asbestoses which had adsorbed amino acids were then washed several times with water and their spectra were taken making the disc in the same method as with the pure asbestoses. The main peaks obtained with the different samples are shown in a separate table (wave length in μm , s = strong, m = medium, w = weak) and the spectra obtained with the different types of asbestoses are shown in the figures 20, 21, 22 and 23.

TABLE 26

The main peaks (in μm) obtained in the infra-red spectra of different asbestoses.

Chrysotile pure	Chrysotile + glutamic acid	Amosite pure	Amosite + glutamic acid	Crocidolite pure	Crocidolite + glutamic acid
6.1(w)	6.1(w)	6.1(w)	6.1(w)	6.1(w)	6.1(w)
-	6.5(w)	-	6.5(w)	-	6.5(w)
-	-	-	-	8.6(m)	8.6(m)
-	-	8.8(m)	8.8(m)	-	-
-	-	9.1(s)	9.1(s)	9.1(s)	9.1(s)
9.2(s)	9.2(s)	-	-	-	-
9.8(s)	9.8(s)	-	-	-	-
-	-	10.0(s)	10.0(s)	-	-
-	-	-	-	10.1(s)	10.1(s)
10.5(s)	10.5(s)	-	-	-	-
-	-	11.1(m)	11.1(m)	11.1(m)	11.1(m)
-	-	12.8(m)	12.8(m)	-	-
-	-	-	-	13.0(m)	13.0(m)
-	-	-	-	13.7(w)	13.7(w)
-	-	14.1(m)	14.1(m)	-	-
-	-	-	-	14.5(m)	14.5(m)
-	-	-	-	15.2(w)	15.2(w)
-	-	15.5(m)	15.5(m)	-	-
-	-	-	-	15.9(m)	15.9(m)
16.5(s)	16.5(s)	-	-	-	-
-	-	-	-	18.5(m)	18.5(m)
-	-	19.6(s)	19.6(s)	-	-
-	-	-	-	20.0(m)	20.0(m)
20.75(s)	20.75(s)	-	-	-	-
-	-	21.9(s)	21.9(s)	-	-
-	-	-	-	22.7(s)	22.7(s)
23.0(s)	-	-	-	-	-
-	-	24.0(s)	24.0(s)	-	-

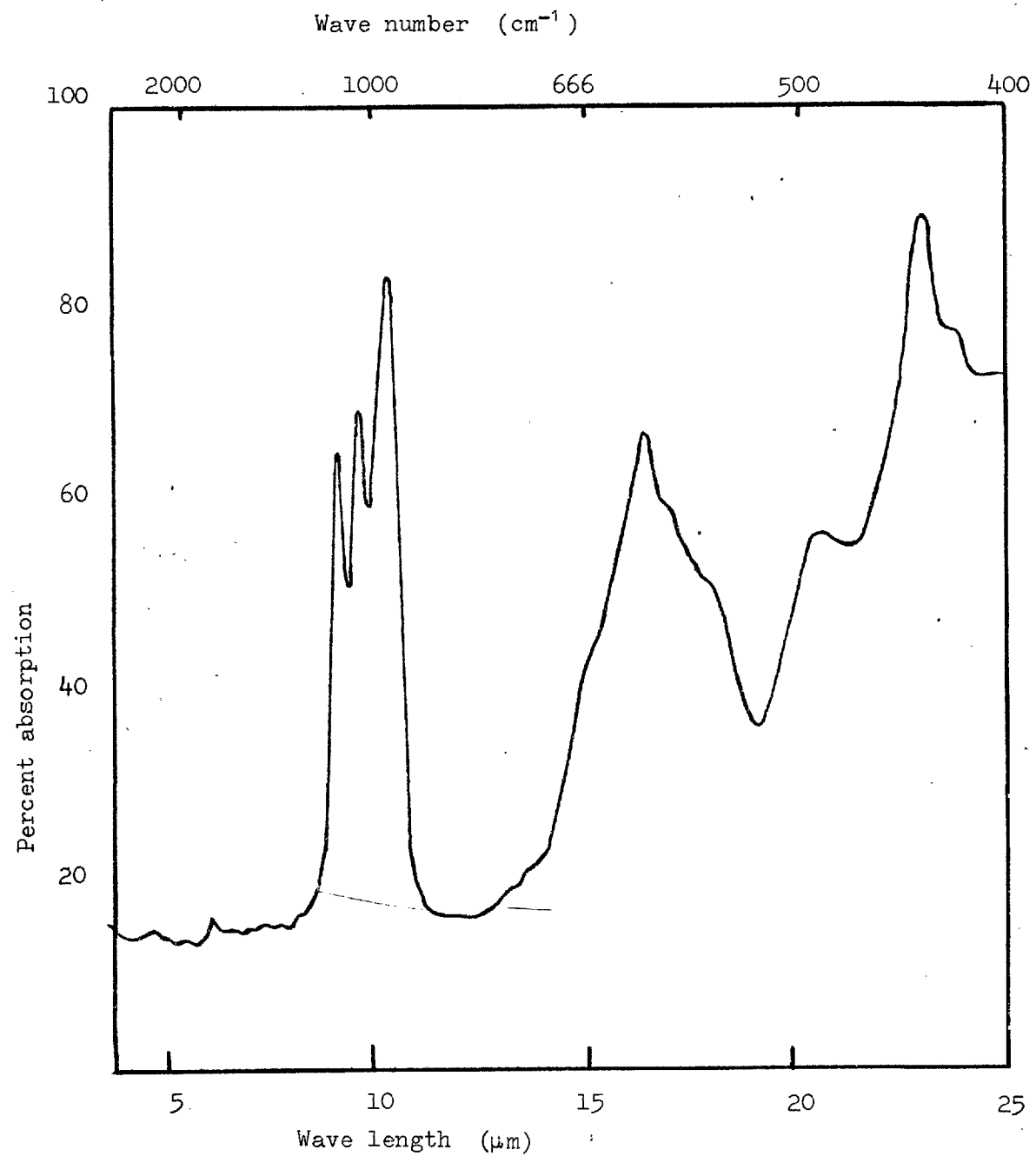


Fig. 20. Infra-red spectrum
of chrysotile.

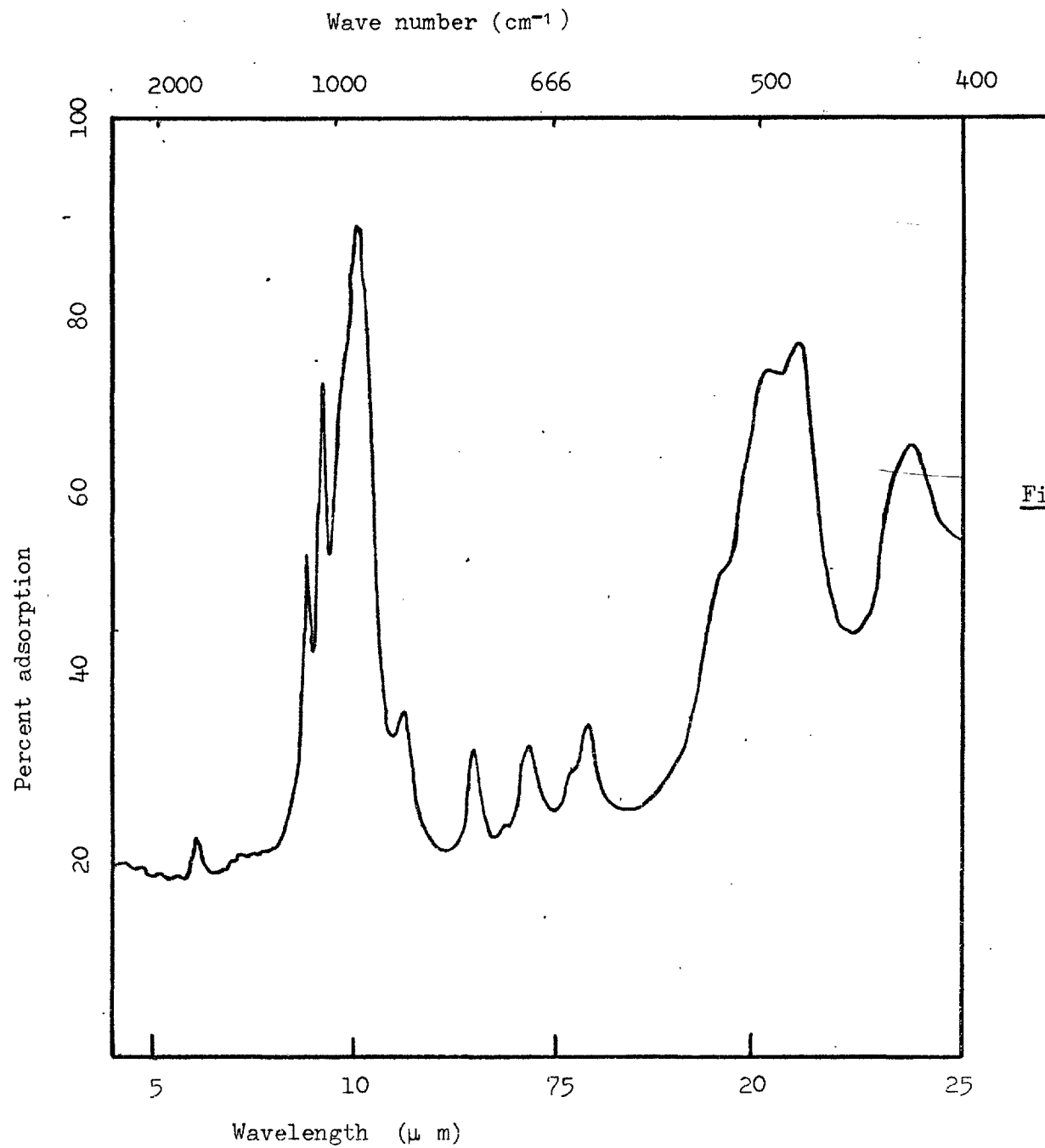


Fig. 21 Infra-red spectrum
of amosite

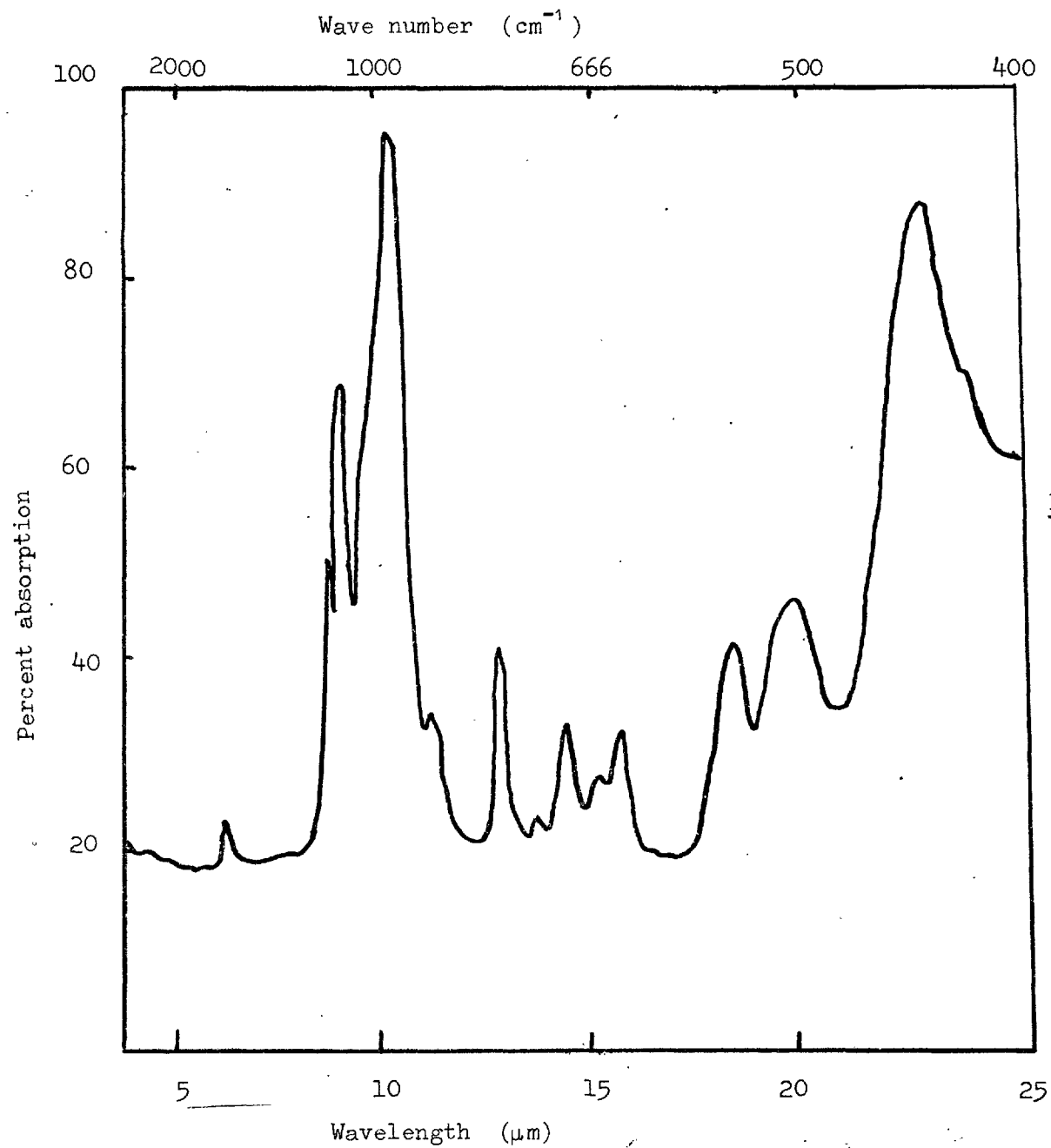


Fig. 22. Infra-red spectrum
of crocidolite

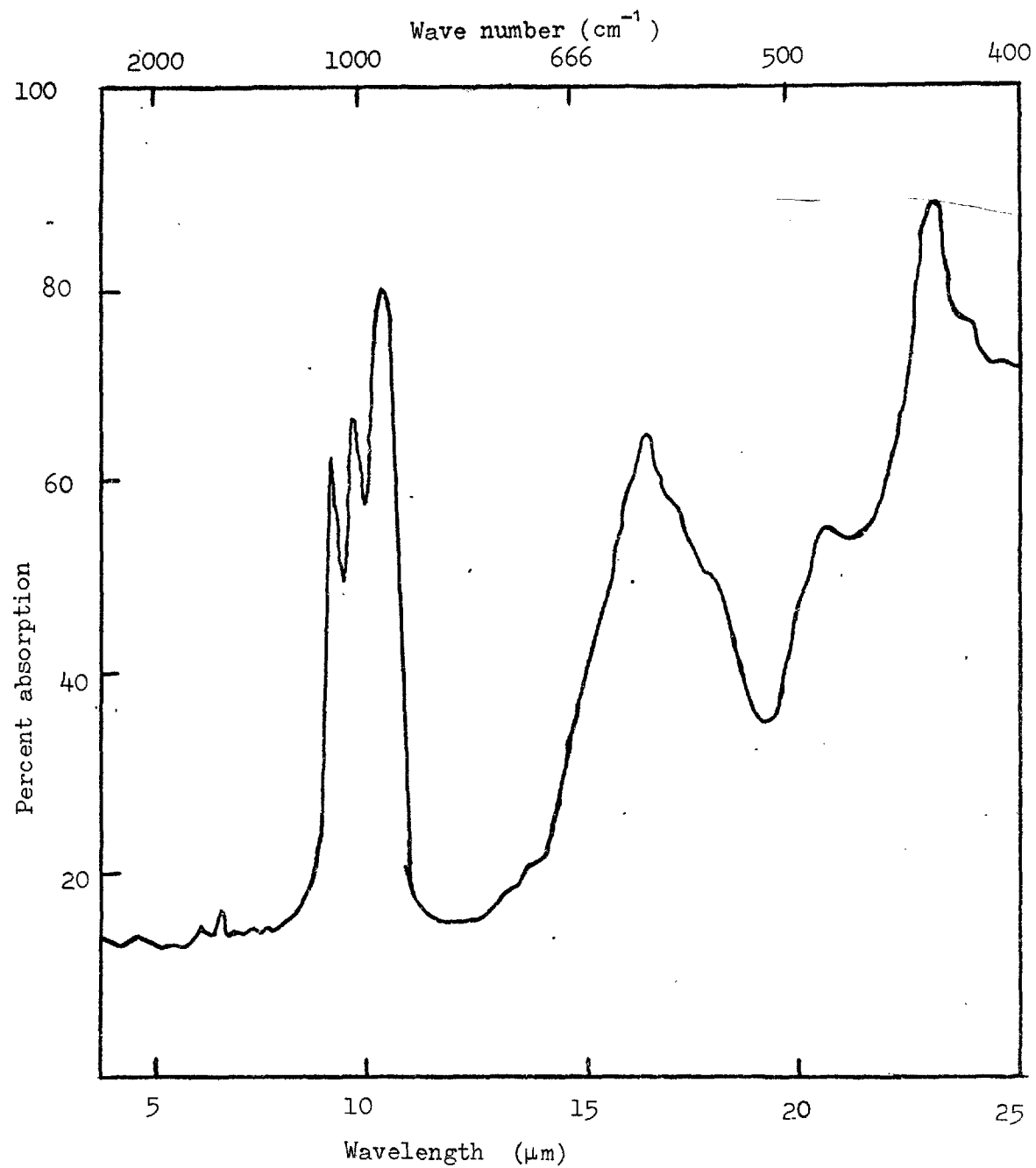


Fig. 23. Infra-red spectrum of chrysotile after adsorption of glutamic acid.

X.2(b) Discussion

Brindley and Zussman (96) studied the infra-red absorption spectra of various serpentine minerals including chrysotile. They observed peaks due to silky fibres at 2.75, 2.95, 6.2, 9.25, 9.85 and 10.5 μm . The peak at 2.75 has been postulated to be due to the hydroxyl groups in the lattice. However, they did not mention anything about the assignment of the other peaks. Saksena (97), who studied the infra-red absorption of many silicates, showed that with chrysotile three distinct bands are obtained in the region 9.2 μm (1085 cm^{-1}), 9.75 μm (1017 cm^{-1}) and 10.4 μm (962 cm^{-1}). From theoretical calculations he has shown that three frequencies are expected in this region due to the Si-O bond in the particular SiO_4 tetrahedron. The peaks obtained in the present experiment (9.2, 9.8 and 10.5 μm) are in agreement with the results obtained by Saksena.

Le Comte (98) studied the infra-red absorption of different amphiboles and showed that amphiboles are characterised by two strong bands close to 10 μm (1000 cm^{-1}), two more feeble bands between 8.4 - 9.5 μm ($1190 - 1052\text{ cm}^{-1}$), another feeble band close to 10.9 μm (917 cm^{-1}) and a band near 13.2 μm (762 cm^{-1}). But he did not assign these bands to any specific groups or bonds. Patterson and O'Connor (99) studied the infra-red absorption of three amphiboles - amosite, crocidolite and tremolite and reported that the spectra for the three amphiboles are sufficiently different for identification but have the same general features. The three amphiboles are characterised by several sharp bands at about 3650 cm^{-1} (2.73 μm) due to OH stretching vibrations, a group of strong bands between 1150 and 800 cm^{-1} (8.78 - 12.5 μm) due to Si-O stretching vibrations, few weaker bands between 800 and 600 cm^{-1} (12.5 - 16.6 μm) due to the vibrations of the silicate chains and a further group of strong absorption bands between 600 and 300 cm^{-1} .

(16.6 - 33.3 μm) which are due to metal-oxygen stretching and silicon-oxygen bending vibrations.

Examination of table 26 and the figures 21, 22 shows that two strong bands appeared within the region 9 - 10.1 μm (9.1 and 10.0 μm with amosite and 9.1 and 10.1 μm with crocidolite), a feeble band at 11.1 μm with both amosite and crocidolite and a stronger band at 12.8 μm with amosite and 13.0 μm with crocidolite. These are in agreement with the results of Le Comte. According to Patterson and O'Connor the two strong bands in the region 9 - 10.1 μm should be due to Si-O stretching vibrations and a number of weak bands in the region 12.8 - 16 μm with both amosite and crocidolite should be due to vibrations of silicate chains and the strong and medium bands within the region 19.6 - 20 μm may be assigned to metal-oxygen stretching and silicon-oxygen bending vibrations. Therefore the results of the present experiments are in good agreement with the published results of infra-red absorption of chrysotile, amosite and crocidolite.

However, from the table and also from fig. 23, it is evident that a weak peak appears at 6.5 μm in case of all asbestoses which had adsorbed some amino acids. (This peak is absent in the case of pure asbestos). Peck et al (100) have found that when either oleic acid or sodium oleate become chemisorbed on hematite, the infra-red band characteristic of antisymmetric vibration of the carbonyl group appears at 6.48 μm . This suggests that the peak obtained at 6.5 μm may be due to a metal-carboxylate bond formation. To confirm this postulate, the infra-red spectra of Mg-acetate and Fe(III)-acetate were taken and both of them showed a sharp peak at 6.5 μm . This evidence supports the hypothesis that a part, at least, of the adsorption of amino acid on the asbestos surface is due to the metal-carboxylate bond formation.

X.3 Adsorption of proteins

Two proteins of types which are prominent in human blood serum were chosen for this experiment - albumin and γ -globulin. Bovine plasma albumin and bovine γ -globulin fraction II were obtained from Armour Pharmaceuticals Ltd. Adsorption experiments were carried out with all the three types of asbestos.

Estimation of albumin and γ -globulin were done by u. v. spectroscopy. Both albumin and γ -globulin have strong absorption at 210 nm.

Two series of experiments were carried out - one adsorption of protein with time (to ascertain the time to reach equilibrium adsorption) and the other with different concentrations.

X.3(a) Adsorption of albumin : dependence on time

Experimental conditions - 0.1 g of asbestos was kept suspended in 20 ml protein solution in polypropylene tubes and kept shaken at 37°C. Two tubes were taken out after definite intervals of time, centrifuged and the amount of albumin in the supernatant was determined. Results, which are the means of two sets of readings, are shown in table 27.

Evidently, adsorption equilibrium is substantially reached within 12 h to 1 day. In the subsequent experiments, i.e. dependence of adsorption of albumin on concentration, the asbestos minerals in albumin solution were allowed to stand one day. (Protracted experiments were avoided because of the liability of mould attack on the protein).

TABLE 27ADSORPTION OF ALBUMIN BY ASBESTOSES : INFLUENCE OF TIME

(1.1 mg albumin added to 0.1 g asbestos)

Time	Amount of albumin adsorbed (mg)		
	chrysotile	amosite	crocidolite
1 h	0.3	0.04	0.1
3 h	0.5	0.1	0.3
6 h	0.6	0.2	0.4
12 h	0.65	0.25	0.4
1 d	0.65	0.25	0.4
2 d	0.65	0.25	0.4
3 d	0.68	0.30	0.5
5 d	0.70	0.30	0.5

X.3(b) Adsorption of albumin on asbestos : influence of concentration

Experimental conditions - 0.1 g of asbestos was kept suspended in 20 ml albumin solution of different concentrations in a series of polypropylene tubes kept shaken at 37°C. After one day the tubes were taken out, centrifuged and the amount of albumin in the supernatant was determined. Results are shown in table 28, and also in figures 24, 25 and 26.

Fig. 24 Adsorption of albumin on crocidolite

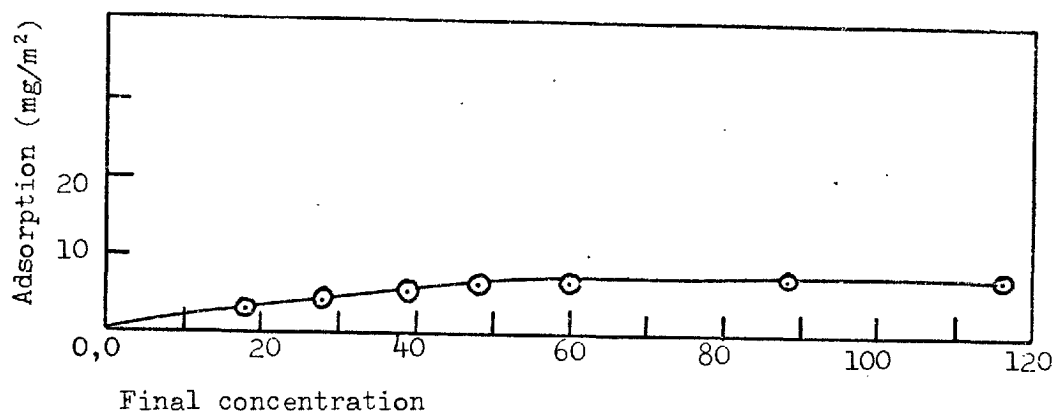
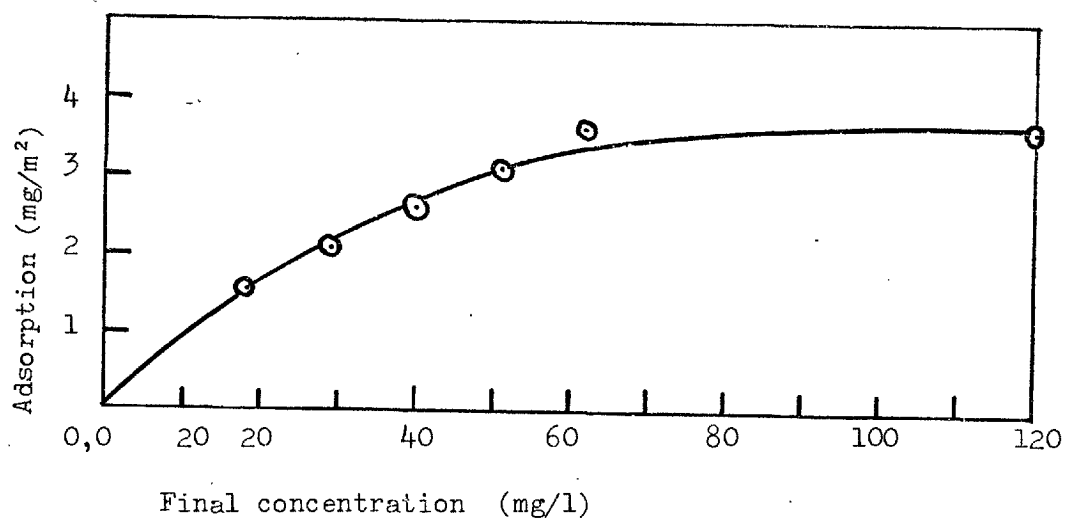


Fig. 25. Adsorption of albumin on amosite

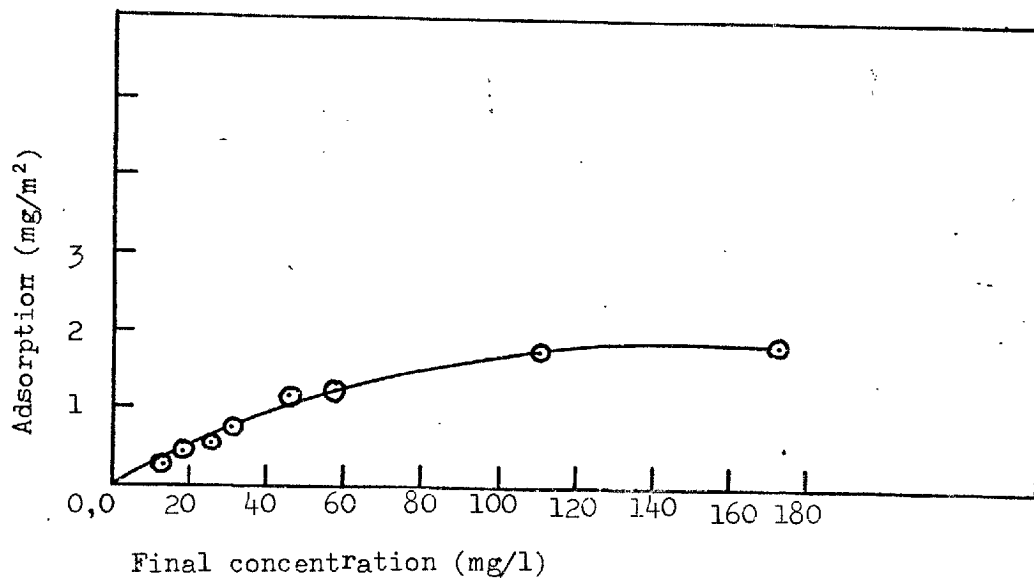


Fig. 26. Adsorption of albumin on chrysotile

TABLE 28

Adsorption of albumin on asbestos : influence of concentration

Initial concn. mg/l	CHRYSOTILE		AMOSITE		CROCIDOLITE	
	Adsorption mg/m ²	Final concn. mg/l	Adsorption mg/m ²	Final concn.	Adsorption mg/m ²	Final concn.
28	0.25	13	3.0	18	1.4	19
43	0.40	18	4.0	28	2.2	28
57	0.50	25	5.0	39	2.6	40
71	0.70	30	6.3	48	3.0	52
85	-	-	6.9	60	3.4	63
113	1.1	45	7.0	88	-	-
130	1.2	57	-	-	-	-
142	-	-	7.0	117	3.4	120
213	1.7	110	-	-	-	-
284	1.8	172	-	-	-	-

X.3(c) Adsorption of γ -globulin : dependence on time

Experimental conditions - 0.1 g asbestos kept suspended in 20 ml γ -globulin solution at 37°C.

From the results on table 29 it is evident that the adsorption equilibrium of γ -globulin on the asbestos surface is attained within 12-24 h. Therefore in the subsequent experiment of globulin adsorption on asbestos

surface the time of standing was chosen to be one day.

TABLE 29

Adsorption of γ -globulin on asbestos with
time

(1.5 mg γ -globulin added to 0.1 g asbestos.)

Time	γ -globulin adsorbed (mg)		
	chrysotile	amosite	crocidolite
1 h	0.3	0.1	0.2
3 h	0.7	0.3	0.5
6 h	1.0	0.7	0.5
12 h	1.2	0.7	0.9
1 d	1.2	0.9	1.0
2 d	1.1	0.9	0.9
3 d	1.2	1.0	1.0

X.3(d) Adsorption of γ -globulin on asbestos surface : dependence on
concentration of γ -globulin

Experimental condition - 0.1 g asbestos kept suspended in 20 ml γ -globulin solution of different concentration and kept shaken at 37°C. After one day the amount of γ -globulin in the supernatant was determined. The results are shown in table 30 and also in figures 27, 28 and 29.

TABLE 30.

Adsorption of γ -globulin on 0.1 g asbestos
minerals dependence on concentration of γ -globulin

γ -globulin added (mg/l)	CHRYSOTILE		AMOSITE		CROCIDOLITE	
	Adspn. (mg/m ²)	Final concn. (mg/l)	Adspn. (mg/m ²)	Final concn. (mg/l)	Adspn. (mg/m ²)	Final concn. (mg/l)
110	1.4	12.5	23	25	12	43
140	2.0	16	30	32	15	52
165	2.2	30	33	47	16	59
190	2.4	40	37	63	-	-
225	2.6	66	43	72	18	106
280	3.0	100	45	118	19	156

The adsorption isotherm obtained with the different asbestoses are shown in the figure. The isotherm obtained with albumin on chrysotile and albumin on crocidolite are approximately of Langmuir type whose equation is $x = \frac{abc}{1 + ac}$, x being the amount adsorbed, c the concentration, 'b' the saturation value. In order to obtain the value of 'b' (saturation value) $1/x$ was plotted against $1/c$ (fig. 30) to obtain a straight line for albumin on crocidolite and from the intercept of the straight line the value of 'b' was calculated to be 3.6 mg/m².

Fig. 27. Adsorption of γ -globulin on crocidolite

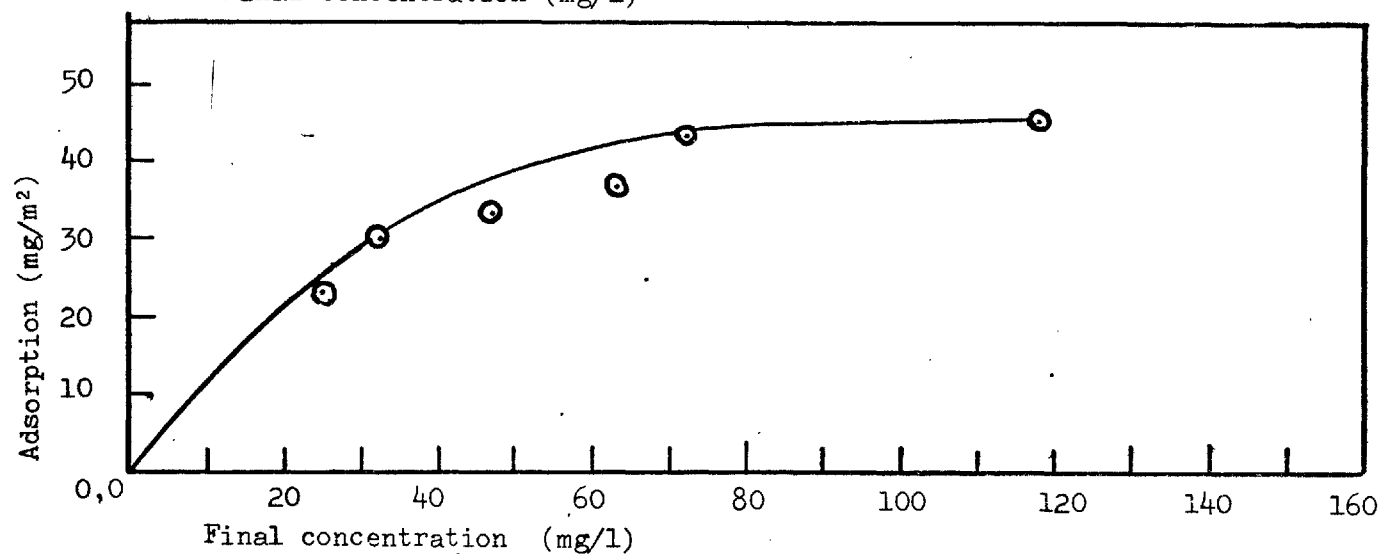
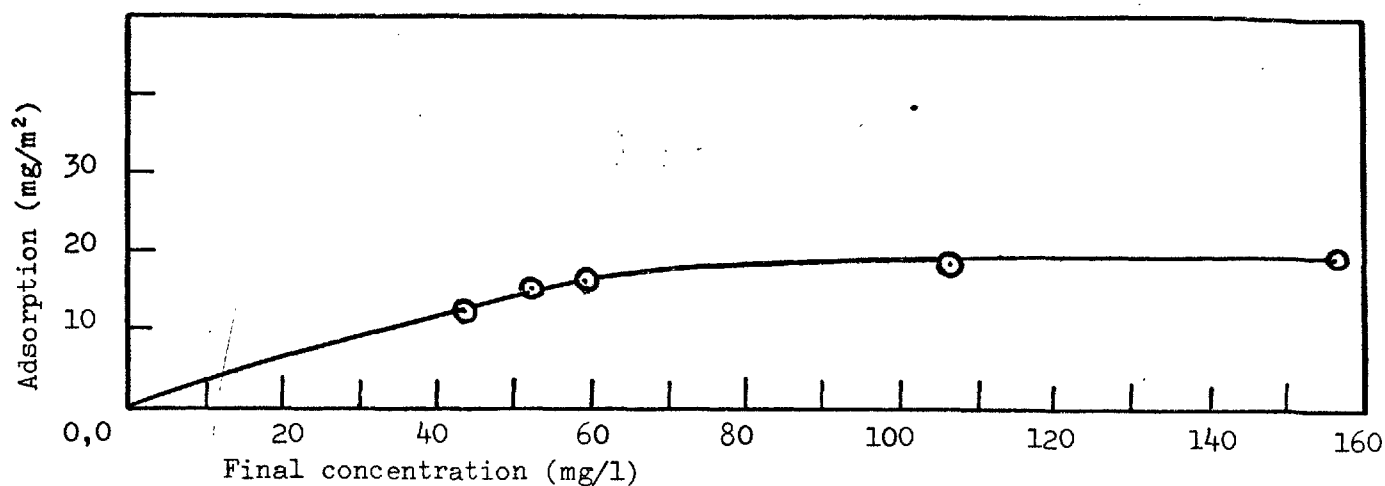


Fig. 28. Adsorption of γ -globulin on amosite

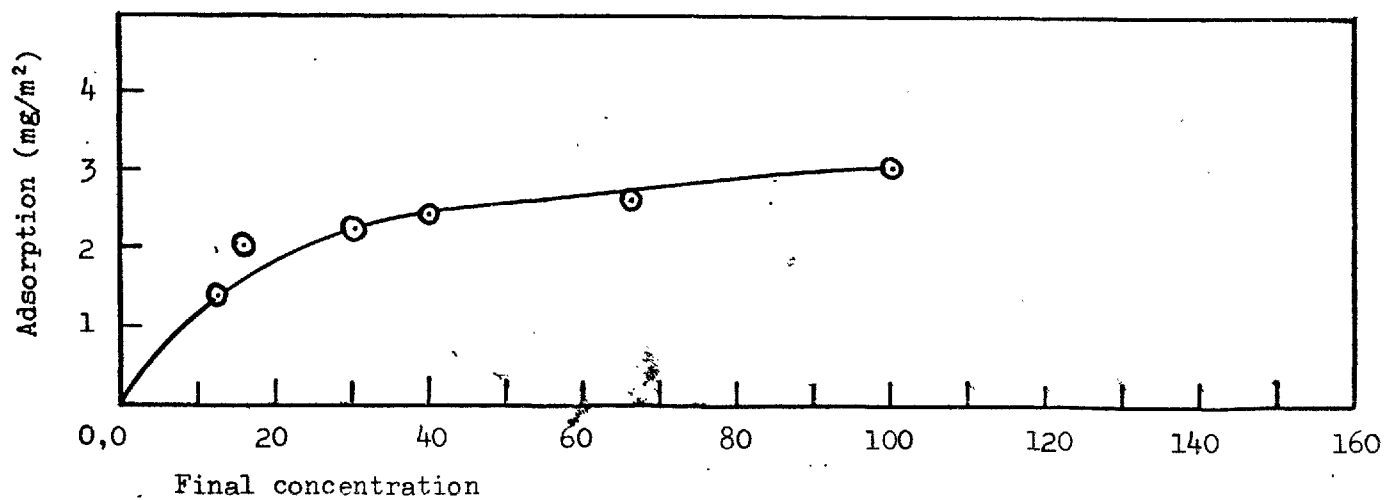
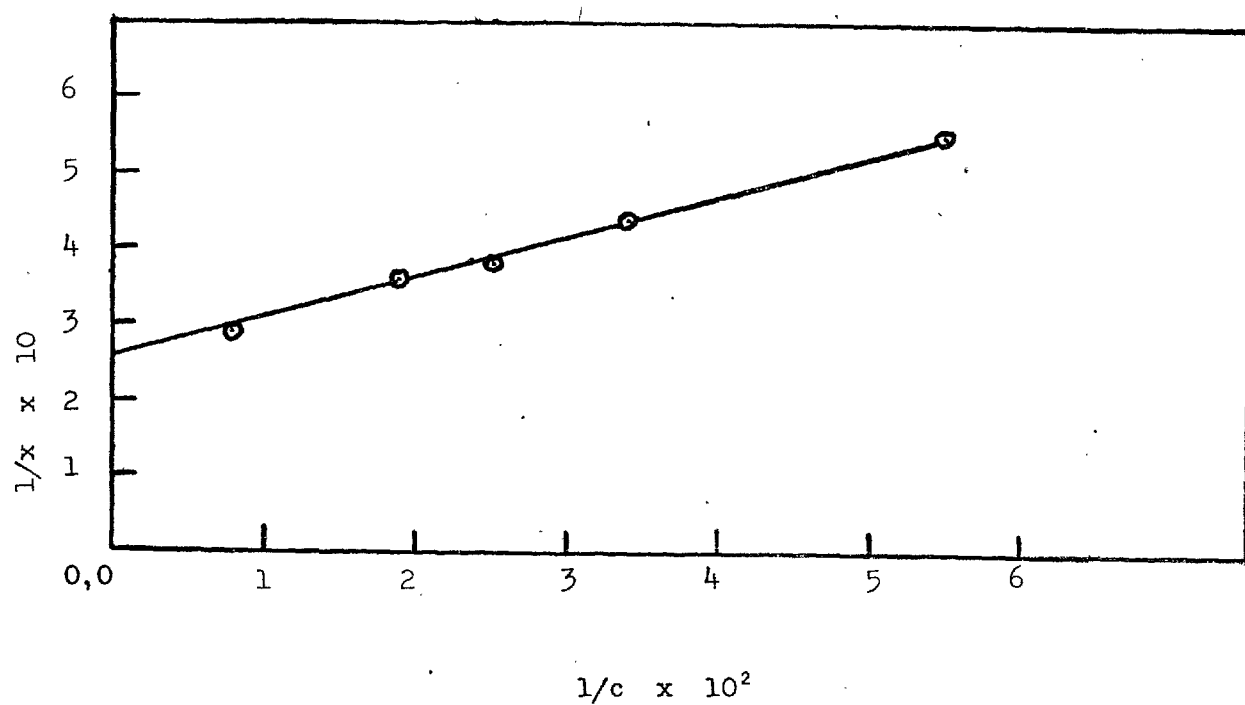


Fig. 29. Adsorption of γ -globulin on chrysotile



x = Amount adsorbed

c = Final concentration

Fig. 30. Adsorption of albumin on crocidolite

X.3(e) Examination of the reversibility of adsorption of proteins

This was made by microelectrophoresis (i.e. zeta-potential determination). Chrysotile normally has a positive surface charge and its zeta-potential as determined by microelectrophoresis is + 44.8 mV. Same chrysotile was allowed to adsorb albumin and the zeta-potential was found to be - 19.5 mV. The above chrysotile with adsorbed albumin was then washed repeatedly with water and the zeta-potential was found to be -19.4 mV. This shows that the albumin that has been strongly adsorbed on the surface of chrysotile has changed the surface from positive to negative. Moreover, the adsorbed layer of albumin cannot be removed by simple washing. Clearly, the adsorption is strong and irreversible.

X.3(f) Discussion

Cockbain (101) studied the physical adsorption of serum albumin at an emulsion interface and showed that albumin forms a monomolecular film. Biswas and Haydon (102) studied the adsorption of B.S.A. on petroleum ether and came to the same conclusion. They claimed that such adsorption is purely physical depending only on the hydrophobic side chains attempting to escape from water to oil phase. Therefore it seems obvious that when proteins are adsorbed in their native state the adsorption should not exceed a monolayer.

If bovine serum albumin is adsorbed in the native state as ellipsoid of semi-axes 69 and 23 Å, (103) could amount to 1.9 mg/m² or 0.03 μmoles/m² for a monolayer. Whereas if adsorbed as close packed spheres of 70 Å

diameter a monolayer coverage works out to be 2.7 mg/m^2 or $0.04 \mu\text{moles/m}^2$. The shape of γ -globulin molecule is still a matter of controversy (104). Depending on different techniques, Valentine (105) and Oncley (106) described the shape of γ -globulin molecule as spheres of $70 \text{ \AA}$ diameter and ellipsoid of $235 \times 44 \text{ \AA}$ semi-axes respectively. Assuming the molecules to be spherical a monolayer coverage works out to be $0.04 \mu \text{ moles/m}^2$ whereas for the ellipsoid shape the monolayer coverage is $0.005 \mu \text{ moles/m}^2$. The values are widely different. This must be associated with the technique employed to determine the shape.

Pankhurst, (107) from a study of the $\pi - A$ curve of monolayers of collagen on water, found that collagen could be spread in a close-packed way to yield a limiting area of $1.3 \text{ m}^2/\text{mg}$ or 0.8 mg/m^2 . Augenstine, (108) from a study of the monolayer of trypsin, obtained a spreading of $1.5 \text{ m}^2/\text{mg}$ or 0.66 mg/m^2 .

The present experimental results obtained with albumin on different asbestoses are 1.8 mg/m^2 or $0.03 \mu \text{ moles/m}^2$ for chrysotile, 7.0 mg/m^2 or $0.10 \mu \text{ moles/m}^2$ for amosite and 3.4 mg/m^2 or $0.05 \mu \text{ moles/m}^2$ for crocidolite. The values obtained for albumin on chrysotile and crocidolite are quite comparable to the theoretical values for a monolayer of spread protein (0.03 and $0.04 \mu \text{ moles/m}^2$), but that on amosite is slightly higher. In the case of the adsorption of γ -globulin, the experimental values are 3.0 mg/m^2 or $0.02 \mu \text{ moles/m}^2$ for chrysotile, 45 mg/m^2 or $0.3 \mu \text{ moles/m}^2$ for amosite and 19 mg/m^2 or $0.1 \mu \text{ moles/m}^2$ for crocidolite. The saturation value on chrysotile is well within the range of theoretical values (0.03 and $0.005 \mu \text{ moles/m}^2$) but those for amosite and crocidolite are very much higher than for a monolayer coverage.

To seek an explanation for the high adsorption of proteins on asbestos the possibility of the metallic ions (Mg^{2+} , Fe^{2+} , Fe^{3+}) on the surface forming any complex with the proteins studied was considered. A good deal of information is available in the literature regarding the interactions of "heavy metal" ions with proteins. There is enough evidence in the literature regarding the interactions of metallic ions like Zn^{2+} , Cd^{2+} , Hg^{2+} , Cu^{2+} , Ca^{2+} , with the protein molecules. No evidence of any specific interaction of ions like Mg^{2+} , Fe^{2+} , Fe^{3+} was obtained from the literature. P. Calissano et al. (109) showed that Ca^{2+} causes conformational change in a large number of proteins whereas Mg^{2+} does not. H. Neurath (110) mentioned that Fe^{2+} forms the least stable complex with nitrogen-oxygen, nitrogen-nitrogen and nitrogen-sulphur bidentate ligand compared to Co, Ni, Cu, Zn, Cd. Therefore, from the literature study it was concluded that Mg^{2+} , Fe^{2+} and Fe^{3+} are unlikely to have any effect on protein other than just forming a metal carboxylate with the carboxyl groups of the amino acids. This conclusion was supported by the following experiment. To albumin and γ -globulin solutions Mg^{2+} , Fe^{2+} and Fe^{3+} salts were added, but no turbidity or precipitation could be observed even on standing. Therefore protein adsorption on the asbestos surface may be related instead, not to the cations but to the "silica" parts of the surface exposed when asbestos is put in water.

It is known that proteins interact with silica and silicates and adsorb at the silica/water interface. A good deal of information is available in the literature regarding the polymerisation of silicic acid, flocculation of silica and different silicates by proteins and simple adsorption studies of protein on silica. Bergman and Nelson (111) studied the polymerisation of silicic acid with gelatin, albumin and globulin. They assumed the surface of silica particles contains the same ($-SiOH$) silanol group as silicic acid.

They found that the interaction of silica is strongest with globulin and decreases from albumin to gelatin. Their results are in agreement with the work of Pernis (112) who percolated serum down a column of quartz powder and found globulin to be preferentially adsorbed. Allison and Harington, (113) from studies on the toxicity of silica, concluded that the toxic effects of silica are due to the capacity of polymeric silicic acid to act as a hydrogen donor in the formation of hydrogen-bonded complexes with active groups such as quaternary and phosphate ester group of phospholipids or to a lesser extent, secondary amide (peptide) groups of protein.

However, with all the three types of asbestoses it has been proved (cf. leaching experiment) that in water they release monomeric silica as silicic acid, polymeric silica, colloidal silica and also some fibrils of asbestos. Therefore it seems possible that serum albumin and γ -globulin could interact with the silicic acid which polymerises, with active sites ($-\text{SiOH}$) on colloidal silica particles and also on the surface silica layer exposed after leaching of the basic layer.

Since chrysotile has micropores (cf. water vapour adsorption experiment) it is possible that the apparent "monolayer" coverage observed may be fortuitous; perhaps the non-accessibility of the micro-pores is compensated by some interaction with silicic acid. Moreover the interaction of silica with protein may possibly explain slightly higher adsorption density of albumin on amosite ($0.10 \mu\text{moles/m}^2$ compared to $0.04 \mu\text{moles/m}^2$) but it cannot definitely explain the exceedingly high values obtained for the adsorption of γ -globulin on amosite and crocidolite.

In order to explain these high results a check was made on the solubility of γ -globulin whose iso-electric point has been reported to be 6.6 (114).

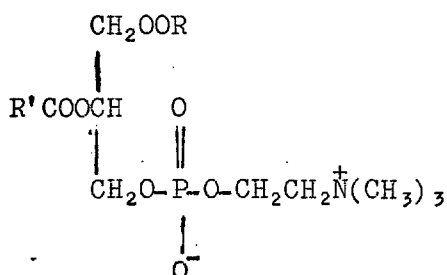
When γ -globulin is dissolved in water (pH = 6.1) the pH goes up to 6.8. A suspension of amosite in γ -globulin shows pH 6.8 and a suspension of crocidolite in γ -globulin solution has a pH about 8. A solution of 300 p.p.m. γ -globulin in pure water was slightly turbid. Therefore, a saturated solution of 75 p.p.m. of γ -globulin was made at a pH 6.8 and an adsorption experiment was carried out with amosite in the usual way. The adsorption was found to be 8 mg/m² or 0.05 μ moles/m² which is quite comparable with the monolayer coverage value (0.04 μ moles/m²). A similar experiment with crocidolite gave a value of 6.5 mg/m² or 0.04 μ moles/m².

Therefore, it can be concluded that the high adsorption values of γ -globulin on amosite and crocidolite are associated with the solubility of γ -globulin at pH near its iso-electric point. The values shown in the table do not represent the true adsorption on the surface, precipitation of undissolved γ -globulin on the surface of minerals definitely took place due to centrifugation. The true adsorption probably does not exceed a monolayer.

In view of the present results it seems likely that in serum fluids asbestos particles would become covered with a monolayer of protein (protein being far more strongly held than simpler molecules).

X.4 Interaction of lipid with asbestos and other minerals

In addition to proteins, lipids form one of the important constituents of all living cells. The main constituents of the cell walls and internal membranes are lipids. The most common lipid that is present in the cell wall is lecithin which is a phospholipid having chemical structure



It is also called phosphatidylcholin.

In connection with the present project it was thought necessary to study the interaction of lipid with the asbestos surface in view of the theory proposed by Allison (115). In the course of his study on the toxic effect of silica and asbestos, Allison found that very short fibres of asbestos were readily and completely taken up by phagocytosis and with longer fibres the cells were closely attached to or enveloped the ends of the fibres. Therefore he proposed that the cytotoxic effect of asbestos is related to a direct interaction of asbestos fibres with cell membranes which are mainly composed of lipids. Pattle (116), who studied the surface-active lining of lung alveoli, believes that the surface-active lining is composed mainly of dipalmitoyl lecithin and may be involved in the formation of asbestos bodies inside the lung.

For the present experiments synthetic lecithin was used. A simple experiment was carried out to test the hydrophilic/oleophilic character of asbestos and other related minerals, and the possible effect of lipids. The experiment is based on the principle of "phase-transfer". Takakuwa and Takamori (117), who studied the phase inversion method as a tool for flotation study, described how it is based on the fact that oil/water emulsions are stabilised by a powdered solid. Whether O/W or W/O emulsion type is obtained depends on whether the contact angle is smaller or larger than 90° .

across the water phase at the solid-oil-water interface. Thus the phase inversion method shows the change in wettability of a mineral observed around the mark line of 90° of contact angle at the mineral-oil-water interface.

In the actual experiment synthetic lecithin (obtained from Koch-Light Laboratory) was dissolved in benzene and the "phase-transfer" experiment was performed with water as the second phase. A similar experiment was done with pure benzene (Analar) alone as one phase and water as the second phase. The results of the experiments are shown in the table.

TABLE 31

Hydrophilic/oleophilic character and the effect of lecithin on different minerals

Mineral	Behaviour in benzene + pure water	Behaviour in benzene + lecithin and water
chrysotile (opened and stored in polypropylene bottle)	not wetted by benzene	wetted by benzene + lecithin
chrysotile (scraped from rocks)	"	"
amosite (opened and stored in polypropylene bottle)	wetted by benzene	"

TABLE 31/continued

Mineral	Behaviour in benzene + pure water	Behaviour in benzene + lecithin and water
amosite (scraped from rocks)	not wetted by benzene	"
crocidolite (opened and stored in polypropylene bottle)	wetted by benzene	"
crocidolite (scraped from rocks)	not wetted by benzene	"
freshly ground quartz	particles collected at the interface and agglomerated	more than 50% of the particles transferred to benzene + lecithin
freshly ground quartz heated to redness	the particles collected at the interface and agglomerated	more than 75% of the particles transferred to benzene + lecithin
quartz aged in water	not wetted by benzene	not wetted by benzene + lecithin
kaolin	not wetted by benzene	not wetted by benzene + lecithin
bentonite (Na-montmorillonite)	"	"
mica (freshly ground)	"	"
calcite	"	"

TABLE 31/continued

Mineral	Behaviour in benzene + pure water	Behaviour in benzene + lecithin and water
feldspar	not wetted by benzene	not wetted by benzene + lecithin
silica gel (freshly ground)	"	"
silica glass (freshly ground)	"	"
fluorite	"	"
chrysotile with pre-adsorbed serum albumin	"	"
talc (directly scraped from the rock)	wetted by benzene	wetted by benzene + lecithin

"wetted by benzene" means the small particles of mineral are wholly transferred to the benzene layer

"not wetted by benzene" means the mineral is in the water phase.

Considering first the behaviour of materials with water and pure benzene - there are four classes of minerals indicated in the table.

(a) Most of them are strongly hydrophilic (e.g. calcite, fluorite, mica,

feldspar) and therefore remain in the water phase, not forming any contact with benzene.

(b) Talc is the only definitely hydrophobic mineral in the list. It is well known that clean talc powder floats when sprinkled on water - i.e. it forms a contact angle at the air/water interface. Bartell and Zuidema (118) measured the contact angle of talc at air/water interface and obtained a value of 86° . This means that the work of adhesion of talc/water is less than the work of cohesion of water/water (namely 144 erg cm^{-2}) whereas for hydrophilic minerals it is commonly much greater (eg. 500 erg cm^{-2}). The actual value of work of adhesion can be calculated from the equation

$$W_{ad} = \gamma_L (1 + \cos \theta)$$

and is found to be $75.9 \text{ ergs cm}^{-2}$. The experiment shows that talc is more strongly oleophilic as well as hydrophobic.

(c) Certain minerals (freshly ground quartz or heated quartz) were observed to collect at the benzene/water interface. This means that contact angle is neither very great nor very small. In other words, the works of adhesion to water and to benzene are approximately equal.

(d) A remarkable result is that although all three asbestos minerals are wetted by water, the amphiboles, amosite and crocidolite which have been opened and stored in polypropylene bottle for a long time were extracted from water into benzene whereas those directly scraped from the rocks remained in water. The same effect was observed when benzene was replaced by n-hexane as the oil phase. This shows that the behaviour of the old opened fibres towards oil is different from that of fresh samples from the rocks.

Contamination with organic substances from the polypropylene bottle may be the cause.

Later investigation showed that the n-hexane used previously contained some impurities. A pure sample of n-hexane (spectroscopic grade) was therefore further purified by shaking with active alumina for about 48 h. Distilled water was further purified by shaking with activated charcoal for about 48 h. The phase-transfer experiment was performed with amosite and the purified samples of n-hexane and water. In order to ascertain the type of impurity (presumably surface-active agents) in the old opened fibres and the minimum amount required to convert the fibres to oleophilic, a few more experiments were performed with the addition of surface-active agents to both water and oil phase. Results of these investigations are tabulated below.

Sample	Impure hexane + impure water	Pure hexane + pure water	Benzene +0.01% stearic acid + water	Benzene + water + 0.01% Na-oleate	Benzene + water + 0.01% CTAB (cetyl trimethyl ammonium bromide)
amosite from rocks	wetted by water	wetted by water	collect at the interface	collect at the interface	transferred to benzene
amosite opened and stored in polypropylene bottle	wetted by hexane	wetted by water	wetted by benzene	wetted by benzene	wetted by benzene

A sample of amosite obtained from the rock and treated with vapour of lubricating oil when subjected to the above test was found to remain in the water phase. Amosite fibre in waste slime (Penge slimes dam concentrate - supplied by Dr. A.A. Hodgson) although carried in plastic bag was found to remain in water phase in the phase-transfer experiment. In the above table, although the results have been shown with amosite, crocidolite was found to give the same type of results.

It is apparent from the above table that anionic surfactants like Na-oleate and stearic acid can make the negatively charged amphibole surface hydrophobic probably by attachment of the polar heads on the metallic ions but the adsorption density is not high enough to make the surface so hydrophobic that the fibres will transfer to the oil phase (although various concentrations of surfactant were tried). But CTAB which is a cationic surfactant, having a quaternary nitrogen atom (a strong base) can easily attach itself to the negative amphibole surface in sufficient surface density to make it strongly hydrophobic or oleophilic. A concentration of 0.004% of CTAB (25 ml surfactant solution + 0.1 g amosite) was sufficient to make the amosite surface hydrophobic and strongly oleophilic. Therefore it appears that the unidentified impurity that must be associated with the old opened fibres could be a cationic surfactant or an amphipathic compound with long hydrocarbon chains like lecithin which also shows the same effect (see below).

Considering now the effect of adding lecithin - its most striking effect is on chrysotile, which it transforms from strongly hydrophilic to strongly oleophilic. The structure of lecithin is "amphipathic" in the sense that one part of the molecule is water-soluble (hydrophilic) and the other

part is oil-soluble (hydrophobic). When a lecithin molecule is introduced into an oil-water interface it spontaneously orients itself with the long chain hydrocarbon portion in the oil phase (104). Presumably lecithin which besides being surface-active is zwitterionic, is chemisorbed by its polar groups (possibly through the negatively charged oxygen atom on the Mg^{2+} sites) on the chrysotile surface with the long hydrocarbon chain away from the surface thus making it hydrophobic or oleophilic.

This conclusion was confirmed experimentally. Chrysotile was first treated with a solution of lecithin in benzene, followed by washing several times with benzene. Finally the benzene was removed by vacuum drying and the dried fibres were found to float in clean water. This shows that the adsorption of lecithin on chrysotile is strong and presumably it is a process of chemisorption. A similar explanation holds good in case of amphiboles - lecithin with the positively charged quaternary nitrogen atom must be involved in a polar interaction with the negatively charged surface of amphiboles.

In another experiment the chrysotile fibres which adsorbed lecithin were subjected to phase-transfer experiment with a solution of serum albumin in water in stead of pure water. The fibres were found to remain in the water phase containing albumin. This shows that protein can adsorb on to the surface already covered by lecithin. This adsorption of protein is probably by hydrophobic association to the previously attached lecithin. Therefore, protein adsorption seems certain to "dominate" the surface in biological fluids.

It seems certain, therefore, that all the three asbestoses will interact strongly with any phospholipid like lecithin. But once they adsorb some protein

adsorption of lipid is inhibited, as shown by the observation that chrysotile with adsorbed protein will not transfer to benzene + lecithin.

In an appendix to the thesis, the surface thermodynamics involved in transfer of small particles from water to oil have been analyzed. As this analysis does not throw any new light on the nature of the phenomena, it will not be discussed further at this point.

CHAPTER XI

SUMMARY AND CONCLUSIONS

The primary aim of this project was to provide information about the inorganic and surface-chemical nature of asbestos minerals which might be a guide to the physiologists concerned with asbestosis and mesothelioma. Since the actual mechanism by which asbestosis is caused has not been established, such information may provide some clue to the proper understanding of its mechanism. It is possible of course, that the asbestos particles act in a purely mechanical manner - simply as hard, sharp particles; but the possibility that their surface-chemical reactivity is involved cannot be eliminated before the nature of this reactivity has been investigated.

Asbestos particles, after entering the lung, would come into contact with various organic and inorganic materials with which they may interact. The reactions of some of the prominent materials with the asbestos minerals were therefore studied in the non-living model system. Leaching kinetics, adsorption of inorganic ions such as Ca^{2+} , Na^+ , adsorption of amino acids, proteins and lipids and measurement of zeta-potentials of the different asbestos are the main investigations made in this project. From the results of the above investigations the following informations were obtained.

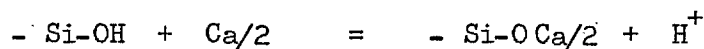
(a) The leaching of chrysotile asbestos is dominated, at least in the early stages, by the release of excess of Mg^{2+} and OH^- from the brucite present as impurity. Release of silica as monomeric and polymeric is relatively slow and does not bear any stoichiometric relation with the release of Mg^{2+} . The solubility of silica is suppressed by the presence

of excess of magnesia. Colloidal particles of silica and of chrysotile itself were detected in the liquid obtained from leaching.

By comparison with chrysotile, amphibole asbestoses (amosite and crocidolite) are relatively inert to the action of water. Leaching of amosite is dominated by the slow release of soluble magnesia and that of crocidolite is dominated by the release of soda. Release of silica is low in both these cases also.

Silica released in the form of colloidal particles and polymeric silicic acid may be involved in some subsequent biological reactions, since silicic acid interacts with proteins.

(b) The amounts of Ca^{2+} and Na^+ adsorbed on the chrysotile surface are too low to suggest a direct ion exchange with Mg^{2+} in chrysotile. Ca^{2+} was found to be adsorbed to the extent of $4 \mu \text{ moles/m}^2$ and Na^+ about $20 \mu \text{ moles/m}^2$. Because of the difference in ionic radii, it is highly unlikely that Ca^{2+} would replace Mg^{2+} in the chrysotile lattice. Evidence has been presented for the hypothesis that the small amount of Ca^{2+} adsorbed may have been involved in the reaction



the $-\text{Si-OH}$ group being exposed on the surface of hydrolysed chrysotile after release of Mg^{2+} . Similarly, the small amount of Na^+ adsorbed may have gone on to the silica by an ion-exchange process.

The quantity of Ca^{2+} or Na^+ adsorbed is quite negligible compared with the reserves in the body fluids; therefore it seems unreasonable to

attach any biological significance to it.

(c) Thermogravimetric analysis of the chrysotile used proved that it was contaminated with about 5% brucite. This observation was further confirmed by X-ray analysis. Most commercial samples of asbestos also contain a certain amount of brucite (eg. 1-20%).

Magnesium hydroxide is appreciably soluble, and raises the pH to about 10.3. Its well known use as a stomach anti-acid suggests that Mg^{2+} is not toxic, even at much higher concentrations than those produced by dissolution of brucite in plain water. But $Mg(OH)_2$ may nevertheless produce local biological reaction with cells (see below).

(d) In order to convert the 5% excess brucite to pure chrysotile, advantage was taken of the hydrothermal method described by Bowen and Tuttle. Results obtained for zeta-potential values, confirmed that this treatment gave a product similar in surface-chemical properties to stoichiometric synthetic chrysotile.

(e) Zeta-potentials of asbestoses from different sources and under different conditions were measured. Chrysotile gave a positive zeta value whereas both the amphiboles showed negative values. Zeta-potentials of chrysotile samples were found to vary, depending on the source; with same forms, even in the same sample, particles of different mobility were observed. This could well be due to different extents of leaching undergone by the sample. (It has been proved that drastic leaching eventually changes the zeta-potential of chrysotile from positive to negative.) A comparison of the micro electrophoretic and electro-osmotic method of

zeta-potential measurement has been made. For chrysotile with high surface conductivity the former method has been found to be more suitable.

(f) Adsorption isotherms of water vapour on chrysotile showed hysteresis, proving the presence of pores. Adsorption of benzene vapour was much less on chrysotile pre-saturated with water vapour.

(g) Adsorption of amino acids (glutamic acid and lysine) on all the three asbestoses has been suggested to involve chemical bond formation through the carboxylic group (indicated by infra-red spectroscopy). Adsorption of the amino acids on chrysotile approximately followed a Langmuir type of isotherm but those on amosite and crocidolite never came to saturation. It was later proved that both amosite and crocidolite become dispersed by amino acids, exposing more and more new surface for further adsorption.

(h) Adsorption studies of albumin and γ -globulin on the three types of asbestoses have proved that these (from dilute solutions) proteins form approximately a monolayer coverage on the three types of asbestoses. Interaction of proteins with the active silica released by leaching has also been thought to be possible. The protein adsorption has been found to be irreversible.

(i) Adsorption of phospholipid on the asbestoses and other related minerals was studied by a wetting experiment. This proved that all the three types of asbestoses adsorb lecithin. But lipid adsorption does not take place if the asbestoses have previously adsorbed some protein. Consequently, initial adsorption of lecithin does not prevent subsequent adsorption of protein.

Discussion

In order to correlate the present findings about the surface chemistry of asbestos with the real problem of asbestosis it is necessary to analyse the present theories of asbestosis.

Asbestosis is a disease in which mainly the lungs are affected first and subsequently other symptoms develop. One of the main characteristics of this disease in human being is the presence of numerous "asbestos bodies". These particles are normally covered with a coating of protein. The main pathological change in asbestosis is lung fibrosis.

An enormous amount of work has been published about the action of asbestos dusts on the lungs of living beings such as guinea pig, rat, etc. But most of these papers discuss the intake of the asbestos particles by the cells of lungs and development of the disease with time. Actual theories as to the mechanism involved in the initiation of asbestosis are not many in the literature and there is no generally accepted explanation of how asbestos produces fibrosis. However, a short review of some of the works so far published about the effect of asbestos on living systems and different explanations put forward are summarised below.

1. Mechanical theories:

Vorwald et al. (120), from their inhalation experiments, concluded that "the disease is caused by an unusual mechanical irritation due to the long fibres; this irritation is related to the peculiar filamented structure of fibre and associated with the flexibility". With ignited chrysotile which lost its peculiar structural shape they did not find any symptoms

of asbestosis. Since it takes place in an organ of high mobility - lung - and also in the peritoneum, where there is also a degree of movement, but not in organs like liver, spleen, etc., they believe the cause to be mechanical one. Although this group of authors suggested the cause of asbestosis to be mechanical irritation, it is not very clear from their work how the irritant action finally leads to the development of fibrosis.

Following this theory, many other workers tried to show evidence that the cause of the disease is associated with the size and shape of the fibres rather than due to any chemical reactions. Schmidt (121) believes that asbestos types chrysotile, amosite and crocidolite are all soft pliable and are dangerous to health as they can enter the alveolar tracts more readily than the hard needle-like fibres of tremolite and anthophyllite. Parazzi et al. (122) studied the cytotoxic effect of asbestos dusts by incubating asbestos dusts in cultures of guineapig macrophages and found that toxicity was largely attributable to the fibrous fraction of the dust samples. From this observation they suggested that toxic action may be related to the physical rather than the chemical nature of the fibre. Bryks and Bertalanffy (123) injected natural chrysotile and synthetic chrysotile separately intratracheally to rats and observed very few changes in rats treated with synthetic chrysotile. They suggested that the greater fibre length of the natural chrysotile may be a significant factor in its greater irritant effect compared to synthetic chrysotile (which has only short fibrils). Stanton and Wrench (124) very recently injected different forms of asbestos and fibrous glass into pleura of rats and observed the development of carcinogenicity. From the result they commented that carcinogenicity of asbestos and fibrous glass seems primarily related to the structural shape of the material rather than physiochemical properties.

2. Chemical theories:

Knox and Beattie (125) tried to give a chemical explanation to the cause of the disease. In their long series of experiments they did not find any relationship between the onset of the disease and the absolute amount of mineral present in the lung. They found the severity of the disease was related to the changes occurring in inhaled material. They suggested that as a result of this change a fibrogenic substance is released which is capable of exerting its effect. But they failed to explain the nature of the fibrogenic substance.

Beattie(126) in his later work showed some evidence that asbestos fibres break up in the lungs. Since the longest fibres cannot be removed from the lung by phagocytosis or cilia action, they get coated with a protective protein to form asbestos bodies which accumulate over the years. He has suggested that rapid fibrosis occurs due to the breakdown of these bodies when the lung is affected by other pathological conditions; when the bodies disintegrate the crystalline bundles are also broken up into small pieces and rapid release of large number of small dust particles could affect sufficient macrophages to produce a considerable degree of fibrosis.

Rath (127) believes that the origin of asbestosis is related to the nature of chrysotile. Since chrysotile has the form of tubular structure, the formation of asbestosis bodies results due to the diffusion of dissolved Si, Fe, and Mg out of the ends of the tubes.

2(a). Dissolved silica theory:

Clark and Holt (39) put forward a more clear chemical theory based on the action of silica released from chrysotile. From the studies on

the solubility of chrysotile they suggested that at lung pH 7 the dissolution of $Mg(OH)_2$ from the surface will be slow and that the surface of $Mg(OH)_2$ may adsorb protein in the initial phase of the production of an asbestos body. But since in an inflammatory reaction the tissues become first alkaline then acidic, the process of dissolution may be accelerated. As the $Mg(OH)_2$ layer is removed the silica will then follow. If silica is released in any form other than orthosilicic acid, it would most likely be in the form of fragments of the silica sheets. These particles will then be ingested by phagocytes as particles of silica dust and finally biological reaction will proceed similar to that in pure silicosis.

In this connection the postulated mechanism of fibrogenesis in silicosis published by Holt and his co-worker should be considered and that in combination with the above theory may serve as a full theory of asbestosis. Holt and Went (128) suggested that simple silicic acid is formed inside the cytoplasm and then diffuses out. Fibrogenesis then takes the following sequence "normally the response of a cell to certain stimuli is the production of a collagen precursor in the form of very small units which are prevented from aggregation by the large amounts of polysaccharide which are secreted simultaneously. Most of the polysaccharide is later removed by polysaccharases, allowing alignment of fibrils and production of fibres with which a small amount of polysaccharide is associated as a cementing substance. In normal fibrogenesis an equilibrium may be established, fibres being built up and others being simultaneously dispersed. When silicic acid is produced along with collagen precursor it is adsorbed irreversibly. Aggregation of collagen chains is prevented by the polysaccharide which is produced by the cells at the same time but once the complex diffuses away from the cells and the polysaccharide is hydrolysed, the

adsorbed silicic acid provides a cement substance which is permanent; there is no dispersion of the fibres".

Holt, Mills and Young (129) from their experiment with rats concluded that high concentrations of chrysotile dusts of small particle size ($< 3 \mu\text{m}$) rapidly produce fibrosis. They suggested the following steps for the development of the disease. "The asbestos worker inhales a mixed dust and may retain fibres of any length below perhaps $100 \mu\text{m}$. Particles in the lung below about $5 \mu\text{m}$ are taken up by phagocytes and if the dust concentration is not too high, they may be removed by lymph-glands. The larger asbestos fibres become coated with protein. The asbestos bodies remain in the lung and accumulate over the years. After some years, perhaps, because of change in the pH, they begin to desintegrate, producing a very large number of asbestos fragments which are collected into phagocytes. These produce a fibrotic process which is similar to that produced by the heavy doses of short fibres".

2(b). Theories based on surface $\text{Mg}(\text{OH})_2$:

More recently many authors have published information about the haemolytic activity of different asbestoses although the relation between haemolysis and fibrosis or asbestosis is not yet definitely established.

Schnitzer and Pundsack (130) studied the haemolytic effect of different asbestoses on sheep erythrocytes. They found that chrysotile was more haemolytic than crocidolite and amosite and that haemolytic effect of chrysotile could be inhibited by the use of EDTA. They further observed a marked correlation between the haemolytic activity and the degree of opening of fibres. Since other mineral sources of magnesium hydroxide

(except nemalite - a fibrous variety of brucite) are not haemolytic, the possible role of surface magnesium hydroxide remains uncertain. Moreover, amphiboles which have a silica-like surface and produce asbestosis, were found to be inactive as haemolytic agents whereas silica in the form of quartz dust is haemolytically active. Because of these apparently contradictory findings they failed to produce a satisfactory chemical explanation for the mechanism of haemolysis by asbestos.

Harington et al (131) studied the haemolytic activities of different asbestoses and found that chrysotile was more haemolytic than amosite and crocidolite. They further observed that haemolysis by chrysotile could be inhibited by EDTA or sialic acid. (Sialic acid, also called N-acetyl neuraminic acid is an amino sugar acid, it forms an important constituent of cell membrane). From these observations they suggested that magnesium ions from the chrysotile surface may combine with the anionic carboxylic group of sialic acid on the cell membrane during haemolysis.

3: Physico-chemical theories:

Davis (132, 133) examined the effect of asbestos dusts on lungs. By electronmicroscopic examination he was able to detect intracellular damage of the cells in the lung and also intracellular crystal disintegration from which he suggested that asbestosis is caused by a combination of mechanical and chemical effects. In his experiment with guineapigs, dust particles were found only in three types of cell - lung macrophages, giant cells and fibroblasts. The concentration of fibroblasts containing dust was more in the areas of large fibrosis. But he failed to produce any definite information about the formation of asbestos bodies and suggested that it could be a complex process. In his subsequent paper, he tried to

explain the formation of dust-containing fibroblasts and giant cells from macrophages.

Supported by some experimental evidence Davis suggested that macrophages are attracted from all directions to an area of chronic irritation caused by a foreign particle and they unite on its surface forming a giant cell which protects the neighbouring cells. He was also able to trace the formation of fibroblast with dust particles and suggested that small giant cell may be involved in the formation of fibroblasts.

Recently Allison (115) has put forward a more clear physico-chemical theory. He studied the interaction of asbestos fibres and macrophage cells and observed that short fibres ($< 5 \mu\text{m}$) were completely taken up by phagocytes whereas longer fibres ($> 30 \mu\text{m}$) were not. The cells were closely attached to - or enveloped - the ends of the fibrils. With very long fibres two or more cells could sometimes be seen attached to a single fibre sometimes with continuity of cytoplasm. These cells attached to long fibres in the presence of serum remained healthy for about a week; but when the fibres were added to macrophages in buffered saline lacking serum, a cytotoxic effect rapidly occurred. Release of proteinaceous cytoplasmic enzyme from the cell, sudden cessation of movement and "blebbing" of the cell membrane were detected within one hour of exposure to asbestos. From these observations he suggested that the rapid cytotoxic effect of asbestos is due to a direct interaction of asbestos fibres with cell membranes, analogous to haemolysis. In his experiments on long-term effects of asbestos fibres on macrophages and mesothelial cells he observed that the fibres were taken up into vacuoles which became secondary lysosome and 20% of the cells were no longer viable. Another striking abnormality he observed was the development in mesothelial cells and to some extent

in macrophages of brown pigmented auto-fluorescent granules in the cytoplasm which increased after ingestion of crocidolite. He further observed the development of an electron-dense matrix surrounding the asbestos particle in the secondary lysosome. This might provide a protective layer between the asbestos particle and the vulnerable membrane of secondary lysosome for which it becomes less toxic than would be expected from its capacity to react with membranes as shown by haemolysis. From these observations Allison suggested that slow progressive damage to the macrophages produced by asbestos may be an important factor in the fibrotic reaction to asbestos.

However, Allison's theory is questionable in some respects - firstly, whether his model experiment on macrophages are relevant to the condition existing inside the lung; secondly, whether the air-borne asbestos particles inside the lung will align themselves in places where they will be able to come in contact with the mesothelial cells of the peritoneum. Some authorities are of the opinion that any particle that touches the mucus-covered trachea would adhere and would subsequently be removed by phagocytosis. These particles would not be the cause of asbestosis. Since cell membranes are rich in phospholipids, the present result on the adsorption of lecithin might be considered to lend some support to the theory of Allison. However, in the present project it has also been proved that the asbestos particles which have already adsorbed some protein would fail to be wetted by lipid. If the asbestos particles came first into contact with the mucus lining the air-ways to the inner lungs, they would change their subsequent interactions with lipids and membranes.

According to Pattle (116) the alveoli of mammalian lung contains fluid lipoprotein lining of $50 \text{ \AA}$ thickness. Thus, the cell walls and

the lining of the alveoli seem to be rather similar in chemical nature. If the cell membrane can be involved in a surface-chemical reaction with the asbestos particles, the alveolar lining will not be excluded. But it seems difficult to ascertain whether air-borne micro-particles of asbestos enter the lung proper without having first made contact with the walls of the trachea..

Therefore, because of the insufficiency of knowledge as to the mechanism how the particles arrive at the lungs proper, no firm conclusions can be made about the subsequent capillary reactions taking place.

4. Immunological theory:

Massey, Lemonde and Fournier-Massey (134) in a recent paper reviewed theories attempting to explain the mechanism of silicosis and asbestosis from the stand point of immunology. Quoting the work of various other experimenters, they have shown evidence that adsorption of proteins on silica denatures the proteins ; this then makes them antigenic, i.e. induces autoimmunological reactions. But finally Massey, Lemonde and Fournier-Massey expressed doubt whether this action of silica could be the fundamental mechanism of fibrogenesis. Nor could they produce any evidence as to whether asbestos alone can be antigenic. The theory remains controversial and unsettled.

5. Theory that carcinogenicity of asbestos is due to trace of organic matter and metal content:

Harrington and Roe (135) were able to extract natural oils from amosite and crocidolite. In the extracted oil they found traces of polycyclic

organic compounds which are supposed to be carcinogenic. From the results of some further preliminary experiments of applying these oils to mouse skin, they suggested that the asbestos oils possess incomplete carcinogenic activity of either tumour-initiating or tumour-promoting type. The same group of authors also suggested that the carcinogenic property of asbestos (chrysotile, amosite and crocidolite) may be associated with their metal content mainly iron, since certain iron complexes (iron-dextran, saccharated iron oxide, ferrous-glutamate) are known to be carcinogenic.

An examination of the results of the present project in the light of the available theories suggests that, besides the processes of normal adsorption of biologically active material, a physical process of preferential wetting of asbestos surface due to capillary forces by the material in the cell membrane may be one of the preliminary steps in the formation of asbestos bodies (cf. Allison's theory). Therefore, further work with non-living membranes composed of the different constituents of living cell membrane (eg. lipid, protein, carbohydrate) and their interaction with asbestos particles may throw some light on the physico-chemical processes involved in the process of slow and progressive damage of cells by asbestos particles.

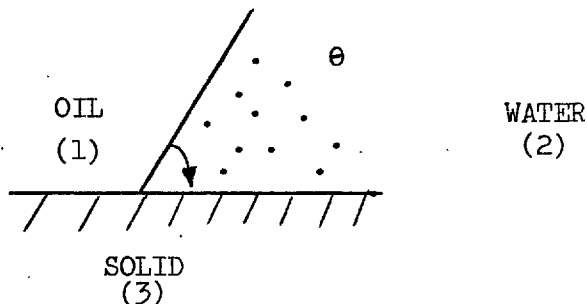
However, at this stage, because of the insufficiency of knowledge as to the mechanism by which the particles arrive at the lungs proper, no firm conclusions can be made about the subsequent capillary reactions taking place. It seems certain that the high energy surface of any fresh mineral particles would interact strongly with the proteins and lipids inside the lung. How their presence leads to the specific diseases of asbestosis and mesothelioma remains, however, completely obscure. It is not even firmly established whether different mineral dusts are really specifically active,

as the differences of "dustiness" and exposure experience with different minerals might largely account for apparent differences of incidences of lung disease. A unique property, for example, of the asbestos minerals is their tendency to break up into separate fibrils when crushed and so release exceedingly light fragments in great numbers, such micro-needles being more readily transported by a current of air than are spheroidal particles of the same mass and, conversely, less easily removed by phagocytosis than, say, cement dust particles. Consequently any further extensive work in the non-living model system may not be of much help until further information is available on possible physiological mechanisms.

APPENDICES

Appendix - 1

Thermodynamic conditions for preferential wetting
by oil or water or a finite contact angle at the
oil/water/solid interface.



Considering two pure liquids oil (1) water (2) mutually saturated there can be three possible cases when a solid is brought in contact:

- the solid is preferentially wetted by water: contact angle θ (defined in phase 2) = 0°
- the solid is preferentially wetted by oil: $\theta = 180^\circ$.
- a finite contact angle at equilibrium is formed.

If the solid is in the form of small particles, shaken with two liquids - in case (a) the particles will remain in the water phase, in case (b) in the oil phase, and in case (c) at the interface of oil and water.

Which case prevails will depend on the work of adhesion of (3) to (2) and (1) i.e. of solid to water and oil. The work of adhesion terms W_{13} and W_{23} (work of adhesion of solid to oil and that of solid to water respectively) are defined by

$$W_{13} = \gamma_1^0 + \gamma_3^0 - \gamma_{13} \quad \text{eqn. (1)}$$

$$W_{23} = \gamma_2^0 + \gamma_3^0 - \gamma_{23} \quad \text{eqn. (2)}$$

The γ terms are surface energies (or tensions), 1^0 and 2^0 mean the vapour/liquid interface, although no vapour phase is present in the system itself.

It is obvious that if $W_{23} \gg W_{13}$, case (a) will prevail while $W_{13} \gg W_{23}$ will give case (b) and case (c) will require W_{13} and W_{23} to be at least of the same order of magnitude.

Limits for a finite contact angle

. . If an equilibrium is formed, by Young's equation

$$\gamma_{13} = \gamma_{23} + \gamma_{12} \cos \theta$$

$$\text{or} \quad \gamma_{13} - \gamma_{23} = \gamma_{12} \cos \theta \quad \text{eqn. (3)}$$

Subtracting equation (1) from (2) and substituting in equation (3)

$$(W_{23} - W_{13}) - (\gamma_2^0 - \gamma_1^0) = \gamma_{12} \cos \theta \quad \text{eqn. (4)}$$

For case (a), $\theta \rightarrow 0^\circ$: $\cos \theta \rightarrow +1$

Therefore case (a) prevails if

$$W_{12} \geq W_{13} + \gamma_2^0 - \gamma_1^0 + \gamma_{12} \quad \text{eqn. (5)}$$

For case (b), $\theta \rightarrow 180^\circ$: $\cos \theta \rightarrow -1$

Therefore case (b) prevails if

$$W_{23} \leq W_{13} + \gamma_2^0 - \gamma_1^0 - \gamma_{12} \quad \text{eqn. (6)}$$

For $\theta = 90^\circ$, $\cos \theta = 0$

$$W_{23} = W_{12} + \gamma_2^0 - \gamma_1^0$$

In the case of benzene and water (mutually saturated) - according to Harkins

$$\gamma_1^0 = 28.9 \text{ erg/cm}^2$$

$$\gamma_2^0 = 62.4 \text{ "}$$

$$\gamma_{12} = 35 \text{ "}$$

i.e.

$$\gamma_2^0 - \gamma_1^0 + \gamma_{12} = 67.5 \text{ (case (a))}$$

$$\gamma_2^0 - \gamma_1^0 - \gamma_{12} = -1.5 \text{ (case (b))}$$

Therefore for $\theta \rightarrow 180^\circ$

$$W_{23} \leq W_{13} - 1.5$$

When the work of adhesion of solid to water is less than the work of adhesion of solid to oil, the solid will be preferentially wetted by the oil phase.

It is obvious that these equations should reduce to the simpler ones for the wetting of a single liquid if phase (1) is now considered to have no cohesive energy i.e. replace oil by vapour.

$$\therefore \gamma_1^0 = 0, W_{13} = 0, \gamma_{12} = \gamma_2^0$$

Equation (4) becomes

$$(W_{23} - 0) - (\gamma_2^0 - 0) = \gamma_2^0 \cos \theta$$

$$W_{23} = \gamma_2^0 (1 + \cos \theta)$$

Equation (5) becomes

$$W_{23} \geq 0 + \gamma_2^0 - 0 + \gamma_2^0$$

$$W_{23} \geq 2 \gamma_2^0$$

i.e.

$$W_{23} \geq W_{22}$$

Work of adhesion	Work of cohesion
---------------------	---------------------

Equation (6) becomes

$$W_{23} \leq 0 + \gamma_2^0 - 0 - \gamma_2^0$$

i.e. $W_{23} \leq 0$, which is physically impossible, since there is a net attraction between any two condensed phases. Therefore the case of $\theta = 180^\circ$ for a single liquid on solid is impossible.

A more rigorous treatment including "equilibrium spreading pressure"

(π) (private communication from Dr Paddey, Kodak Research Laboratory) leads to the same conclusion.

APPENDIX II

ELECTRONMICROGRAPHS.



Fig. 31. Electronmicrograph of chrysotile (Bells)
dispersed in water with surfactant.
(Magnification: 21,850 x)



Fig. 32. Electronmicrograph of amosite dispersed
in water with surfactant.
(Magnification : 8,400 x)



Fig. 33. Electronmicrograph of crocidolite mechanically dispersed in water.
(Magnification : 10,580 x)

REFERENCES

1. Hodgson, A.A.
"fibrous Silicates"
Roy. Inst. Chem. Lect. Series, No. 4, 1965.
2. Deer, W.A., Howie, R.A. and Zussman, J.
"Rock Forming Minerals"
(Longmans, London, 1963), 2, 203-48.
3. Gard, J.A. (Editor)
"Electron optical investigation of clays"
(Mineralogical Society, 1971), 255-75.
4. Deer, W.A., Howie, R.A. and Zussman, J.
"Rock Forming Minerals"
(Longmans, London, 1963), 3, 170-90.
5. Bowen, N.L. and Tuttle, O.F.
"The System $\text{MgO-SiO}_2\text{-H}_2\text{O}$ "
Bull. Geol. Soc. Am., 60, 1949, 439-60.
6. Hendry, N.W.
"The Geology, Occurences and Major Uses of Asbestos"
Ann. NY. Acad. Sci., 132, 1965, 12-22.
7. Warren, B.E. and Bragg, L.W.
"The Structure of Chrysotile, $\text{H}_4\text{Mg}_3\text{Si}_2\text{O}_9$ "
Z. Krystallog., 76, 1930, 201-10.
8. Warren, B.E. and Haring, K.W.
"The Random Structure of Chrysotile"
Phys. Rev., 59, 1941, 925.
9. Whittaker, E.J.W.
"The Structure of Chrysotile"
Acta Cryst., 6, 1953, 747-48.

10. Bates, T.F., Sand, B.L. and Mink, J.F.
"Tubular Crystals of Chrysotile Asbestos"
Science, 111, 1950, 512-13.
11. Turkevich, J. and Hiller, T.
"Electron Microscopy of Colloidal Systems"
Anal. Chem., 21, 1949, 475-85.
12. Noll, W. and Kercher, H.
"On the morphology of chrysotile asbestos"
Naturwiss, 37, 1950, 540-41.
13. Pundsack, F.L.
"The properties of asbestos. II. The density and structure of chrysotile"
J. Phys. Chem., 60, 1956, 361-64.
14. Whittaker, E.J.W.
"Structure of Chrysotile. V. Diffuse Reflexions and Fibre Texture"
Acta Cryst., 23, 1957, 1949-55.
15. Yada, K.
"Study of Chrysotile Asbestos by a High Resolution Electron Microscope"
Acta Cryst., 23, 1967, 704-07.
16. Whittaker, E.J.W.
"The Structure of Chrysotile!"
Acta Cryst., 6, 1953, 747-48.
17. Whittaker, E.J.W.
"An Orthorhombic Variety of Chrysotile"
Acta Cryst., 4, 1951, 187-88.
18. Whittaker, E.J.W.
"The Structure of Chrysotile. II Clino-Chrysotile."
Acta Cryst., 9, 1956, 855-61
19. Whittaker, E.J.W.
"The Structure of Chrysotile. III Ortho-Chrysotile".
Acta Cryst., 9, 1956, 862-64.

20. Whittaker, E.J.W.
 "The Structure of Chrysotile. IV. Para-Chrysotile"
Acta Cryst., 9, 1956, 865-67
21. Harington, J.S.
 "Chemical Studies of Asbestos"
Ann. NY. Acad. Sci., 132, 1965, 31-47.
22. Vermaas, F.H.S.
 "The Amphibole Asbestos of South Africa"
Trans. Geol. Soc. South Africa, 55, 1952, 199-231
23. Gaze, R.
 "Physical and Molecular Structure of Asbestos"
Ann. NY. Acad. Sci., 132, 1965, 23-30.
24. Warren. B.E.
 "The Structure of tremolite, $H_2CaMg_5(SiO_2)_8$ "
Z. Krystallog., 72, 1929, 42-57.
25. Pauling, L.
 "Nature of the Chemical Bond"
 (Oxford and I.B.H. Co. Calcutta, 1960), 167.
26. Gibb, T.N. and Greenwood, N.N.
 "Chemical Applications of the Mössbauer Effect."
Trans. Faraday Soc., 61, 1965, 1317-23
27. Spiel, S. and Leinweber, J.P.
 "Asbestos Minerals in Modern Technology"
Env. Res., 2, 1969, 166-208.
28. Addison, C.C., Addison, W.E. and Sharp, J.H.
 "Amphiboles. Part I. The Oxidation of Crocidolite."
J. Chem. Soc., 278, 1962, 1468-71
29. Addison, W.E. Neal, G.H. and Sharp, J.H.
 "Amphiboles. Part II. The Kinetics of Oxidation of Crocidolite."
J. Chem. Soc., 279, 1962, 1472-75.

30. Addison, W.E. and Sharp, J.H.
"Amphiboles. Part III. The Reduction of Crocidolite"
J. Chem. Soc., 716, 1962, 3693-98.
31. Hodgson, A.A., Freeman, A.G. and Taylor, H.F.W.
"The Thermal Decomposition of Amosite".
Mineralog. Mag., 35, 1965, 445-63.
32. Hodgson, A.A. Freeman, A.G. and Taylor, H.F.W.
"The Thermal Decomposition of Crocidolite from Koegas,
South Africa".
Mineralog. Mag., 35, 1965, 5-30.
33. Hodgson, A.A.
"The Thermal Decomposition of Miscellaneous Crocidolite"
Mineralog. Mag., 35, 1965, 291-305.
34. Stumm, W. and Morgan, J.J.
"Aquatic Chemistry"
(Willey-Interscience, New York, 1970), 194.
35. Irving, S.N.
"Dangerous Properties of Industrial Materials"
(Rheinhold Publishing Corporation, NY., 1957), 440.
36. McVitte, J.C.
"Asbestosis in Great Britain."
Ann. N.Y. Acad. Sci., 132, 1965, 128-38.
37. Selikoff, I.J. and Churg, J.
"The occurence of asbestosis among insulation workers in
the United States".
Ann. NY. Acad. Sci., 132, 1965, 139-55.
38. "Problems arising from the use of asbestos".
Memorandum of the Senior Medical Inspector's Advisory Panel."
(H.M.'s Stationery Office, 1967).

39. Clark, S.G. and Holt, P.F.
"Studies of the Chemical Properties of Chrysotile in Relation to Asbestosis".
Ann. Occup. Hyg., 3, 1960, 22-29.
40. Clark, S.G. and Holt, P.F.
"Dissolution of Chrysotile in Water, Acid and Alkali"
Nature, 185, 1966, 237.
41. David, D.J.
"The Determination of Exchangeable Sodium, Potassium, Calcium and Magnesium Ions in Soil by Atomic Absorption Spectroscopy".
Analyst., 85, 1960, 495-503.
42. Wallace, F.J.
"The Determination of Magnesium in Aluminium Alloys by Atomic Absorption Spectroscopy".
Analyst., 88, 1963, 259-65.
43. Willis, J.B.
"Determination of Calcium and Magnesium in Urine by Atomic Absorption Spectroscopy".
Analyt. Chem., 33, 1961, 556-61.
44. Jeffery, P.G. and Wilson, A.D.
"A Combined Gravimetric and Photometric Method for Determining Silica in Silicate Rocks and Minerals".
Analyst., 85, 1960, 478-86.
45. Iler, R.K.
"Colloid Chemistry of Silica and Silicates"
(Cornell University Press, New York, 1955) 20-21.
46. Hostetler, P.B.
"The stability and surface energy of brucite in water at 25°C".
Am. J. Sci., 261, 1963, 238-58.

47. Badollet, M.S.
 "Asbestos, A Mineral of Unparalleled Properties"
Trans. Can. Inst. Mining Met., 54, 1951, 151-60.
48. Pundsack, F.L.
 "The properties of asbestos, I. The colloidal and surface chemistry of chrysotile".
J. Phys. Chem., 59, 1955, 892.
49. Pundsack, F.L. and Reimschuessel, G.
 "The properties of asbestos. III Basicity of chrysotile suspensions".
J. Phys. Chem., 60, 1956, 1218-22.
50. Hostetler, P.B. and Christ, C.L.
 "Studies in the system $\text{MgO-SiO}_2\text{-CO}_2\text{-H}_2\text{O}(l)$. The activity-product constant of chrysotile".
Geochim. et. Cosmochim., 32, 1968, 485-97.
51. Choi, I. and Smith, R.W.
 "Kinetic Study of Dissolution of Asbestos Fibres in Water".
J. Coll. Sci., 42, 1972, 253-62.
52. Atkinson, A.W. and Rickards, A.L.
 "Acid decomposition of highly opened chrysotile".
Physics and Chemistry of Asbestos Minerals (Second Int. Conf. Louvain, 1971), paper 3:1.
53. Monkman, L.J.
 "Some chemical and mineralogical aspects of the acid decomposition of chrysotile"
Physics and Chemistry of Asbestos Minerals (Second Int. Conf. Louvain, 1971), paper 3:2.
54. Millot, G.
 "Geology of Clays"
 (Chapman and Hall, London, 1970,) 61.

55. Wey, R. and Siffert, B.M.
"Synthesis of sepiolite at ordinary temperature".
C.R. Acad. Sci., 254, 1962, 1460-61.
56. Private communication from Turner Brothers Asbestos Co.
57. Mellor, J.W.
"Comprehensive Treatise of Inorganic Chemistry"
(Longmans, London, 1923), IV, 290.
58. Whittaker, E.J.W. and Zussman, J.
"The characterisation of serpentine minerals by X-ray diffraction".
Mineralog. Mag., 31, 1956, 107-26.
59. Deer, W.A. Howie, R.A. and Zussman, J.
"An Introduction to Rock Forming Minerals"
(Longmans, London, 1966), 248.
60. Atkinson, A.W. and Gettins, R.B.
"Estimation of Fibril Lengths in Chrysotile Asbestos Fibres".
Nature, 226, 1970, 937-38.
61. Atkinson, R.J.
Research Report (unpublished),
Department of Mineral Technology, Imperial College, London.
62. Gettins, R.B. and Mellon, F.J.
"Adsorption of surface-active agent on chrysotile asbestos"
"Physics and Chemistry of Asbestos Minerals".
(Second Int. Conf. Louvain, 1971) paper 4:1.
63. Novak, I.J.
"Asbestos Dispersions".
U.S. Patent, 2, 626, 213, 1953.
64. Reh binder, P.A. and Lichtman, V.
"Effect of surface-active media on strains and rupture in solid".
Second Int. Conf. Surface Activity, III, 1953, 563.

65. Reh binder, P.A. and Shchukin, E.D.
"Surface Phenomena in Solids during Deformation and Fracture Processes"
Progress in Surface Science, (Editor, Davison, S.G., Pergamon Press, 1972).
66. Long, C.
"Biochemists' Handbook" (E.& F.N. Spon. Ltd., 1961), 839-93.
67. Bragg, L. and Claringbull, G.F.
"Crystal Structures of Minerals"
(G. Bell and Sons Ltd., 1965), 286.
68. Clark, S.W. and Cooke, S.R.B.
"Adsorption of calcium, magnesium and sodium ion by quartz"
Trans. A.I.M.E., 241, 1968, 334-41.
69. Willis, J.B.
"The determination of metal in blood serum by atomic absorption spectroscopy"
Spectrochimica Acta., 16, 1960, 257-72.
70. French, C.M. and Howard, J.P.
"Adsorption on Silica Gel"
Chemistry and Industry, June, 1956, 572.
71. Churms, S.C.
"Inorganic ion exchangers, part IV"
The South African Ind. Chem., May, 1965, 87-96.
72. Strazheska, D.N. and Yankovskaya, G.F.
"Investigation of adsorption of electrolytes on silica-gel by radio-active indicators"
Ukrain Khim. Zhur., 25, 1959, 471-76.
73. Gregg, S.J. and Sing, K.S.W.
"Adsorption Surface Area and Porosity"
(Academic Press, London, 1967), 107.

74. Young, G.J. and Healey, F.H.
"The Physical Structure of Asbestos"
J. Phys. Chem., 58, 1954, 881-84.
75. Young, G.J. and Healey, F.H.
"The Surface Properties of Chrysotile Asbestos"
J. Phys. Chem., 58, 1954, 885-86.
76. Yada, K.
"Study of the micro-structure of chrysotile by high resolution electron microscopy"
Acta Cryst., 27, 1971, 659-64.
77. Wells, F.G.
"The hydrothermal alteration of serpentine"
Am. J. Sci., 18, 1929, 35.
78. Syromytnikov, F.V.
"The problem of the transfer of silica by water vapours"
Econ. Geol. 30, 1935, 89.
79. Jander, W. and Wührer, J.
"Synthesis of chrysotile"
Z. Anor. Allg. Chem., 235, 1938, 273-94.
80. Yang, J.C.
"Growth of Synthetic Chrysotile"
Am. Mineralog., 46, 1961, 748-52.
81. Ovcharenko, F.D. and others.
"The Colloid Chemistry of Palygorskite"
(The Israel Program for Scientific Translation, Jerusalem, 1964), 17.
82. Henry, D.C.
"The Cataphoresis of Suspended Particles, Part I, The Equation of Cataphoresis."
Proc. Roy. Soc., A133, 1931, 106-29.

83. Overbeek, J. Th. G.,
"Quantitative interpretation of the electrophoretic velocity
of colloids"
Adv. Coll. Sci., 3, 1950, 97-136.
84. Booth, F.
"The cataphoresis of spherical, solid non-conducting particles
in a symmetrical electrolyte"
Proc. Roy. Soc., A203, 1950, 514-33
85. Parks, G.A.
"Aqueous surface chemistry of oxides and complex oxide mineral"
Equilibrium Concepts in Natural Water Systems (Washington:
American Chem. Soc., 1967, Adv. Chem. Ser. 67), 148.
86. Thiessen, P.A.
"Changeable adsorption in colloids"
Z. Electrochem., 48, 1942, 675-81.
87. Huber, V.O. and Weigl, J.
"Influence of electrokinetic charge of inorganic fillers on
different processes of paper making"
Wochenblatt für Papierfabrikation, 10, 1969, 359-70.
88. Redinha, J.S. and Kitchener, J.A.
Min. Tech. Progress Report (Imperial College), 43, 1972, 82-87.
89. Private communication from Dr. A.A. Hodgson, Cape Asbestos Co.,
London.
90. Zucker, G.L.
Ph.D. Thesis, Columbia University, 1959.
91. Churaev, N.V. and Deryaguin, B.V.
"Influence of overlapping of diffuse ionic layers on electrokinetic
effects in thin films and pores"
Coll. J. U.S.S.R., 28, 1966, 608-12.

92. Martinez, E. and Zucker, G.L.
 "Asbestos Ore Body Minerals Studied by Zeta-Potential Measurements".
J. Phys. Chem., 64, 1960, 924-26.
93. Gracheva, O.I. and Epinateva, V.I.
 "Electrokinetic properties of chrysotile from various U.S.S.R
 deposits"
Trans. Vses. Nauch-Issled. Proekt: Inst. Asbestosem. Izdevi,
Nyagkikh Krovelnykh Gridroizol. Mater., 26, 1971, 22-49.
94. Naumann, A.W. and Drescher, W.H.
 "Colloidal Suspension of Chrysotile Asbestos: Surface Charge
 Enhancement"
J. Coll. Sci., 27, 1968, 133-40.
95. "Stability Constants", Special Publication No. 17 (Chem. Soc.,
 London), 52-53.
96. Brindley, G.W. and Zussman, J.
 "Infra-red absorption data for serpentine minerals"
Amer. Mineralog., 44, 1959, 185-88.
97. Saksena, B.D.
 "Infra-red absorption studies of some silicate structures"
Trans. Faraday Soc., 57, 1961, 240-55.
98. Le Comte, J.
 "Infra-red Spectroscopy"
Handbuch der Physik, (Springer Verlag, 1958) 26, 839.
99. Patterson, J.H. and O'Connor, D.J.
 "Chemical Studies of Amphibole Asbestos"
Aust. J. Chem., 19, 1966, 1155-64.

100. Peck, A.S., Raby, L.H. and Wadsworth, M.E.
 "An infra-red Study of flotation of hematite with oleic acid
 and sodium oleate"
Trans. A.I.M.E., 235, 1966, 301-07.
101. Cockbain, E.G.
 "Adsorption of Serum Albumin and Sodium Dodecyl Sulfate at
 Emulsion Interface"
J. Coll. Sci., 11, 1956, 575-84.
102. Biswas, B. and Haydon, D.A.
 "The rheology of some interfacially adsorbed films of
 macromolecules. I. Elastic and creep phenomena".
Proc. Roy. Soc., A271, 1963, 296-316.
103. Moser, P. Squire, P.G. and O'Konski, C.T.
 "Electric Polarisation of Proteins-Dielectric Dispersion and
 Kerr-Effect Studies of Isotonic Bovine Albumin"
J. Phys. Chem., 70, 1966, 744.
104. Hair, M.L.
 "The Chemistry of Biosurfaces"
 (Dekkar Inc. NY. 1971), I, 96.
105. Vallentine, R.C.
 "The Shape of Protein molecules suggested by electron microscopy"
Nature, 184, 1959, 1839-41.
106. Oncley, J.L.
 "Physical+chemical characteristics of certain proteins of normal
 human plasma".
J. Phys. Chem., 51, 1947, 134.
107. Pankhurst, K.G.A. and Danielli, J.F.
 "Surface Phenomena in Chemistry and Biology"
 (Pergamon Press, London, 1958), 103.

108. Augenstine, G.L. and Roy, B.R.
 "Trypsin monolayers at the water-air interface. I. Film
 characteristic and recovery of enzymatic activity".
J. Phys. Chem., 60, 1956, 1193-99.
109. Calissano, P., Moore, B.W. and Friesen, A.
 "Effect of Calcium Ion on S-100, a Protein of Nervous System"
Biochemistry, 8, 1969, 4318-26.
110. Neurath, H.
 "The Proteins"
 (Academic Press, 1970) V, 66-69.
111. Bergman, I. and Nelson, E.S.
 "The polymerisation of silicic acid with proteins and other
 hydrogen-bonding agent"
J. Coll. Sci., 17, 1962, 823-37.
112. Pernis, B. and Balligeli, M.
 "Adsorption of silica; its possible significance in the
 causation of silicosis"
Med. Lavoro, 46, (1955), 1-13.
113. Nash, T., Allison, A.C. and Harington, J.
 "Physico-chemical properties of silica in relation to its toxicity"
Nature, 210, 1966, 259-61.
114. Hess, E.L. and Deutsch, H.F.
 "Biophysical Studies of Blood Plasma"
J. Am. Chem. Soc., 71, 1949, 1376.
115. Allison, A.C.
 "Lysosomes and the Toxicity of Particulate Pollutants"
Arch. Intern. Med., 28, 1971, 131-39.
116. Pattle, R.E.
 "Surface Lining of Lung Alveoli"
Physiolog. Rev., 45, 1965, 48-79.

117. Takakuwa, T. and Takamori, T.
"Phase inversion method for flotation study"
Proc. 6th Int. Min. Proces. Congr. (Pergamon Press, 1963), 1-11.
118. Bartell, F.E. and Zuidema, H.H.
"Wetting Characteristics of Solids of Low Surface Tension such
as Talc, Waxes and Resins."
J. Am. Chem. Soc., 58, 1936, 1449-54.
119. Satake, K. Okuyama T. et al.
"The spectrophotometric determination of amine, amino acid and peptide
with 2,4,6, Trinitrobenzene sulphonic acid."
The J. Biochem., 47, 1960, 654-60.
120. Vorwald, A.J., Durkan, T.M. and Pratt, P.C.
"Experimental Studies of Asbestosis"
Arch. Industr. Hyg., 3, 1951, 1-43.
121. Schmidt, K.G.
"Asbestos types: their optical investigation and their
pathological action".
Staub., 20, 1960, 173-80.
122. Parazzi, E. and Pernis, B.
"Cytotoxicity of asbestos dusts"
Med. Lavaro., 59, 1967, 561-76.
123. Bryks, S. and Bartalanffy, F.D.
Cytodynamic reactivity of mesothelium. Pleural reaction to
crysotile asbestos".
Arch. Env. Health, 23, 1971, 469-72.
124. Stanton, M.F. and Wrench, C.
"Mechanism of mesothelioma induction with asbestos and fibrous glass"
J. Nat. Cancer Inst., 48, 1972, 797-821.

125. Knox, J.F. and Beattie, J.
"Mineral content of lungs after exposure to asbestos dust"
Arch. Industr. Hyg., 10, 1954, 23-34.
126. Beattie, J.
"The Asbestosis Body"
Inhaled Particles and Vapours (Edited by C.N. Davis, Pergamon Press, 1961), 434-41
127. Rath, R.
"The form of changes in the formation of asbestosis bodies"
Beitr. Silikose-Forsch., 81, 1964, 3-10.
128. Holt, P.F. and Went, C.W.
"Studies on the nature of silicosis. A suggested mechanism of fibrogenesis"
Brit. J. Industr. Med., 17, 1960, 25-30
129. Holt, P.F. Mills, J. and Young, D.K.
"The early effects of chrysotile asbestos dust on the rat lung"
J. Path. Bacteriology, 87, 1964, 15-23.
130. Schnitzer, R.J. and Pundsack, F.L.
"Asbestos Hemolysis"
Env. Res., 3, 1970, 1-13.
131. Harington, J.S. Miller, K. and Macnab, G.
"Hemolysis by Asbestos"
Env. Res., 4, 1971, 95-117.
132. Davis, J.M.G.
"An electron microscopy study of the effect of asbestos dust on the lung".
Brit. J. Expl. Path., 44, 1964, 454-65.
133. Davis, J.M.G.
"The ultra-structural changes that occur during transformation of giant cells and fibroblasts in experimental asbestosis".
Brit. J. Expl. Path., 44, 1964, 568-75.

134. Massey, D., Lemonde, J. and Fournier-Massey, G.

"The immunological factors of asbestosis"

J. Union Med. Canada, 100, 1971, 1588-71.

135. Harington, J.S. and Roe, F.J.C.

"Studies of carcinogenesis of asbestos fibres and their
natural oils"

Ann. NY. Acad. Sci., 132, 1965, 439-50.