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Electrokinetic Behaviour of Asbestos Minerals

As a Function of Aging Time in Water

Ronald C. Smith
A thesis submitted in partial fulfillment of the
requirements for the degree of Master of Science in
Metallurgy

by

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ABSTRACT

The electrokinetic behaviour and dissolution in water of several ferromagnesium silicates were studied as a function of their aging time. The particular magnesium silicates studied were asbestiform and nonasbestiform varieties of serpentine, and crocidolite, a fibrous member of the amphibole group. Acid treated and untreated samples of the three minerals were studied.

Changes in the pH, point of zero charge (pzc) and electrophoretic mobilities were noted for various aging times upto ten weeks for two different (weight/volume) suspensions of these minerals. Concentrations of magnesium, iron and silicon were measured in the leachates at intermediate time intervals.

It was observed that the pzc's of these minerals are variable quantities and are dependent on the history of the minerals, on the ionic constituents of the suspensions and hence, on the pH of the suspensions. It was also noted that the dissolution of the magnesium silicates is a zero order kinetic reaction and that such a study can throw more light on the disputed structure of chrysotile.

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INTRODUCTION

Considerable data are available in the scientific literature about the behaviour of minerals in aqueous environments at high temperatures and pressures. Recently, attempts have been made to determine the behaviour of aqueous mineral suspensions at low temperatures and pressures. Not much is known, however, about the mechanism and rate of dissolution of many important groups of minerals. In some cases this may be because of extremely slow approaches of the dissolution reactions to equilibrium. It is often contended that the dissolution of suspended mineral particles in an aqueous medium is governed by a change in the surface charge of the mineral in suspension. The present investigation deals with the change in the surface charge of some asbestos minerals as a function of their aging time in water.

All asbestos minerals are essentially magnesium silicates containing comparatively high percentages of ferrous and ferric iron. In the present investigation, several asbestiform and one nonasbestiform ferromagnesium silicates were studied.

THE MAGNESIUM SILICATES:

The asbestiform minerals that are of value in industry are often classified according to their mineralogical constituents, chemical composition and crystalline form. They have been divided into the following distinct groups.

CLASSIFIED GROUPING OF THE RECOGNIZED
 ASBESTOS MINERALS¹

A. Serpentine Group:

Monoclinic - (1) Chrysotile
 (2) Picrolite

B. Amphibole Group:

Monoclinic - (1) Crocidolite
 (2) Tremolite
 (3) Actinolite

Ortho-
 rhombic - (1) Anthophyllite
 (2) Amosite

Chrysotile and crocidolite are the two monoclinic asbestiform minerals that have been selected here to represent the serpentine and amphibole groups respectively. In addition, a nonfibrous sample of serpentine was chosen for study. In short, this study is limited to chrysotile, crocidolite and serpentine, two asbestiform and one nonasbestiform magnesium silicates.

CHRYSOTILE, CROCIDOLITE AND SERPENTINE:

Serpentine is known to exist as a transformation product of olivine. It exhibits two different physical forms, but generally, has the same chemical composition. Chrysotile is a fibrous variety of serpentine and is classed as a hydrated magnesium orthosilicate containing a high percentage of magnesium and of water. In addition, chrysotile usually contains varying amounts of Fe^{**} and Fe⁺⁺⁺ oxides and alumina.

Its chemical composition may be expressed as $Mg_3Si_2O_5(OH)_8$. The nonfibrous variety, serpentine, has the same chemical composition, but is a noncrystalline layer silicate. An $Mg(OH)_2$ sheet is joined with an Si_2O_5 sheet by oxygen sharing. In the next layer, the $Mg(OH)_2$ sheet is joined to the oxygens of the Si_2O_5 sheet by hydrogen bonding. It is sometimes seen to exhibit monoclinic habit. Crocidolite is, chemically, a metasilicate of soda, ferrous and ferric oxides with water and magnesia. Its composition is extremely variable and could be represented by the formula, $2(Na_2O), 6(Fe, Mg)O, 2Fe_2O_3, 17SiO_2, 3H_2O$.²

SURFACE PROPERTIES - ELECTRICAL DOUBLE LAYER:

By "surface properties", as far as this investigation is concerned, it is meant the "aqueous surface properties". When an oxide or silicate mineral is fractured in air and subsequently immersed in water, it has been postulated that, positive and negative sites on the mineral surface attract OH^- and H^+ ions resulting into the hydroxylated surface on the mineral. It has been observed that when immersed in aqueous solutions, solid silicates and oxides develop an electrical charge. The origin of this charge at a solid-liquid interface has been definitely linked with the ionic strength of the solutions, the dissociation of the suspended mineral in the liquid phase and lately, to the presence of other ionic species in the suspension.

One possible mechanism for the production of surface charge on the minerals is the amphoteric dissociation of the surface hydroxyl

groups. The charge, according to another mechanism, is supposed to originate through an adsorption on the mineral surface of charged hydrolysis products of its dissolution or through a complete exchange of charged species of the liquid phase for those of the mineral surface.³ If no other ionic species is specifically adsorbed on the mineral surface, the charge on the mineral is determined by H^+ , OH^- and/or hydrolysis products that are adsorbed on the mineral surface. For this reason, they are called potential determining ions (pdi). This concept is discussed in greater detail in available literature.^{4,5}

In a suspension, at the solid-liquid interface, there exists what is called the "electrical double layer". In Stern's model⁶ of the electrical double layer, the inner layer has been described as "the anchored layer of charged ions, the charge being opposite to that on the mineral surface". The value of the potential difference applied in order to bring a unit (opposite) charge from an infinite distance in the bulk of the liquid to the plane of shear of the solid-liquid interface is called the zeta potential. Figure 1 is a pictorial representation of the electrical double layer and the variation of potential with distance in the diffuse layer.

It is the magnitude and sign of the zeta potential which acts as an indicator for the nature and extent of the charge at an aqueous surface. The point of zero charge, pzc, of the mineral is a very useful reference in order to predict the charge dependant behaviour of the minerals and their suspensions. The pzc has been defined as the pH at which the surface charge on the solid from all sources is zero, that is,

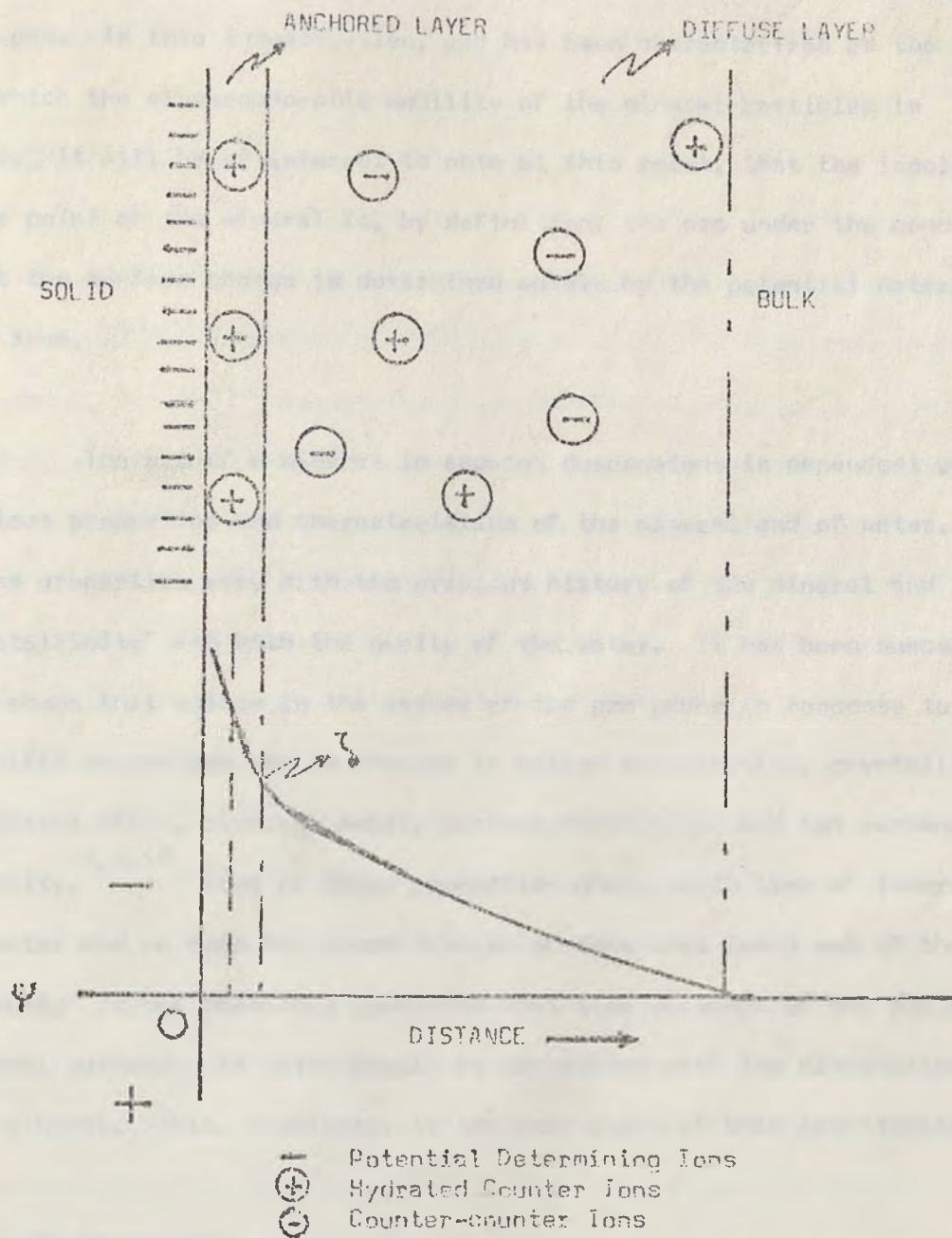


Figure 1. Stern's Model of the Electrical Double Layer

the zeta potential is zero.⁷ The surface of the mineral in suspension exhibits a negative charge in solutions which are more basic than the

pzc and it exhibits a positive charge in the solutions more acidic than the pzc. In this investigation, pzc has been characterized as the pH at which the electrophoretic mobility of the mineral particles is zero. It will be of interest to note at this point, that the isoelectric point of the mineral is, by definition, the pzc under the condition that the surface charge is determined solely by the potential determining ions.

The pzc of a mineral in aqueous suspensions is dependent upon various properties and characteristics of the mineral and of water. These properties vary with the previous history of the mineral and its crystallinity and with the purity of the water. It has been successfully shown that shifts in the values of the pzc occur in response to specific adsorption and to changes in cation coordination, crystallinity, hydration state, cleavage habit, surface composition and ion exchange capacity.^{8,9,10} Some of these properties change with time of immersion in water and so does the concentration of ions that leach out of the mineral. It has been thus contended that time variance of the pzc of a mineral suspended in water should be correlated with the dissolution of the mineral. This, precisely, is the main point of this investigation.

GOALS OF THIS STUDY:

One goal of this study is to determine, for the first time, the change in the pzc's of chrysotile, crocidolite and serpentine as a function of their aging time in water. Secondly, the change in the pzc's is to be correlated with the change in the pH of the suspension and change

in the concentrations of various ionic species or polynuclear hydroxocomplexes in the suspensions.

IMPORTANCE OF THIS STUDY:

A careful look at the following pages will reveal that this is the study of aqueous surface properties of a vitally important group of minerals. Asbestos minerals have been shown to be hazardous to health and to possess carcinogenic properties. The study of their electrokinetic behaviour will prove to be very important, because it is believed that "the aqueous surface properties and adsorptive properties in general, play a very significant role in initial adsorption of various oils and metal contaminants on the fibers and their behaviour in lungs and other organs."¹¹

In addition, van Olphen¹² and Mysels¹³ have reviewed the important role the surface charge of the mineral plays in ion exchange, rheology, sedimentation rate, adsorption of flotation reagents and flocculation. Colloids, presumably possessing a surface charge, have been found to be useful in removing traces of rare metals from solutions and it is quite probable that they will be very important agents for controlling concentrations of several elements in sea water.

MATERIALS AND EXPERIMENTAL DETAILS

The following section on general experimental procedures gives an outline of the techniques employed and materials used during various steps of the investigation. Some theoretical aspects relevant to the procedure and affecting the techniques have been discussed.

MINERAL PREPARATION:

Description and Preliminary Identification:-

Naturally occurring minerals cannot be expected to possess a high degree of chemical purity. Synthetically prepared minerals can be made chemically pure, but it is rather a complicated process. Also few methods exist which can reproduce the unique physical characteristics (eg. the extremely thin fibers) of the natural asbestos minerals. For this and many other reasons all the minerals used here were natural. They were purchased from M/s. Wards Natural Science Establishment, Inc. of Rochester, New York. The minerals were in a relative high state of purity and were obtained from locations famous for the respective minerals. Thus, chrysotile, the fibrous variety of serpentine, was obtained from Quebec, Canada and crocidolite, the fibrous member of the amphibole group, came from Prieska District of Griqualand in Southwest Africa. The Kijmar mining district of Quebec, Canada was the source of nonfibrous serpentine.

For preliminary identification and characterization, each mineral was compared with its standard physical characteristics as found

in literature. Standard characteristics of chrysotile, crocidolite and serpentine are listed in Table I.

TABLE I^{14,15}

STANDARD CHARACTERISTICS OF
CHRYSTILE, CROCIDOLITE AND SERPENTINE

PROPERTY	CHRYSTILE	CROCIDOLITE	SERPENTINE
Colour	Greenish White	Dark Blue	Greenish White
Crystal Structure	Fibrous	Fibrous	Nonfibrous
Crystal System	Monoclinic	Monoclinic	Monoclinic
Lustre	Silky	Silky to dull	Dull
Hardness*	3 - 4	4	4
Cleavage	010 perfect	110 perfect	010 perfect
Composition	Hydrous silicate of magnesia	Silicate of Na, Fe, Mg.	Hydrous silicate of magnesia

* Hardness determined on Moh's scale.

The three minerals used in this investigation were found to be matching quite well with their standard physical properties.

This primary labelling was followed by optical examination and X-ray diffraction. For the X-ray diffraction study and also for the electrophoresis and leaching study, particles of very fine mesh size were required. The primarily identified, hand picked minerals were

therefore, ground.

Grinding:-

Depending upon the crystal structures of the minerals, two different methods were employed. For serpentine, the nonfibrous ferro-magnesium silicate, conventional primary hand crushing with a $1\frac{1}{2}$ " stainless steel mortar and pestle was used. This was followed by final size reduction in agate mortar and pestle. Use was made of acetone to prevent lighter particles from flying off because of the impact of the pestle. The ground mineral was then sieved through a standard screen of 325 mesh size (44 microns). The -325 mesh serpentine was then stored in styrene vials for further processing.

The two fibrous asbestos minerals could not be ground by this method. Placing the mortar in dry ice and then grinding also proved to be unsatisfactory. In literature, no satisfactory method is available for dry grinding of asbestos. There is an easier way of wet grinding asbestos, which consists of suspending the fibers in distilled water and then applying ultrasonic vibrations to the suspensions. As our study is concerned mainly with aqueous suspensions and time variance of surface charges, the possibility of employing the method was ruled out. Finally, the fibrous magnesium silicates were ground with the use of pica mill. The pica mill is manufactured by Pittsburgh Manufacturing Corporation of Pittsburgh, Pennsylvania and essentially consists of a motor-driven shaft on which are mounted frames which have a vibratory motion when the motor is turned on. The sample and a ball are kept in a hollow cylindrical container (vial) with lids on both the sides, which is mounted on the frame and screwed tight. The vials used in this

experiment were made of Tungsten Carbide and so were the balls placed in the vials. This machine is, in essence, a miniature ball mill.

Tungsten carbide is very resistant to wear and supposedly, does not greatly contaminate the ground sample. This procedure proved to be a very slow yet satisfactory way of dry grinding the fibrous minerals. The ground minerals were, again, screened through a 325 mesh standard sieve and the -325 mesh material was stored in styrene vials.

At this stage of the experiment, three ground minerals were obtained. The next stage was that of final identification by means of X-ray diffraction and other studies.

Final Identification - X-ray Diffraction:-

For the spectrographic analyses of the three samples, a Bausch and Lomb Littrow Spectrograph no. 1778 was used in conjunction with a Jarrel-Ash Power Supply. Carbon electrodes were used with a DC arc operating at 7 amperes for half a minute. The results of the Emission Spectrograph analyses may be found in Table II.

TABLE II ¹⁶

MINERAL	ELEMENTS PRESENT	STOICHIOMETRIC EXPRESSION
Chrysotile	Fe, Al, Mg, Si	$(Mg_{5.75}Al_{0.75})(Si_{3.25}Fe_{0.25})_{10}(OH)_8$
Crocidolite	Fe, Na, Mg, Si	$(Na_2Fe_2Mg_{0.5})Si_8O_{22}(OH)_2$
Serpentine	Fe, Al, Mg, Si	$(Mg_{5.75}Al_{0.75})(Si_{3.25}Fe_{0.25})_{10}(OH)_8$

Identification of the ground minerals was also made using X-ray diffraction analysis. The X-ray diffraction patterns were obtained with a North American Phillips Company Diffractometer. As all the samples were -325 mesh, they were put directly into powder sample holders for diffraction studies. The scanning speed used was 1 degree per minute. The slits were 1 degree divergence and scatter, and the receiving slit was 0.005". All the patterns were obtained with a copper X-ray tube operating at 35 kilovolts and 15 miliamps. A nickel filter was used to eliminate copper K_{β} radiations. The d spacings observed are shown in Table III. Also shown are the ASTM standards for the minerals.

TABLE III

d SPACINGS OF ASBESTOS MINERALS

SAMPLE # 1	SAMPLE # 2	SERPENTINE
CHRYSOTILE	SERPENTINE	ASTM 11-386
7.20	7.22	7.25
4.43	4.53	4.61
3.90	3.85	3.91
3.63	3.63	3.62
2.50	2.49	2.50
..	2.14	2.15
..	1.79	1.79
..	1.73	1.73
1.54	..	1.54

SAMPLE # 3	CROCIDOLITE
CROCIDOLITE	ASTM 14-230
8.19	8.42
4.51	4.52
3.83	3.88
3.66	3.67
3.39	3.43
3.08	3.08
2.73	2.73
2.69	2.68

Within allowable limits of experimental error and insignificant amounts of impurities, all the ASTM standards confirm the mineral indicated. Except for crocidolite, X-ray patterns for chrysotile and serpentine both, showed identifiable peaks.

At this stage, the different plastic vials containing the ground -325 mesh samples were legitimately labelled as chrysotile, crocidolite and serpentine. The next stage of the experiment was to suspend them in water and start the study of their surface charge as a function of time.

REAGENTS AND LABORATORY WARE:

In order to avoid the contamination of the mineral surface with silica, laboratory glassware was not used. All the beakers, flasks, pipettes and funnels were made of polyethylene. The minerals were suspended in distilled, deionized, double boiled water. The only purpose of boiling water two times was to remove as much of the dissolved carbonic acid gas as possible. For rinsing the laboratory ware and for other purposes, only distilled and deionized water was used. NaOH and HCl were used to adjust the pH of the system. Buffer solutions of various pH values in the related pH ranges were prepared using standard procedures. All the chemicals used were of reagent grade. The suspensions were stored in a glove box which was intermittently filled with Nitrogen gas. In order to absorb any carbon dioxide from Nitrogen that entered the glove box, a plug of Ascarite was placed in between the Nitrogen cylinder and the glove box.

SAMPLE PREPARATION:

The mineral samples collected in plastic vials were then one by one treated as follows. The samples were thoroughly mixed and divided into two equal parts. One part was subjected to the action of 18% conc. HCl for two hours. After all the metallics and other impurities were supposedly leached out, the sample was thoroughly rinsed with distilled, deionized water to remove any chlorine or other acidic material. A 7% loss in weight was observed for chrysotile, which was also observed for serpentine. The loss in the weight of crocidolite was only about 4%. The acid leached sample was then dried overnight at about 110 degrees F. The other half of all the three minerals was not processed at all. At this stage of the experiment, six samples on the whole were obtained as follows:

Chrysotile	(1)	Acid Treated
	(2)	Untreated
Crocidolite	(1)	Acid Treated
	(2)	Untreated
Serpentine	(1)	Acid Treated
	(2)	Untreated

At this time, the suspensions in water were to be prepared out of these samples. It was decided to study the change in the pzc and change in the concentrations of Mg^{++} , Fe^{++} and Si^{4+} in the leachate for the period of about two months taking intermittent time intervals. For this reason, large quantities of the suspensions were made. Two different suspension densities were obtained for the six samples. A 1% susp-

ension was obtained by suspending 3 grammes of the ground mineral in 300 ml. water. Similarly, 300 ml. of water containing 6 grammes of the ground mineral as a suspension resulted in a 2% suspension. Thus, at the beginning of the actual core of the investigation, there were twelve suspensions in all to be studied, e.g.

Chrysetile	Acid Treated	1% susp.
				2% susp.
		Untreated	1% susp.
				2% susp.

and similarly four for each of the other two minerals.

INSTRUMENTS:

The instruments utilized during this study could not be said to be "very complicated" or "complex", but they were extremely sensitive to the procedure used and were such that even a slight carelessness would create a multiple damage or would give ambiguous results.

The pH Meter:-

As this study is mainly the study of the surface charge with pH of the system as a preliminary variable, the pH meter was a very important part of the study. The pH meter used during the investigation was a Corning model - 10 with expanded scale. This instrument has been found to be very sensitive with a good response to the slightest change in the value of the pH of the solution in question. The pH meter was standardized before making any pzc measurement. The standard glass electrodes alongwith a reference electrode were used. The electrodes

were rinsed with distilled, deionized water and then wiped clean after and before dipping them in any liquid. These simple precautions were very rigidly followed.

The Zeta Meter:--

The instrument used for the measurements of electrophoretic mobilities of various mineral particles at different pH values and hence the pzc's of the minerals, was a commercial microelectrophoresis apparatus manufactured by M/s. Zeta Meter, Inc. of New York City, New York. There are many other ways in which a surface charge could be measured. Some theoretical aspects of the working of this instrument are discussed in Appendix I. The microelectrophoresis device or "zeta meter" essentially consists of a plexiglass cell with two hollow cylinders connected by a narrow tube. A difference of potential is applied at either end of the cell from an external source. The anode and the cathode are platinum-iridium electrodes. At pH values lower than 3.0 and higher than 11.0, use is made of molybdenum anode. A high powered microscope with calibrated eyepieces is focussed on the minute mineral particles, the suspension of which is filled in both the cylinders of the cell and which are lighted by an external light source. When the current is switched on, the particles move either towards the cathode or towards the anode depending upon the charge they carry. Measurement is made of the time taken by a carefully selected particle to traverse one full division of the calibrated eyepiece. The value of the electrophoretic mobility for the measured time length is then obtained from a chart supplied by the manufacturers and is expressed in microns per second per

volt per centimetre. The arrangement of the pH meter and the zeta meter is shown in figure 2.

Alongwith the measurement of the surface charge of the minerals at various time intervals, measurements were also made of the concentrations of Mg^{++} , Fe^{++} and Si^{4+} in the leachant. An adequate aliquot of the mineral suspension was taken out of the plastic beaker at the end of the predecided time period. After noting the pH of the suspension and measuring the pzc of the particles, the suspension was filtered through Whatman filter paper number 42. The filtrate was stored in a styrene vial for a subsequent chemical analysis.

CHEMICAL ANALYSIS TECHNIQUES:

For the quantitative analysis of the leachant, two different techniques were utilized. The silica contents of the leachants were measured by a simple colorimetric method, while atomic absorption spectrophotometry was used to determine the iron and magnesium contents of the leachants.

Atomic Absorption Spectrometry:-

This is one of the most commonly used methods for the analyses of various aqueous solutions. The basic principles on which the method is based are very clearly explained in standard literature on analytical chemistry.¹⁷ Standard iron and magnesium solutions were prepared and used for the analyses of the leachants. Use was made of a Perkin Elmer 303 Atomic Absorption Instrument having a digital concentration readout. Standard error was ± 0.05 ppm at 1 ppm Mg^{++} and ± 0.08 ppm at 1 ppm Fe^{++} .



Figure 2 Set up of the pH meter and the Zeta Meter

Colorimetry:-

A Bausch and Lomb Spectronic - 20 colorimeter was utilized for the determination of silicon as a yellow coloured silicomolybdate complex, which on reduction with sodium sulfide forms the molybdate blue complex. This is a standard method for the analysis of silica and the standard error at 1 ppm of SiO_2 was determined to be 0.07 ppm. The principle of working of this method is described by Rainwater and Thatcher.¹⁸

SOME TECHNICAL DETAILS OF THE PROCEDURE:

The 1% and 2% suspensions (w/v) of acid treated and untreated, ground, -325 mesh chrysotile, crocidolite and serpentine were made in distilled, deionized, double boiled water, pH of which was adjusted to 6.5. The suspensions were stored in a CO_2 free N_2 atmosphere. The temperature of the chamber was around 25 to 28 degrees centigrade. The pH and the electrophoretic mobilities were measured for the time intervals of 1 day, 1 week, 3 weeks, 5 weeks, 8 weeks and 10 weeks after the initial measurements at the time the suspensions were made. A 30 ml. aliquot of each of the suspensions was taken out at the time of the surface charge measurement. When measuring the pzc's at various time intervals, distilled, deionized water was taken in a plastic beaker. The pH of the water was adjusted to a particular value by HCl or NaOH. To this beaker containing water of known pH, five drops of the aged suspension of the mineral were added. The beaker was shaken for about

thirty seconds and the zeta meter cell was completely filled with the contents of the beaker. The time taken by a mineral particle to traverse one full division or a computable fraction of it for a potential difference of 100 volts for both, normal and reverse current directions, was measured. Care was taken to trace only those particles which were in sharp focus. The final pH of the suspension was noted down. The zeta meter electrodes and the cell were always rinsed with 0.1N HClO₄, washed with distilled, deionized water and wiped dry before taking the next reading. For all the mineral samples at various time intervals, values of pzc's were found.

RESULTS

At the end of the leaching study, some very interesting data were collected for the three magnesium silicates in question. The maximum aging time was ten weeks for all the minerals and pH, pzc, electrophoretic mobility, etc., were measured for the time intervals of one day, one week, three weeks, five weeks, eight weeks and ten weeks using techniques and equipment described earlier. The data have been represented hereunder in two forms, tabular form and graphical form.

During the course of this study, time has been considered as the master variable, but the fact that the pH of the system is a more effective variable cannot be ignored. The pzc of the minerals after a decided period of aging time has been measured with pH as the primary variable. This will be clear by reference to Appendix II. It is believed that with pH as the main variable, some discrepancy in results is not always avoidable. The concentrations of Mg^{++} , Fe^{++} and Si^{4+} species in the leachants have been determined by atomic absorption spectrometry and colorimetry and have been found to be, surprisingly enough, reproducible for three to four times.

As mentioned earlier in Chapter II, for every mineral, there are two different samples; one of which had not been treated with any chemical before suspension, while the other one had been kept for two hours in 18% concentrated hydrochloric acid. For every sample, again, two different suspensions were made, one being a 1% (w/v) suspension and the other one 2%. Thus, the pH, electrophoretic mobility, pzc and

the Fe^{++} , Mg^{++} and Si^{4+} contents for various known time intervals have been measured for four different suspensions of every mineral.

Chrysotile:- Table IV-A represents the data for the 1% and 2% suspensions of acid treated chrysotile. Table IV-B has similar data for the untreated chrysotile samples. The electrophoretic mobilities are represented in microns per second per volt per centimetre and the concentrations of iron, magnesium and silica in the leachants are in parts per million (ppm).

It is quite apparent from tables IV-A and IV-B that there are differences in suspension pH's and the magnitude and sign of the charge carried by the mineral depending upon the history of the mineral. The pzc of the acid treated mineral in both the suspensions is around that for quartz and does not vary by a considerable amount as the suspension is aged. This is not true, however, for the untreated chrysotile sample. Both suspensions of the untreated sample show a rather high pH, which tends to decrease gradually with time. There seem to be many factors interrelated with this. The electrophoretic mobility of the mineral particle in these two suspensions is from the anode to the cathode clearly indicating a positive charge, which, however, is found to change to a negative value after a two months aging. Is that the time when the mineral, just immersed in water of pH 6.5, itself reaches its pzc by some way, e.g. dissolution of charge carrying species or adsorption of species carrying the opposite charge? It is also interesting to note that the concentration of magnesium in the leachant after various time intervals bears a linear relationship with the aging time.

TABLE IV-A

ELECTROKINETIC DATA FOR ACID TREATED CHRYSOTILE

1% Suspension : Chrysotile in Water

Aging Time	pH	zpm	pzc	Fe ⁺⁺	Mg ⁺⁺	Si ⁴⁺
0	6.13	...	3.0
1 day	6.61	-0.64	3.3	0.3	1.4	0.5
7 days	7.11	-0.91	2.6	0.2	2.0	0.6
21 days	7.43	-1.02	2.8	0.3	1.5	0.9
35 days	7.67	-1.03	2.9	0.4	2.0	1.0
55 days	7.74	-1.05	3.0	0.4	2.3	1.0
70 days	7.85	-1.05	2.9	0.5	2.8	1.2

2% Suspension : Chrysotile in Water

0	5.96	...	3.9
1 day	6.85	-0.79	3.4	0.2	1.7	0.8
7 days	7.16	-0.95	2.9	0.4	2.3	1.1
21 days	7.32	-1.13	3.5	0.3	2.5	1.2
35 days	7.50	-1.16	3.6	0.2	2.6	1.4
56 days	7.68	-1.01	3.6	0.4	2.8	1.6
70 days	7.91	-1.11	3.7	0.4	3.0	2.0

TABLE IV-B

ELECTROKINETIC DATA FOR UNTREATED CHRYSOTILE

1% Suspension : Chrysotile in Water

Aging Time	pH	epm	pzc	Fe ⁺⁺	Mg ⁺⁺	Si ⁴⁺
0	10.11	1.8
1 day	9.42	0.55	10.3	2.1	29.0	0.1
7 days	8.91	0.70	9.9	3.5	25.0	0.2
21 days	9.03	0.67	9.9	4.8	31.0	0.3
35 days	8.96	0.60	9.0	4.9	38.0	0.1
56 days	8.94	-0.56	8.7	4.7	46.0	0.1
70 days	8.92	-0.63	8.7	6.1	49.0	0.4

2% Suspension : Chrysotile in Water

0	10.05	1.8
1 day	9.34	0.46	9.7	3.9	30.0	0.2
7 days	8.76	0.52	9.4	5.8	48.0	0.2
21 days	8.79	0.37	9.3	9.7	53.0	0.3
35 days	8.61	0.39	9.1	6.3	60.0	0.4
56 days	8.68	0.24	9.0	4.2	71.0	0.4
70 days	8.84	-0.71	8.7	5.3	78.0	0.5

Serpentine:- As chrysotile and serpentine are members of the serpentine and have the same chemical composition, it was expected that there would be some similarities in their electrokinetic behaviour. It has, however, been observed that serpentine gives a different response, especially for the values of pH, pzc and electrophoretic mobility. This will be clear from tables V-A and V-B, which, as in chrysotile, list data for acid treated and untreated samples of serpentine respectively. It can be seen from the tables that more Mg^{++} is extracted out of the surface than Fe^{++} or Si^{4+} are. This is also true in the case of chrysotile. The pzc shown by the acid treated sample is again that of or nearly equal to that of quartz. The charge on the mineral surface for both, acid treated and untreated samples, is negative thus suggesting that the pzc of the mineral is lower than the pH of the suspension at that time. One interesting factor observed here is the gradual decrease in the magnitude of the surface charge with time. The pH of the suspension also seems to be decreasing with time in the case of the untreated sample. Will the value of the electrophoretic mobility be zero after a considerable length of time? And will the pH of the suspension be at the observed pzc? An increase in the pH of the suspension of the acid treated sample could be attributed to exposure of inner $Mg(OH)_2$ layers to the liquid phase. There are many interrelated factors here also. The difference observed in the behaviour of the two members of the serpentine group seems to be because of the difference in their physical forms. Structures of the asbestiform and nonasbestiform minerals are discussed in detail in the next chapter.

TABLE V-A

ELECTROKINETIC DATA FOR ACID TREATED SERPENTINE

1% Suspension : Serpentine in Water

Aging Time	pH	zpm	pzc	Fe ⁺⁺	Mg ⁺⁺	Si ⁴⁺
0	6.70	-1.20	3.4
1 day	7.16	-1.40	2.3	0.3	1.2	0.6
7 days	7.78	-1.00	2.4	0.4	1.9	0.8
21 days	8.21	-1.00	2.5	0.4	2.3	0.8
35 days	8.61	-0.97	2.7	0.5	2.4	0.9
56 days	8.17	-0.83	2.8	0.6	2.6	1.0
70 days	8.21	-0.99	2.9	0.6	2.8	1.1

2% Suspension : Serpentine in Water

0	6.62	-1.20	2.9
1 day	7.24	-1.34	2.8	0.4	2.0	0.9
7 days	7.68	-0.75	2.8	0.6	3.7	1.0
21 days	7.79	-0.71	2.7	0.7	4.3	1.0
35 days	7.94	-0.63	2.7	0.7	4.6	1.2
56 days	7.89	-0.91	2.7	0.8	4.8	1.3
70 days	7.87	-0.88	2.7	0.9	4.8	1.5

TABLE V-5

ELECTROKINETIC DATA FOR UNTREATED SERPENTINE

1% Suspension : Serpentine in Water

Aging Time	pH	epm	pzc	Fe ⁺⁺	Mg ⁺⁺	Si ⁴⁺
0	9.89	1.02	6.0
1 day	9.68	-0.57	8.4	2.2	24.0	0.1
7 days	9.34	-0.45	5.9	3.0	39.0	0.2
21 days	9.29	-0.39	5.8	3.4	43.0	0.2
35 days	9.18	-0.37	6.2	3.5	46.0	0.3
56 days	9.11	-0.46	6.7	3.6	49.0	0.4
70 days	9.03	-0.42	7.1	3.8	52.0	0.4

2% Suspension : Serpentine in Water

0	9.82	1.08	10.00
1 day	9.43	-0.95	6.90	4.1	38.0	0.2
7 days	9.15	-0.74	6.10	6.2	57.0	0.3
21 days	9.03	-0.68	5.90	6.7	68.0	0.4
35 days	8.95	-0.62	5.80	7.1	77.0	0.4
56 days	8.89	-0.72	5.80	7.6	84.0	0.5
70 days	8.86	-0.70	6.00	7.4	91.0	0.6

Crocidolite:- Not many attempts have been made to determine the electrokinetic behaviour of the fibrous member of the amphibole group. Crocidolite has not been investigated sufficiently for its form, its electrophoretic mobility, its pzc and its dissolution in water or any other solvent. Being a fibrous magnesium silicate, it did show a high pH value for all its suspensions, but the surface charge was negative throughout with a larger magnitude than in the case of chrysotile or serpentine. In the case of the untreated sample of crocidolite, it is surprising to find that the concentration of iron and silicon is more in the leachant after every interval of aging time than that of magnesium. All the observations are tabulated in tables VI-A and VI-B.

GRAPHICAL REPRESENTATION:

In order to facilitate an easy comparison of the various phenomena observed for the three minerals, the observations tabulated in tables IV-A, IV-B, V-A, V-B, VI-A and VI-B have been represented in figures 3, 4, 5, 6, 7, 8, 9 and 10.

TABLE VI-A

ELECTROKINETIC DATA FOR ACID TREATED CROCIDOLITE

1% Suspension : Crocidolite in Water

Agging Time	pH	epm	pzc	Fe ⁺⁺	Nig ⁺⁺	Si ⁴⁺
0	6.58	-2.51	3.4
1 day	6.07	-2.91	3.5	0.2	0.2	1.0
7 days	6.48	-3.15	2.4	0.3	0.4	1.3
21 days	6.56	-2.97	2.3	0.1	0.4	1.7
35 days	6.62	-2.92	2.3	0.4	0.5	2.2
56 days	6.71	-2.88	2.2	0.2	0.3	2.8
70 days	6.79	-2.91	2.2	0.8	0.6	3.4

2% Suspension : Crocidolite in Water

0	6.51	-2.51	3.5
1 day	6.49	-3.62	2.5	0.2	0.1	1.8
7 days	6.53	-3.41	2.1	0.3	0.1	2.9
21 days	6.61	-3.37	2.0	0.3	0.2	3.7
35 days	6.57	-3.18	2.0	0.3	0.3	4.8
56 days	6.52	-2.95	2.1	0.1	0.3	5.1
70 days	6.55	-2.90	2.2	0.3	0.5	5.3

TABLE VI-8

ELECTROKINETIC DATA FOR UNTREATED CROCIDOLITE

1% Suspension : Crocidolite in Water

Aging Time	pH	epm	pzc	Fe ⁺⁺	Mg ⁺⁺	Si ⁴⁺
0	9.95	-3.15	3.7
1 day	9.81	-2.21	3.4	0.5	0.3	2.5
7 days	9.63	-2.08	3.3	1.1	0.3	2.9
21 days	9.42	-1.91	3.2	2.0	0.5	3.1
35 days	9.31	-1.79	3.2	2.4	0.4	3.2
56 days	9.14	-1.67	3.2	3.2	0.5	3.0
70 days	9.11	-1.52	3.2	3.5	0.6	3.4

2% Suspension : Crocidolite in Water

0	9.91	-3.19	4.4
1 day	9.73	-3.40	3.4	0.8	0.5	3.1
7 days	9.57	-3.51	2.7	1.5	0.7	3.4
21 days	9.39	-3.58	3.3	3.3	0.9	3.8
35 days	9.24	-3.69	3.3	5.0	0.8	3.6
56 days	9.17	-3.73	3.2	6.0	0.7	3.9
70 days	9.15	-3.59	3.1	7.3	0.8	4.2

1% and 2% Suspensions of UNTREATED

Chrysotile, Crocidolite and Serpentine

Chrysotile 1% Suspension —●— Chrysotile 2% Susp. —●—
 Crocidolite 1% Suspension —□— Crocidolite 2% Susp. —□—
 Serpentine 1% Suspension —△— Serpentine 2% Susp. —△—

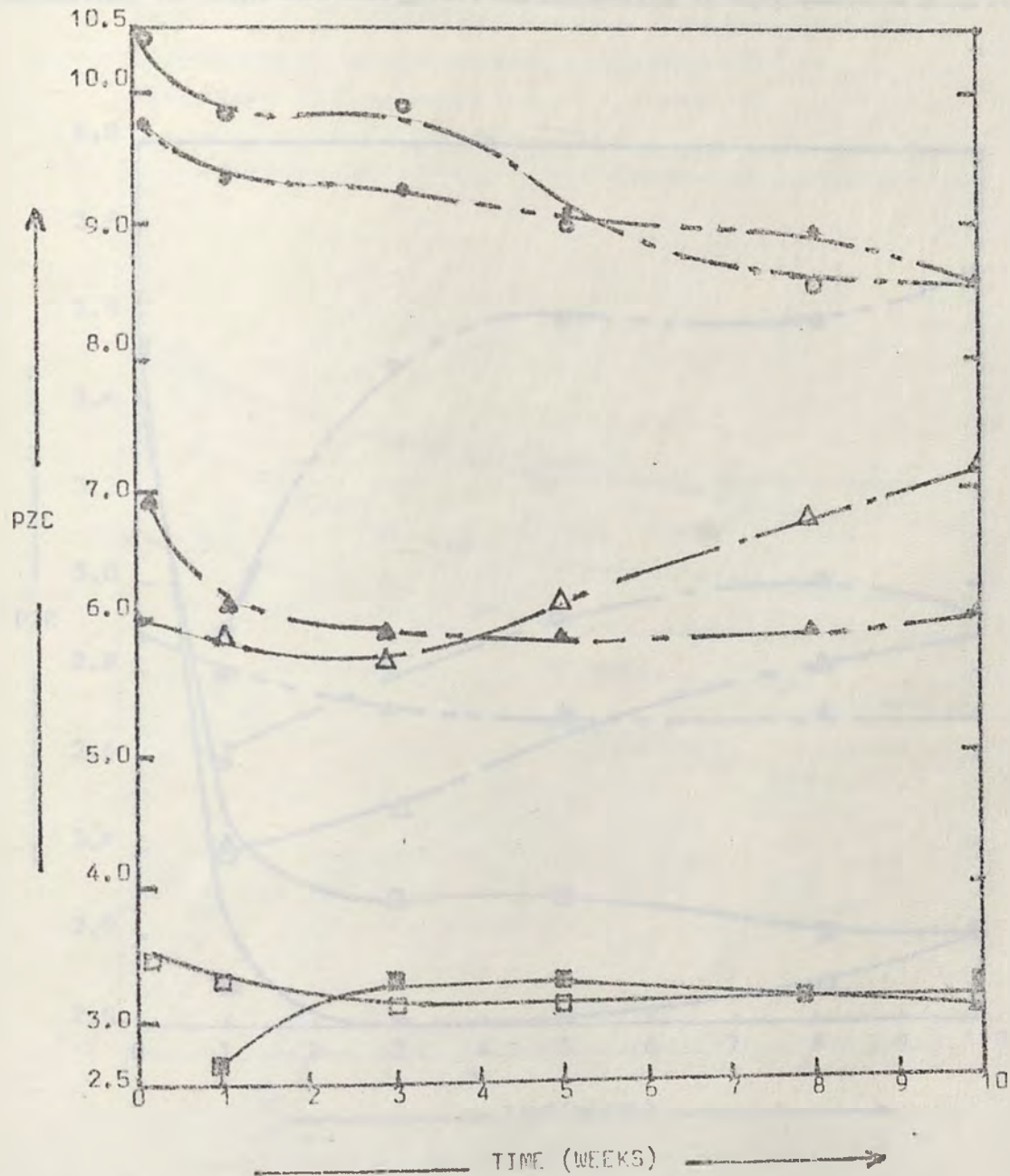


Figure 3-A Plot of PZC (pH) versus Aging Time (weeks)

1% and 2% Suspensions of ACID TREATED
Chrysotile, Crocidolite and Serpentine.

Chrysotile 1% Susp. ———○——— Chrysotile 2% Susp. ———●———
 Crocidolite 1% Susp. ———□——— Crocidolite 2% Susp. ———■———
 Serpentine 1% Susp. ———△——— Serpentine 2% Susp. ———▲———

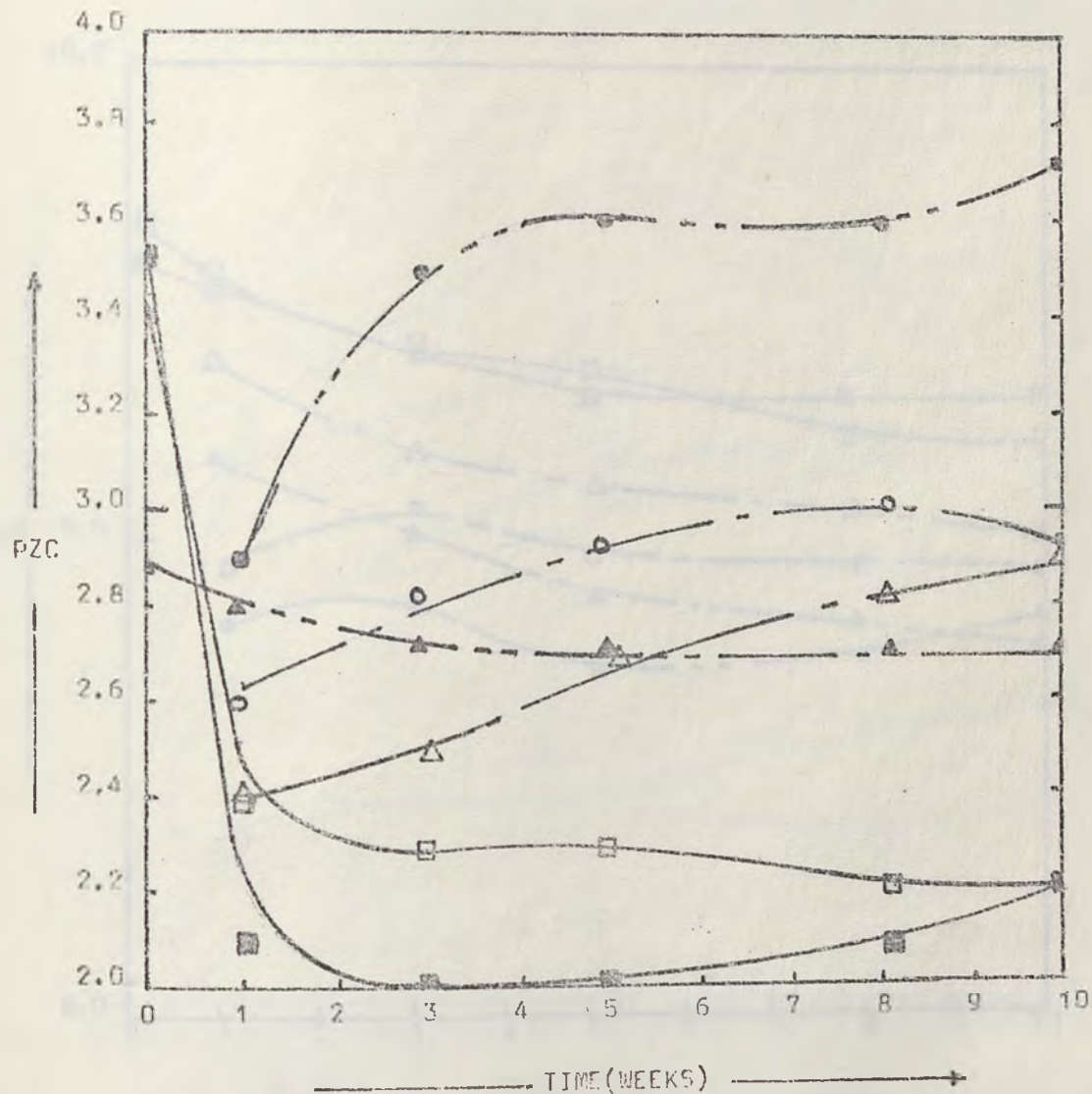


Figure 3-8 Plot of PZC (pH) versus Aging Time (weeks)

1% and 2% Suspensions of UNTREATED
Chrysotile, Crocidolite and Serpentina

Chrysotile 1% Suspension : ———— ○ ————
 Chrysotile 2% Suspension : ———— ● ————
 Crocidolite 1% Suspension : ———— □ ————
 Crocidolite 2% Suspension : ———— ■ ————
 Serpentina 1% Suspension : ———— △ ————
 Serpentina 2% Suspension : ———— ▲ ————

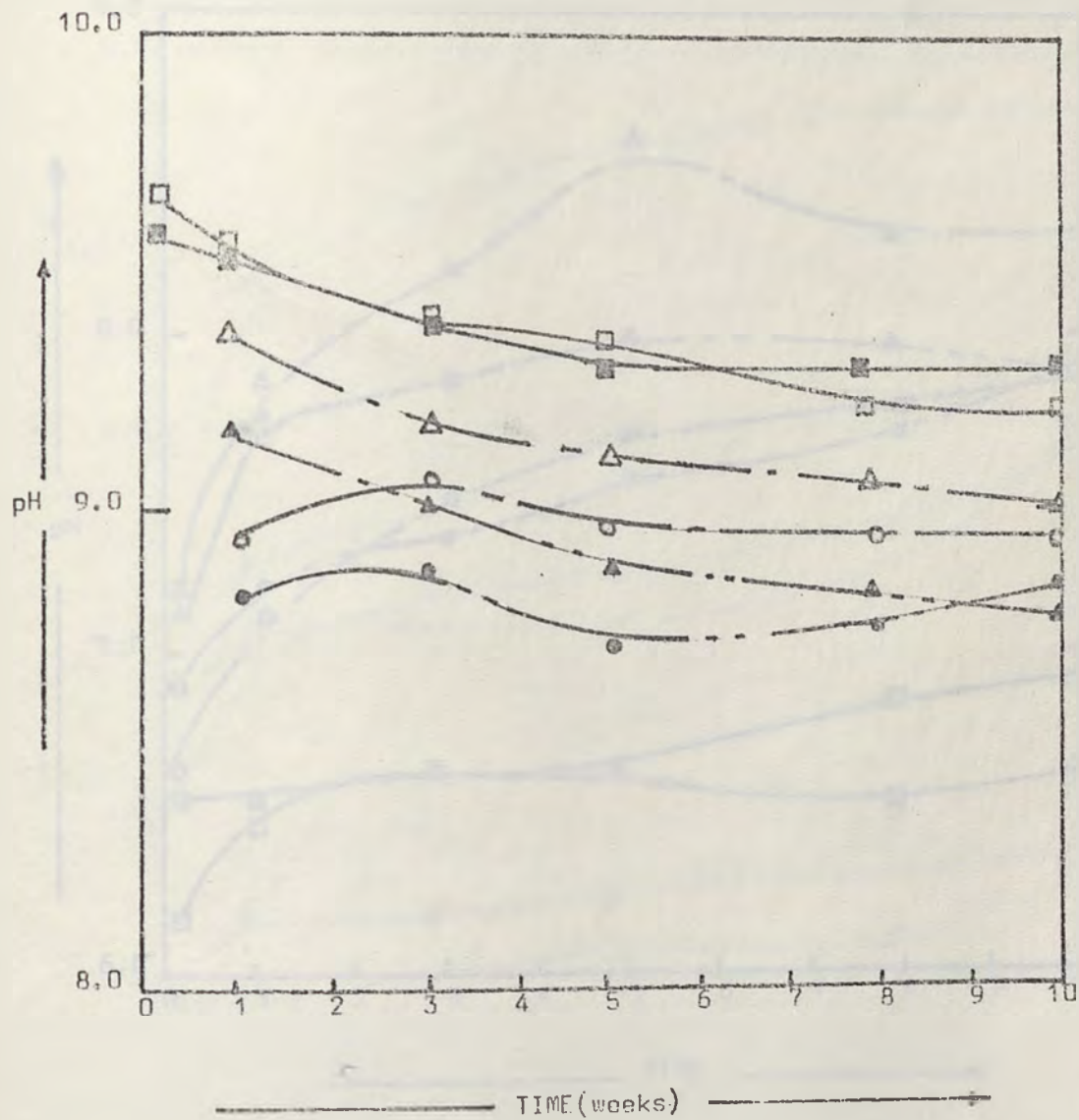


Figure 4-A Plot of pH versus Aging Time (weeks)

1% and 2% Suspensions of ACID TREATED
Chrysotile, Crocidolite and Serpentine.

Chrysotile 1% Susp. ——— ○ ——— Chrysotile 2% Susp. ——— ● ———
 Crocidolite 1% Susp. ——— □ ——— Crocidolite 2% Susp. ——— ■ ———
 Serpentine 1% Susp. ——— △ ——— Serpentine 2% Susp. ——— ▲ ———

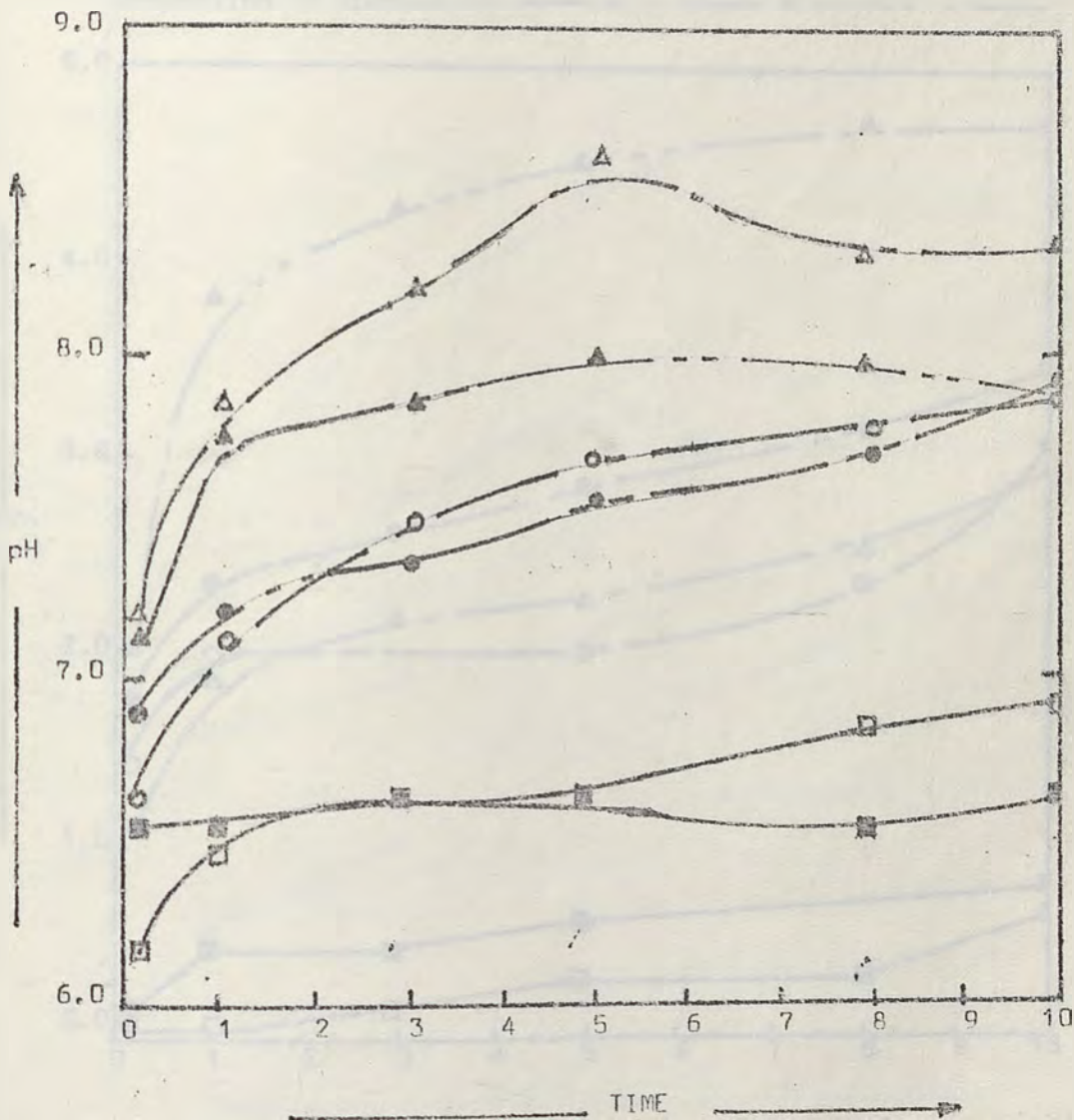


Figure 4-8 Plot of pH versus Aging Time (weeks)

1% and 2% Suspensions of ACID TREATED
Chrysotile, Crocidolite and Serpentine.

Chrysotile 1% Suspension : ——— ○ ———
 Chrysotile 2% Suspension : ——— ● ———
 Crocidolite 1% Suspension : ——— □ ———
 Crocidolite 2% Suspension : ——— ■ ———
 Serpentine 1% Suspension : ——— △ ———
 Serpentine 2% Suspension : ——— ▲ ———

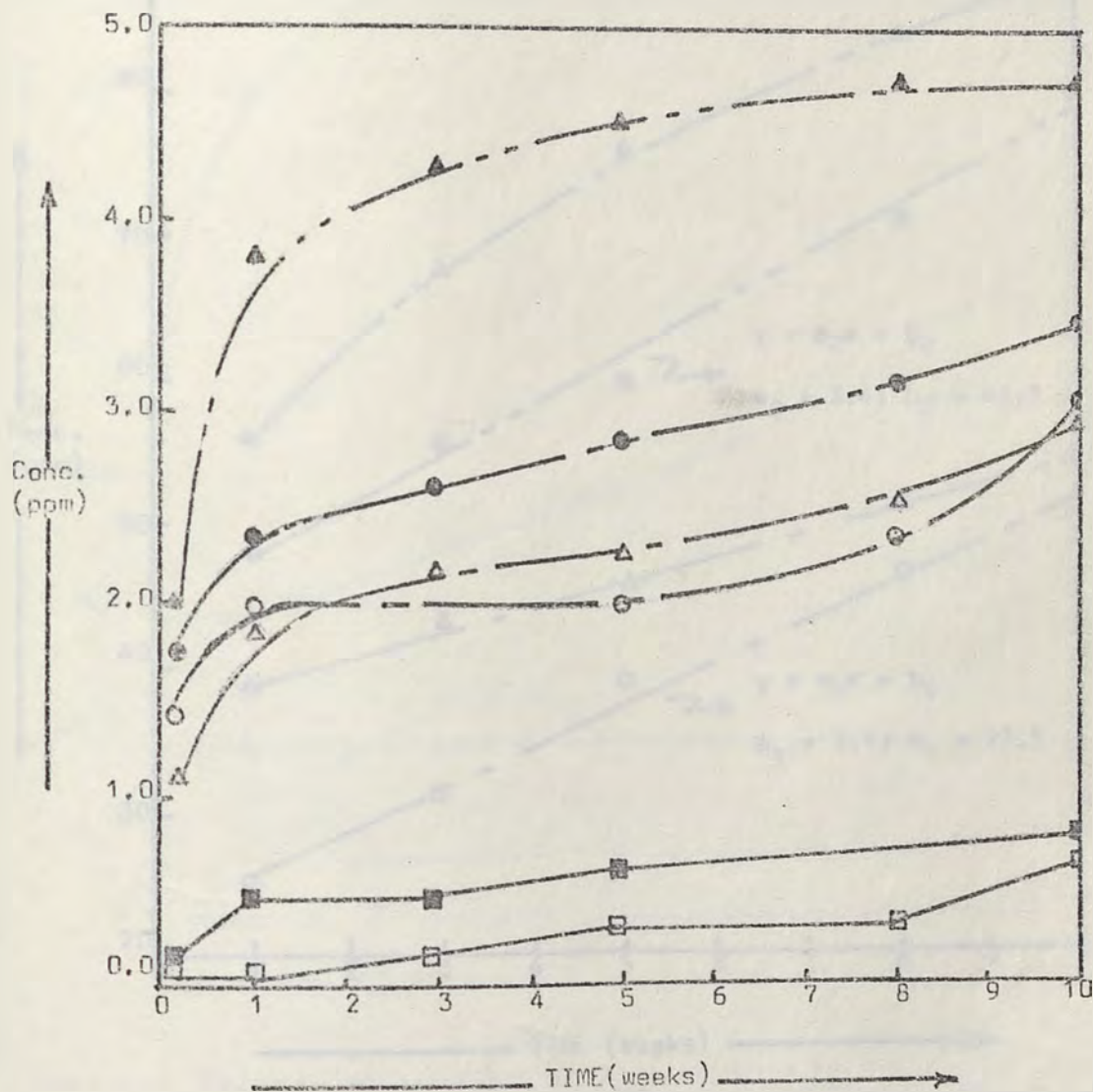


Figure 5 Plot of Concentration of Mg^{++} (ppm) versus Aging Time (weeks)

1% and 2% Suspensions of UNTREATED
Chrysotile and Serpentine

Chrysotile 1% Suspension : ———— ○ ————
 Chrysotile 2% Suspension : ———— ⊙ ————
 Serpentine 1% Suspension : ———— △ ————
 Serpentine 2% Suspension : ———— ▲ ————

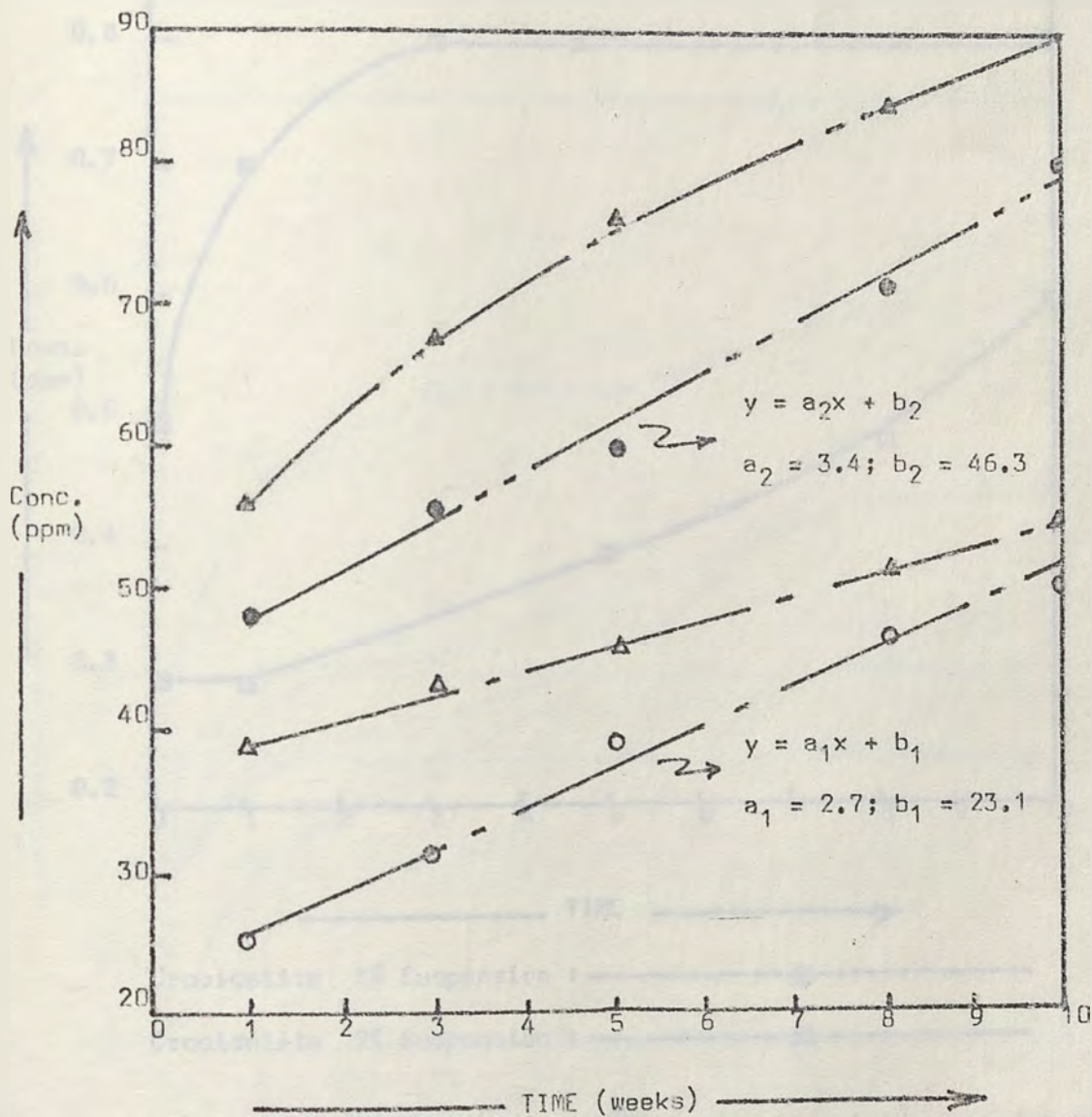


Figure 6-A Plot of Concentration of Mg^{++} (ppm) versus Aging Time (weeks)

1% and 2% Suspensions of UNTREATED
Crocidolite

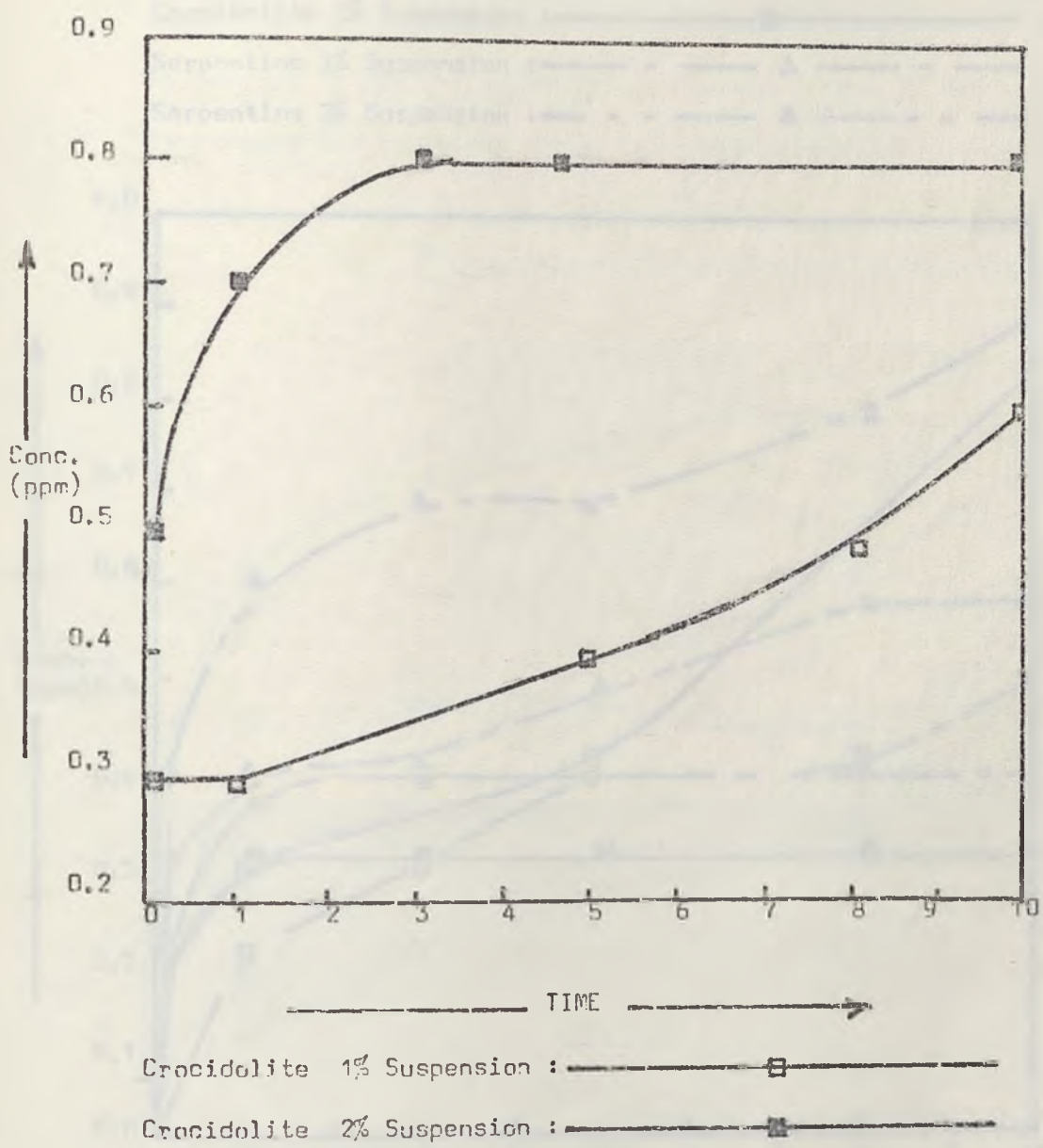


Figure 6-8 Plot of Concentration of Mg⁺⁺ (ppm) versus Aging Time (weeks)

1% and 2% Suspensions of ACID TREATED
Chrysotile, Crocidolite and Serpentine :-

Chrysotile 1% Suspension : ———— ○ ————
 Chrysotile 2% Suspension : ———— ⊙ ————
 Crocidolite 1% Suspension : ———— □ ————
 Crocidolite 2% Suspension : ———— ⊠ ————
 Serpentine 1% Suspension : ———— △ ————
 Serpentine 2% Suspension : ———— ▲ ————

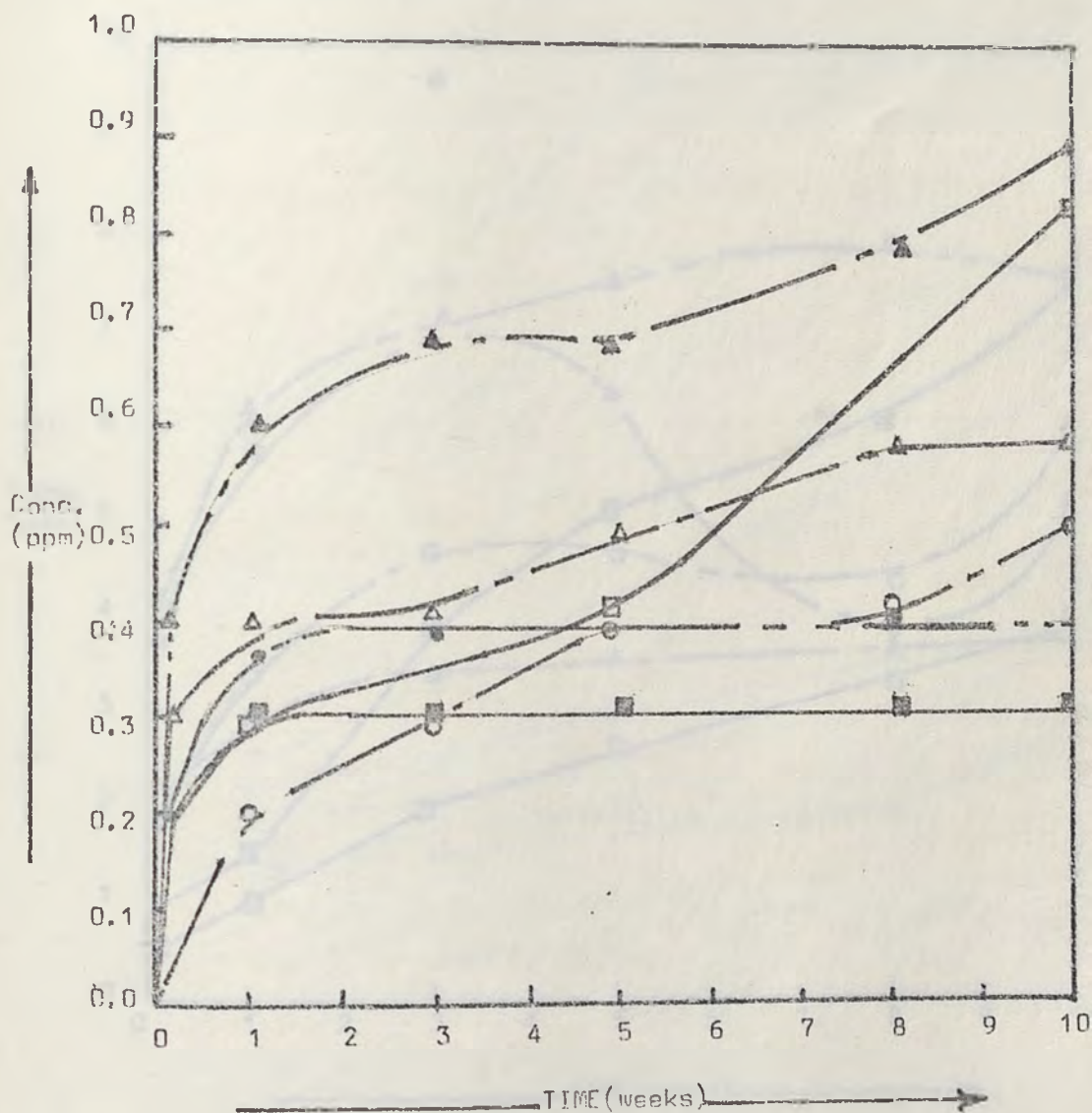


Figure 7 Plot of Concentration of Fe⁺⁺ (ppm) versus Aging Time (weeks)

1% and 2% Suspensions of UNTREATED
Chrysotile, Crocidolite and Serpentine

Chrysotile 1% Suspension : ———— ○ ————
 Chrysotile 2% Suspension : ———— ⊙ ————
 Crocidolite 1% Suspension : ———— □ ————
 Crocidolite 2% Suspension : ———— ⊠ ————
 Serpentine 1% Suspension : ———— △ ————
 Serpentine 2% Suspension : ———— ▲ ————

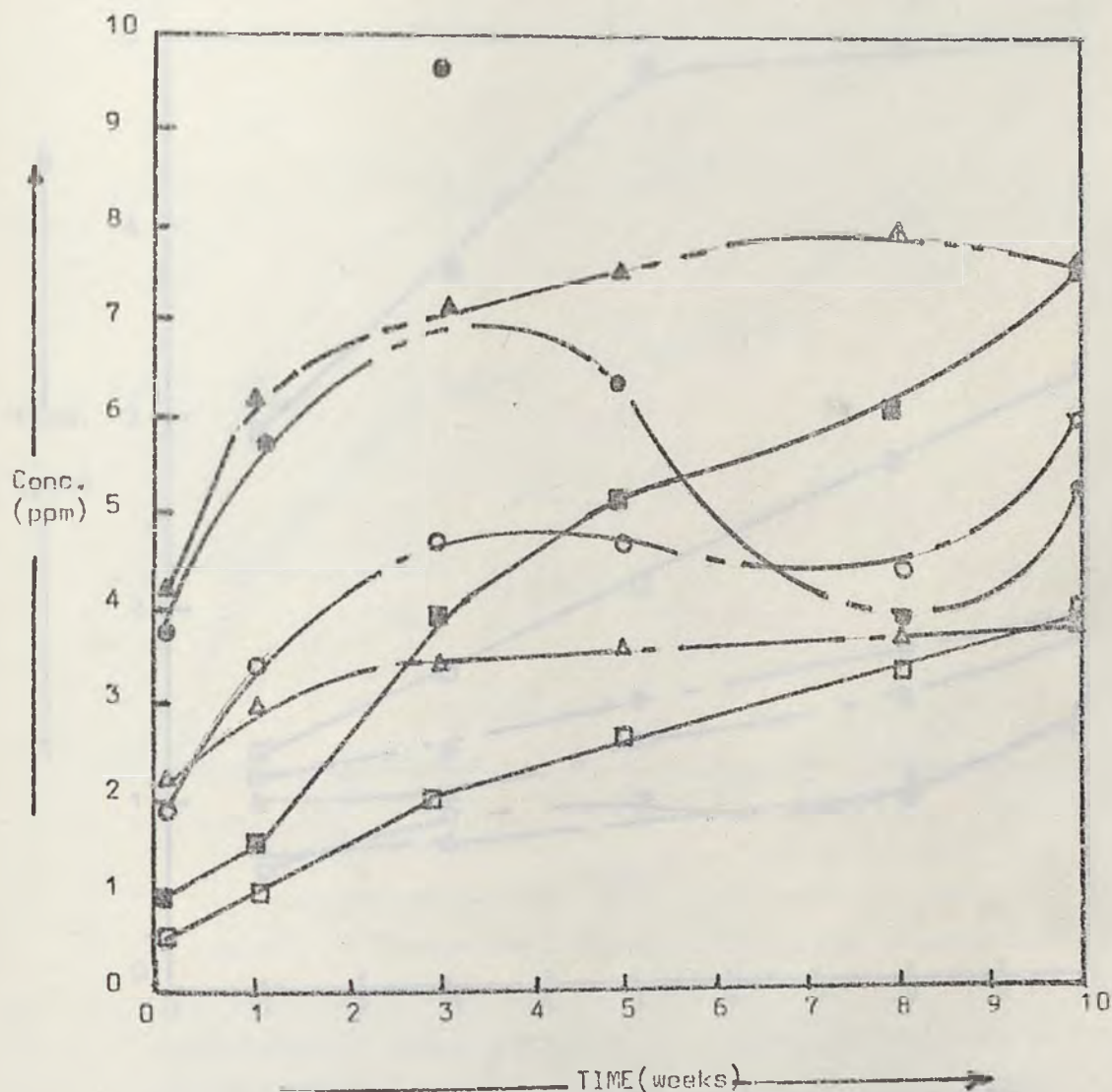


Figure 8 Plot of Concentration of Fe⁺⁺ (ppm) versus Aging Time (weeks)

1% and 2% Suspensions of ACID TREATED
Chrysotile, Crocidolite and Serpentine.

Chrysotile 1% Suspension : ———— ○ ————
 Chrysotile 2% Suspension : ———— ● ————
 Crocidolite 1% Suspension : ———— □ ————
 Crocidolite 2% Suspension : ———— ■ ————
 Serpentine 1% Suspension : ———— ▲ ————
 Serpentine 2% Suspension : ———— ▲ ————

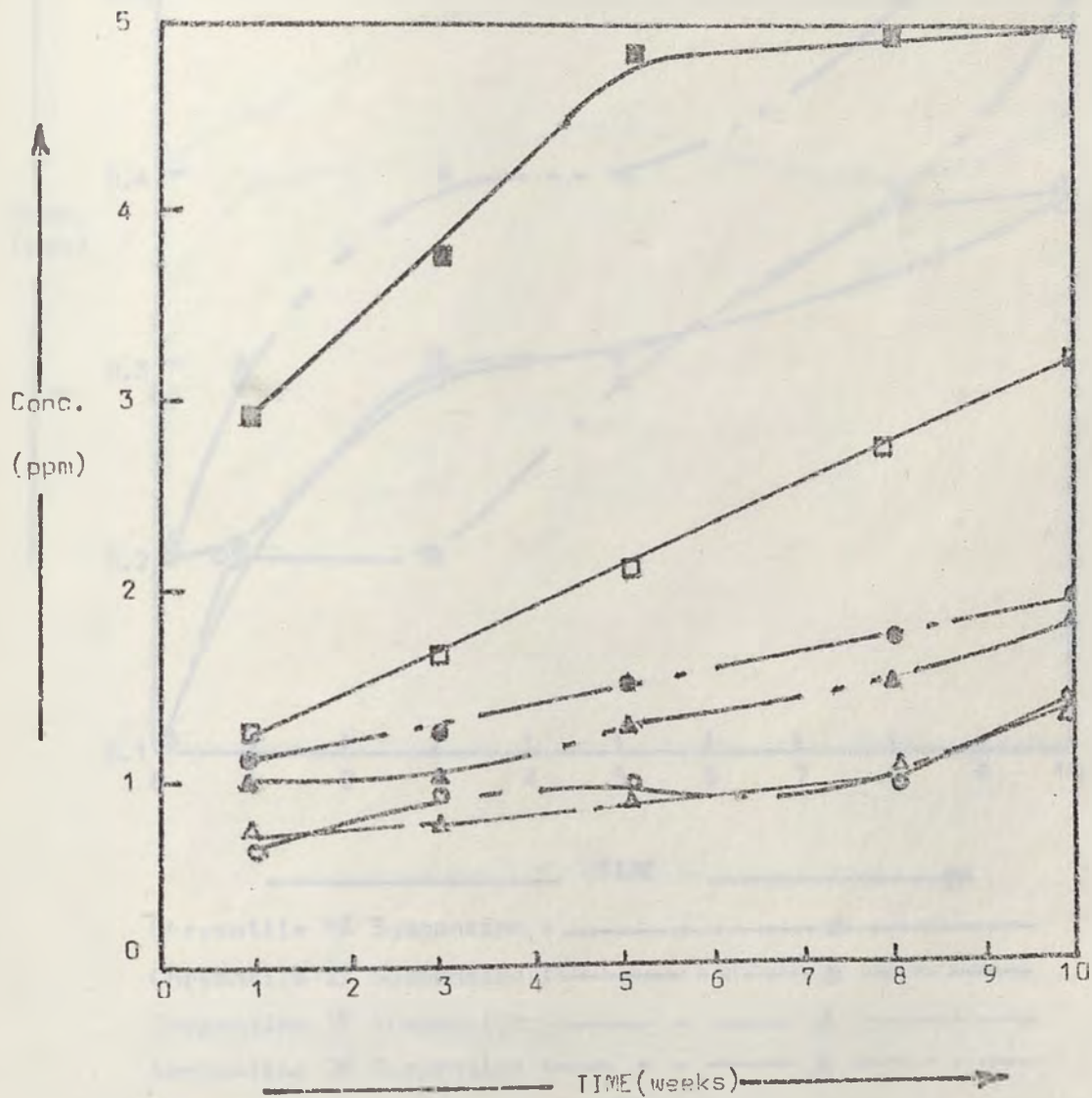


Figure 9 Plot of Concentration of Si^{4+} (ppm) versus Aging Time (weeks)

1% and 2% Suspensions of UNTREATED
Chrysotile and Serpentine

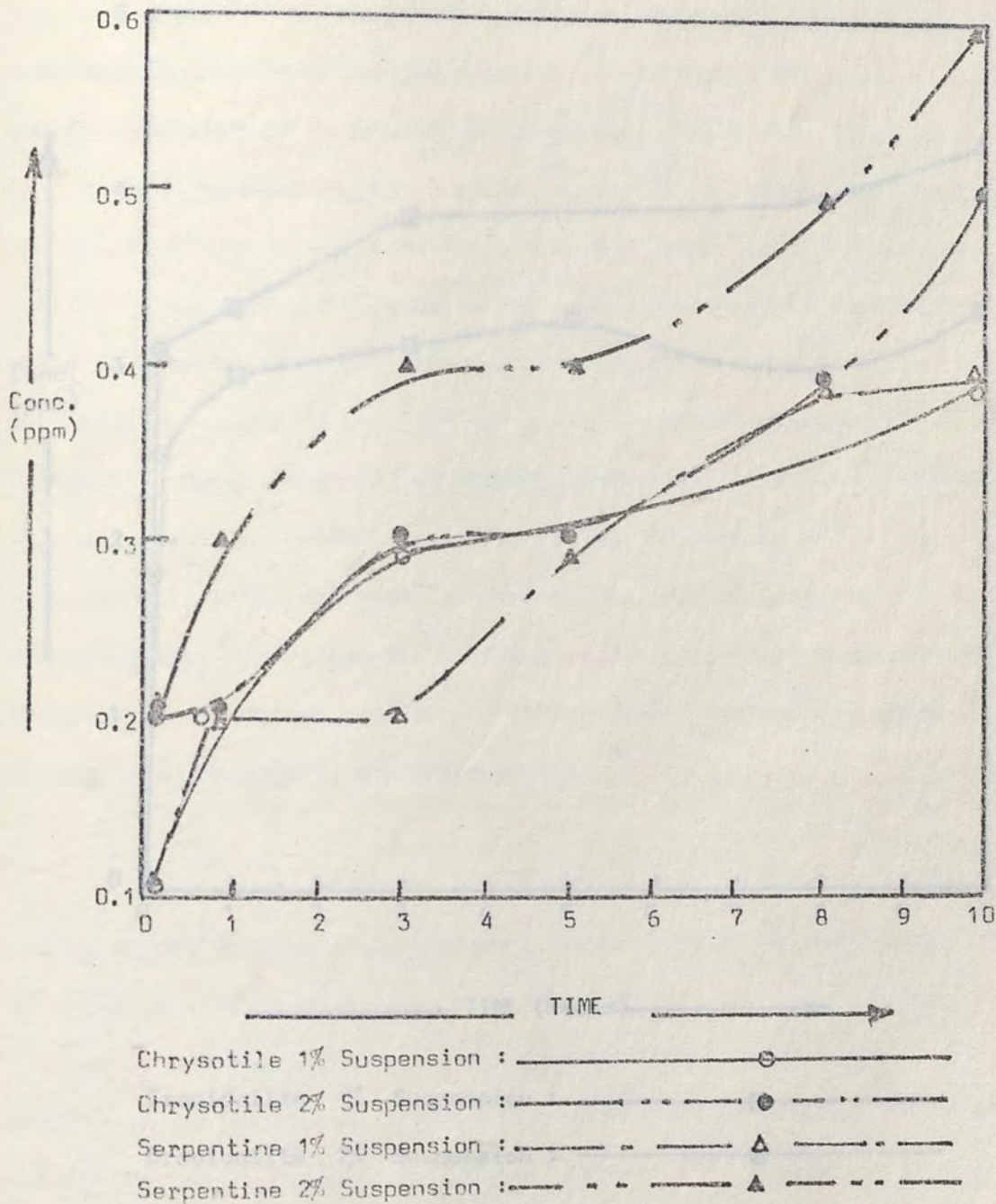


Figure 10-A Plot of Concentration of Si^{4+} (ppm) versus Aging Time (weeks)

1% and 2% Suspensions of UNTREATED
Crocidolite

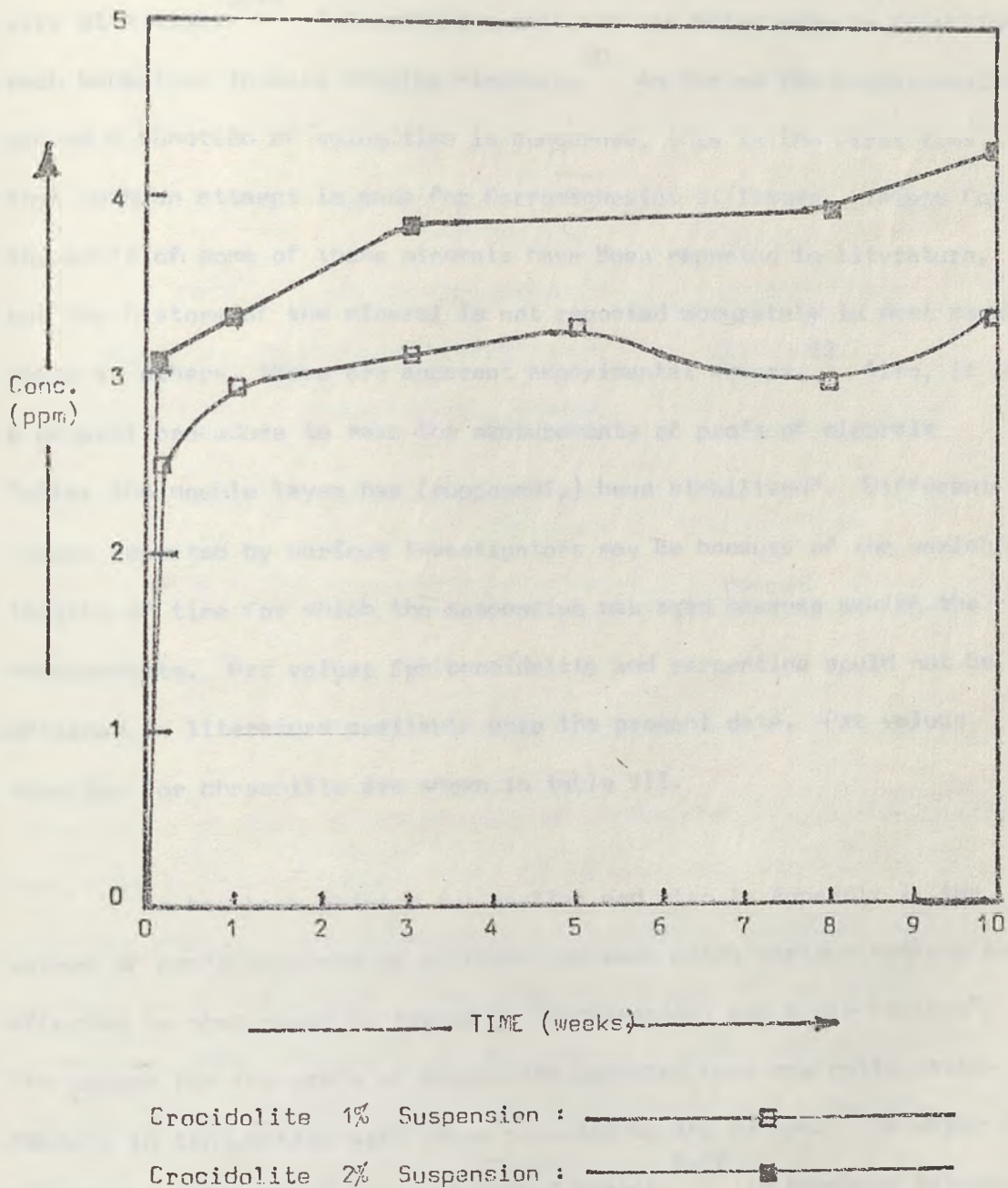


Figure 10-B Plot of Concentration of Si^{4+} (ppm) versus Aging Time (weeks)

DISCUSSION

It is a recognized fact that pzc's of certain simple oxides vary with time.^{5,19} Attempts have been and are being made to investigate such behaviour in more complex minerals.²⁰ As far as the measurement of pzc as a function of aging time is concerned, this is the first time that such an attempt is made for ferromagnesium silicates. Values for the pzc's of some of these minerals have been reported in literature, but the history of the mineral is not reported accurately in most cases,²¹ while in others, there are apparent experimental errors.²² Also, it is a general procedure to make the measurements of pzc's of minerals "after the double layer has (supposedly) been stabilized". Different values reported by various investigators may be because of the variable lengths of time for which the suspension was aged because making the measurements. Pzc values for crocidolite and serpentine could not be obtained in literature available upto the present date. Pzc values reported for chrysotile are shown in table VII.

As has been pointed out earlier and also in Appendix I, the values of pzc's obtained by different persons using various methods are affected by what could be termed as "instrumental and human factors". The values for the pzc's of chrysotile reported here are quite satisfactory in conjunction with those reported by the others. The value of pzc of chrysotile calculated by Parks' formula^{5,23} is anywhere between 8.2 and 12.5. It can further be seen from table IV-8 that for both the

TABLE VII

PZC of Chrysotile

PZC	REMARKS	REFERENCE
8.2 - 12.5	calculated	Luce (23)
11.8	streaming potential	Martinez and Zucker (24)
10.8 - 11.0	adsorption of acetate ions	Chwastiak (21)
10.0	microelectrophoresis	Pundsack (25)
8.3, 9.8, 11.1	microelectrophoresis	Riddick (22)
10.1	microelectrophoresis 7 weeks aging	Picuf (16)
10.3	microelectrophoresis 1 day aging	Present Study
8.7	microelectrophoresis 10 weeks aging	Present Study

suspensions of the untreated sample of chrysotile, the pzc was around 8.7 after a 10 weeks' aging time. It is contended that the pzc will not show any change in its value after a considerable length of time which remains to be determined. This time will be when the potential determining ions present at the interface are enough to nullify the effects of each other. This is the definition of pzc. What are these potential determining ions in our case? Are they OH^- and H^+ or are they the hydrolysis products of Mg^{++} and Si^{4+} e.g. MgOH^+ and H_3SiO_4^- ? Or is there the presence of other polynuclear species? For dilute

aqueous solutions, no magnesium-silica complex ions have been reported.²⁶

For a detailed discussion and interpretation of the potential determining ions and the pzc's, it is essential to get an idea of the distribution of all significant ionic species as a function of the pH of the system in question. In our case of magnesium silicates, the following stability ^{Constants} constants are enough for calculating the concentrations of all significant ionic species:

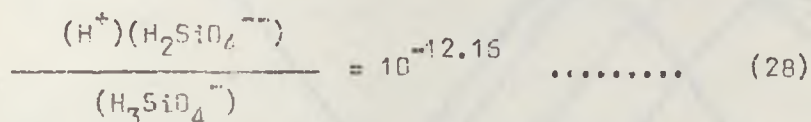
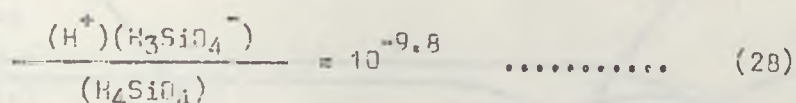
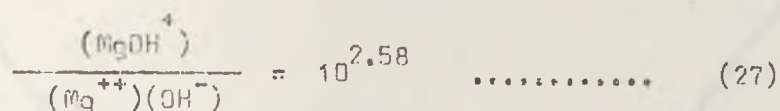


Figure 11 shows the distribution of ionic species as a function of pH at arbitrary total concentrations of Mg^{++} and Si^{4+} . The positive charge on chrysotile below pH 10 and the negative charge above this pH must be accounted for by the potential determining ions. It can be seen from figure 11 that between pH 10 and 11, the concentration of Mg^{++} and OH^- is equal. There is no decrease in the concentration of Mg^{++} ions below pH 10 which could also account for the positive charge shown by the chrysotile surface at pH values below pH 10. On the other hand, the concentration of Mg^{++} ions above pH 11 tends to decrease, while that of OH^- tends to increase, thus accounting for a negative charge on the surface at pH above 11. This locates the pzc in between pH 10 and 11.

Plot of Log Activity (moles/litre) versus pH

Total Arbitrary Concentration of $Mg^{++} = 1.5 \times 10^{-5}$ moles/litre
and of $Si^{4+} = 10^{-4}$ moles/litre.

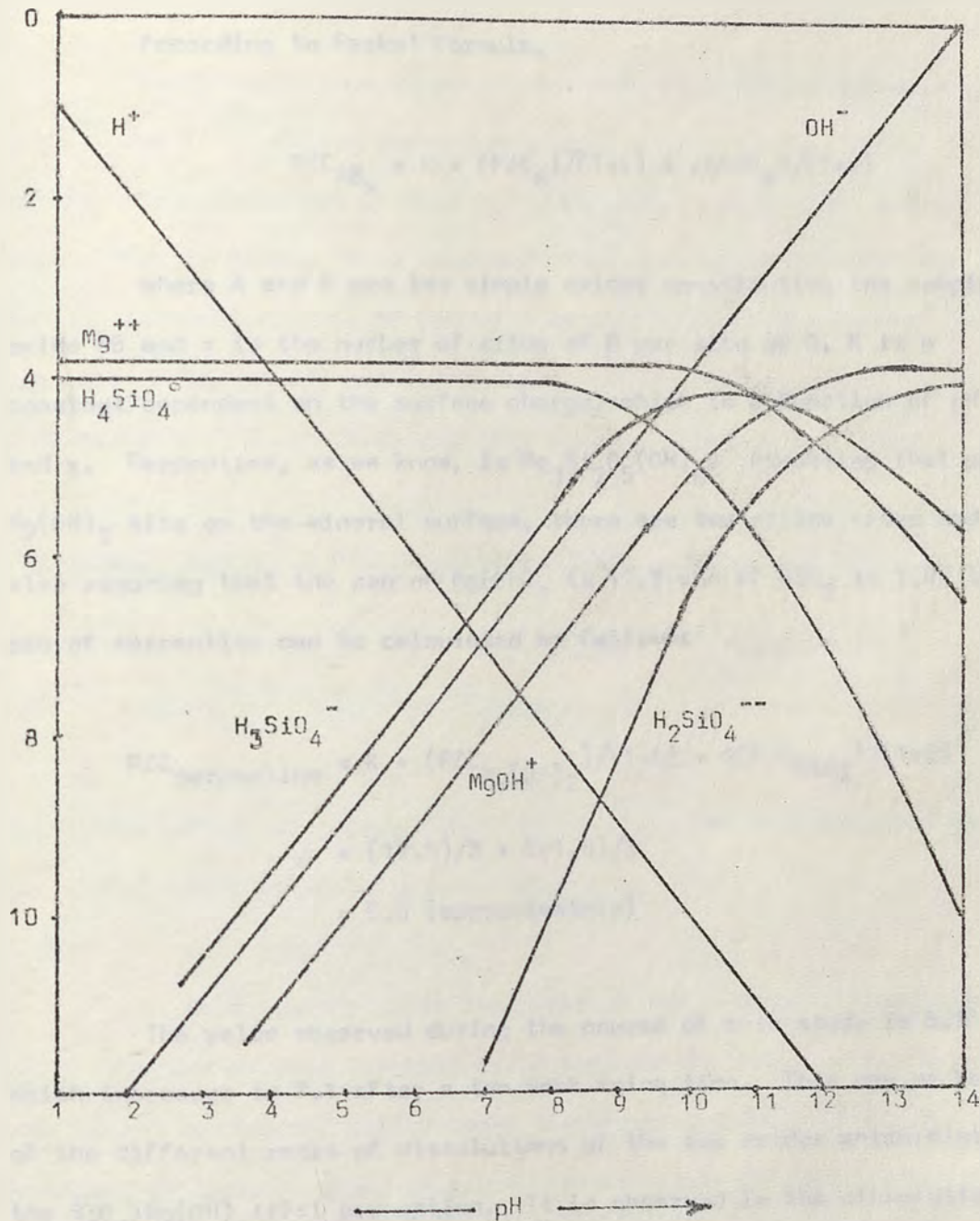


Figure 11 Log Activity Diagram for Mg-Si-H₂O System

As far as the pzc's of nonfibrous serpentine and crocidolite are concerned, no value has been reported in literature. However, an attempt is made to justify the values reported here, by comparing them with those calculated by Parks' formula.

According to Parks' formula,

$$PZC_{AB_x} = K + (PZC_A)/(1+x) + x(PZC_B)/(1+x)$$

where A and B are two simple oxides constituting the complex oxide AB and x is the number of sites of B per site of A. K is a constant dependent on the surface charge, which is a function of pH and x. Serpentine, as we know, is $Mg_3Si_2O_5(OH)_8$. Assuming that per $Mg(OH)_2$ site on the mineral surface, there are two silica sites and also assuming that the pzc of $Mg(OH)_2$ is 12.5 and of SiO_2 is 1.8, the pzc of serpentine can be calculated as follows:

$$\begin{aligned} PZC_{\text{serpentine}} &= K + (PZC_{Mg(OH)_2})/(1+2) + 2(PZC_{SiO_2})/(1+2) \\ &= (12.5)/3 + 2(1.8)/3 \\ &= 5.3 \text{ (approximately)} \end{aligned}$$

The value observed during the course of this study is 5.8 which increases to 7.1 after a ten week aging time. This may be because of the different rates of dissolutions of the two oxides which disturbs the $SiO_2:Mg(OH)_2::2:1$ proportion. It is observed in the dissolution study reported here that the rate at which Mg^{++} leaches out of the surface is far more than that at which Si^{4+} leaches out of the surface.

This could not, however, be taken as the most logical explanation, because there are several other complexities and interdependences of various sites of other species and impurities claiming their own charge on the situation. This can be more clarified by consideration of our next mineral, crocidolite.

Crocidolite is a magnesium silicate with considerable amount of Fe^{++} and Fe^{+++} oxides present along with silica and magnesia. We have earlier assumed the pzc of $\text{Mg}(\text{OH})_2$ to be 12.5. Let us also assume that that of FeO is around 11.8. Assuming that the number of sites of $\text{Mg}(\text{OH})_2$ is equal to that of $\text{Fe}(\text{OH})_2$, we can consider the overall pzc of a complex oxide of MgO and FeO to be at the arithmetic mean of 11.8 and 12.5 is 12.2. Let us designate this complex oxide as A. Then,

$$\begin{aligned} \text{PZC}_{\text{crocidolite}} &= \text{PZC}_{\text{SiO}_2\text{-A}} = (3/4)(\text{PZC}_{\text{SiO}_2}) + (1/4)(\text{PZC}_A) \\ &= (3/4)(1.8) + (1/4)(12.2) \\ &= 4.4 \end{aligned}$$

this is assuming, of course, that $\text{SiO}_2:\text{A}::3:1$. We have observed that the pzc of crocidolite is around 4.4.

As this similarity in the observed and calculated values of the pzc's is based on many assumptions as regards the pzc's of various constituent oxides and also because the very basic formula for the calculations is largely based on assumptions and has its own limits of empiricism, the safest possible way is to conclude that the pzc's of

magnesium silicates should not be considered a constant, but a variable quantity because of their more easily dissolved cations.

As the suspension is aged, again referring to table IV-B it can be seen that the pH of the suspension decreases. This may be because of the formation of surface MgOH and SiOH groups. The dissociation of MgOH and SiOH groups is pH dependent. This decrease in the pH of the suspension might be responsible for a decrease in the electrophoretic mobility of the particles, thus having a direct tendency to decrease the pzc of the minerals. It is contended that the pH of the suspension will increase after a certain aging time as a result of the exposure of more acidic silica sites.

It is reported that the extraction of magnesium and soluble silica is dependant on the acidity or basicity of the suspension and also on the temperature at which the leaching is carried out.²⁹ This type of study should prove to be of much interest and quite informative. The study reported here, however, takes into account the dissolution of Mg^{++} , Fe^{+++} AND Si^{4+} at room temperature and at natural pH of the suspension. As can be seen, the only two variables are the history of the mineral and the suspension densities of all the suspensions in water. In the absence of any temperature other than the room temperature and also with no more than two suspension densities, the data may seem more specific than general. No attempt is hence made to generalize these data for another suspension density or to determine whether the dissolution is diffusion controlled. It is not known what is the extent of

the effect of the change in pH on dissolution. It is certain, however, that pH changes do affect dissolution.²⁹

Researchers in the field of asbestos and other ferromagnesium minerals hold different views as regards the structure of the asbestiform minerals. The sheet structure with alternate sheets of $Mg(OH)_2$ and $Si-O$ is generally accepted for the nonfibrous serpentine. Figure 12 is a schematic representation of the idealized structure of serpentine.³⁰

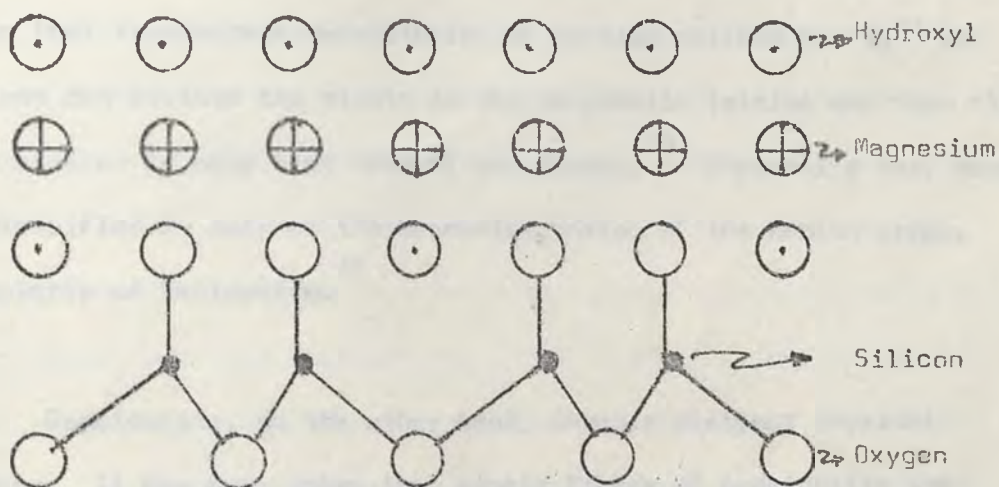


Figure 12 Idealized Structure of Serpentine

For the structure of the fibrous variety of serpentine, however, two schools of thoughts exist and both have convincing evidence in their favour. Chrysotile was classified first as an amphibole structure with a repeating $Si_4O_{11}^{-6}$ unit³¹ which was then revised to a sheet type structure with a repeating $Si_4O_{10}^{-3}$ unit.³² During the earlier part of the 'fifties, electron micrographs of chrysotile were published^{33,34,35} which clearly showed the fibers in the form of hollow tubes.

The hollow tubular structure has, however, been ruled out as 'highly improbable' as it is not compatible with experimentally determined density values for sealed, solid blocks of asbestos fibers.³⁶ The tubular structure is supposed to be formed as a result of the bending of the Si-O-Mg-OH layers in order to relieve strain caused by differences in the dimensions of the intermeshing layers.³³ This type of strain effect was predicted as early as 1930.³⁷

The tubular hypothesis has further been substantiated by showing that isomorphous substitution of various cations for Mg⁺⁺ or Si⁴⁺ ions can relieve the strain in the chrysotile lattice and form flat plates similar to many clay mineral structures.³⁸ Chrysotile has, hence, been classified by many as the magnesium analog of the kaolin group, particularly of Halloysite.³⁹

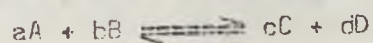
Crocidolite, on the other hand, shows a distinct physical structure. It has been shown that single fibers of crocidolite are in the form of laths.⁴⁰ Electron microscopy shows that crocidolite fibers are actually ribbons.⁴¹

While it is not certain what is the actual structure of the two fibrous minerals, it is sure that the fibers have an outer layer of magnesium hydroxide and an inner layer of silica. This is supported by high alkalinity of their suspensions in water. On the other hand, it is contended that if the outer layer of Mg(OH)₂ is somehow removed, the inner silica layer should be exposed to the liquid. This has been

shown by the data gathered during the present investigation. All the three minerals, when treated for two hours with 18% concentrated HCl, lost the outer layer of readily dissolved $Mg(OH)_2$ and showed surface charge and electrophoretic behaviour almost similar to that of silica. They all exhibited pzc values between 2 and 3, not showing substantial change by aging. The pzc values for silica (quartz) reported in literature are also found to be lying anywhere between 1.5 and 3 and not changing with the aging time of the suspension.²⁰

Another important aspect of the present investigation is the study of the kinetics of dissolution of the magnesium silicates in question. The possibility of employing various methods for measuring rates of reactions primarily depends upon the system being studied. The experimental techniques applicable to hydrometallurgical systems such as these, are more limited than those applicable to solid-gas or gas-gas reactions. The reaction is called homogeneous when it occurs within only one phase of a system. In hydrometallurgical systems, we commonly come across solution diffusion which is a homogeneous reaction and which is a main phenomenon in dissolution of minerals. In systems involving dissolution of a solid (also precipitation of a solid, which is just the reverse), diffusion through a zone adjacent to the solid-liquid interface controls the rate.⁴²

A chemical reaction could be represented by the equation:



The rates in the forward (r_f) and the backward (r_b) directions are expressed as

$$r_f = k_f (A)^a (B)^b \quad \text{and} \quad r_b = k_b (C)^c (D)^d \quad \text{where}$$

k_f and k_b are the rate constants for the forward and the backward reactions. Considering only the forward reaction, the order (n) is equal to the sum of the exponents ($a+b$). Therefore, any reaction rate involves a product of concentration raised to some power according to the equation

$dc/dt = \pm k c_i^{n_i}$ where c is the concentration of the species which changes as a result of the reaction.⁴²

Considering a reaction of the order n with respect to reactant c , the general differential rate equation is

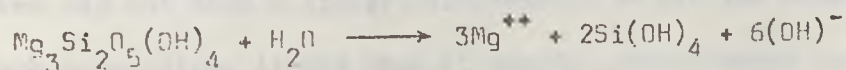
$$dc/dt = -k(c)^n.$$

When $n = 1$, the reaction is first order and upon integration becomes

$$\ln(c_0/c) = kt.$$

Similarly, for a zero order reaction, $dc/dt = k$ ie $c = kt$. Zero order kinetics result from the fact that the concentrations of all the reactants in a rate step remain constant during the reaction.⁴² Crystal growth from saturated solutions and many heterogeneous solid-gas and solid-liquid reactions are examples of zero order reactions.

The dissolution of the serpentines could be represented as



It is interesting to note that in the case of Mg^{++} leached out of untreated chrysotile samples, the plot of concentration versus aging time is a straight line obeying a linear equation of the form $y = mx + c$ where m is the slope of the straight line and c , the intercept made on the vertical axis. This is shown in figure 6. The values of the slope and the intercept for both the suspensions have been estimated by the method of least squares⁴³ and it has been found that the best linear unbiased estimates for the slopes of the straight lines are 2.7 and 3.4 for 1% and 2% suspensions respectively, and those for the intercepts are 23.1 and 46.3 for the two suspensions. It is further interesting to note that 23.1, the intercept made by the line for 1% suspension is almost half of that made by the line for 2% suspension. Suspension density thus seems to be a governing factor. This type of linear relationship seems to exist for other suspensions and dissolution of other species of the same suspension. This is evident from figures 6, 8 and 10. In some of the cases it is observed that the plot is not exactly a straight line. In order to throw more light on this matter, another approach has been taken.

The same data could be looked at in another way to draw a similar conclusion. The concentrations of Mg^{++} , Fe^{++} and Si^{4+} in the suspensions of chrysotile, crocidolite and serpentine in moles per litre, when plotted on the semilogarithmic scale with their corresponding aging times did not show a linear relationship in all the cases, but for some of the suspensions it did show linearity, which tended to curve out

after a considerable length of time. This could be explained by a possible re-adsorption of the dissolved species on the mineral surface. Also, it must be kept in mind that zero order reactions some times show behaviour of a first order reaction which is because of an incomplete adsorption of the products taking place because of low pressures. The linearity observed in these cases (represented in figure 13) is just a limiting case of the plots in figure 6 and has resulted due to the change of units of concentration which has caused the contraction of the scale. This further helps substantiate the conclusion that this dissolution is a zero order kinetic reaction. Looking at the similarity (although the two are exactly reverse of one another) between the processes of dissolution and precipitation, it is evident that the initial time period which is assigned to the phenomena of "Nucleation and Growth" in precipitation or recrystallization needs special attention. No attempt has therefore been made to give emphasis to the amount of Mg^{++} , Fe^{++} and Si^{4+} dissolved in water for aging times of upto one week.

The amounts of magnesium, iron and silicon that leach out of the mineral surface is dependent not only on the history of the sample, but also on the sample concentration itself. Thus more of iron and silicon species were detected in the leachant of the untreated crocidolite sample than magnesium was, while chrysotile and serpentine lost more of their magnesium in the aging suspensions because the magnesium content in the serpentines was initially higher. The initial composition of the minerals, however, should not be a guiding criterion.

Figure 13-A Plot of Conc. of Mg^{++} (moles/litre) versus Aging Time (weeks)
 1% and 2% Suspensions of Untreated Chrysotile and Serpentine

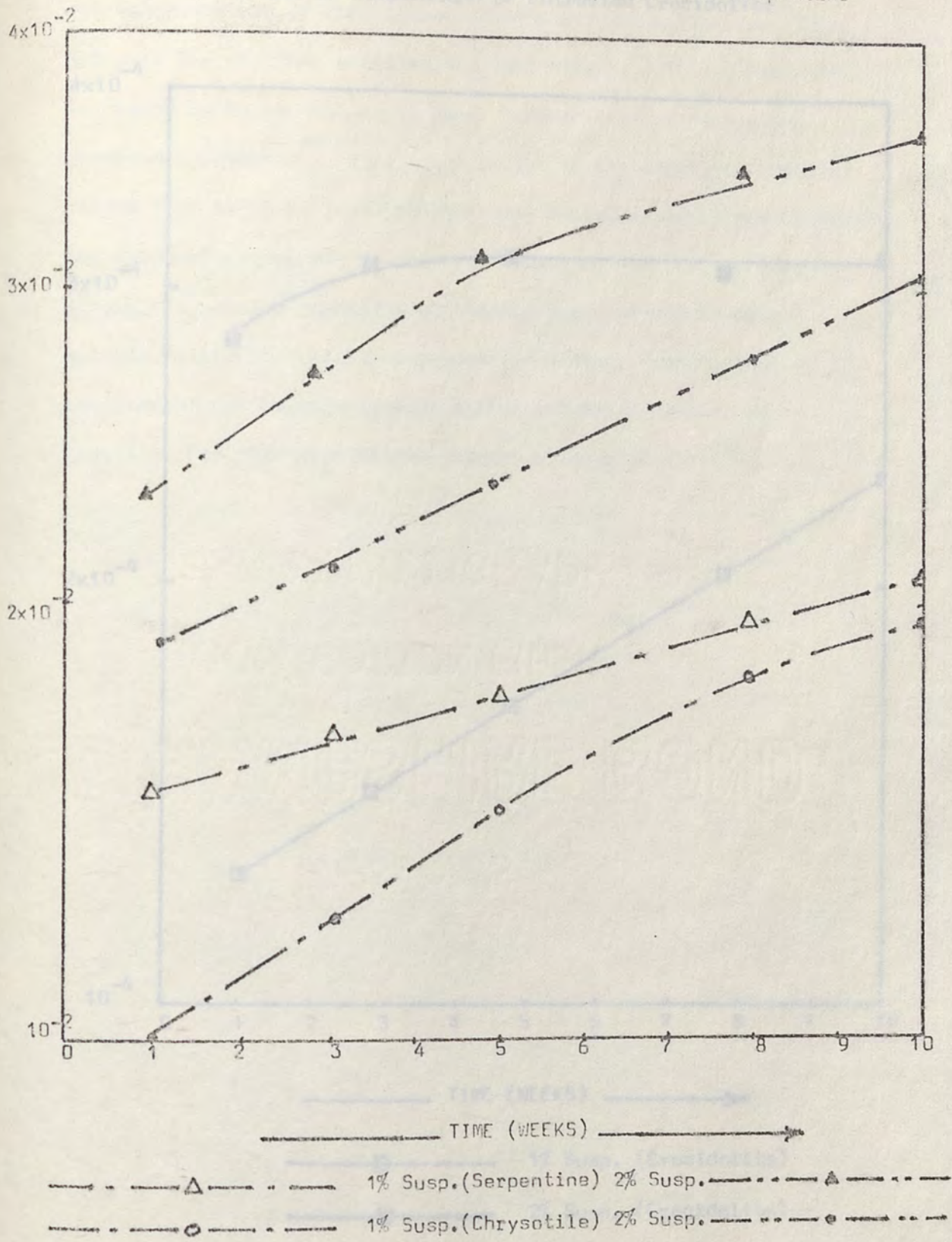
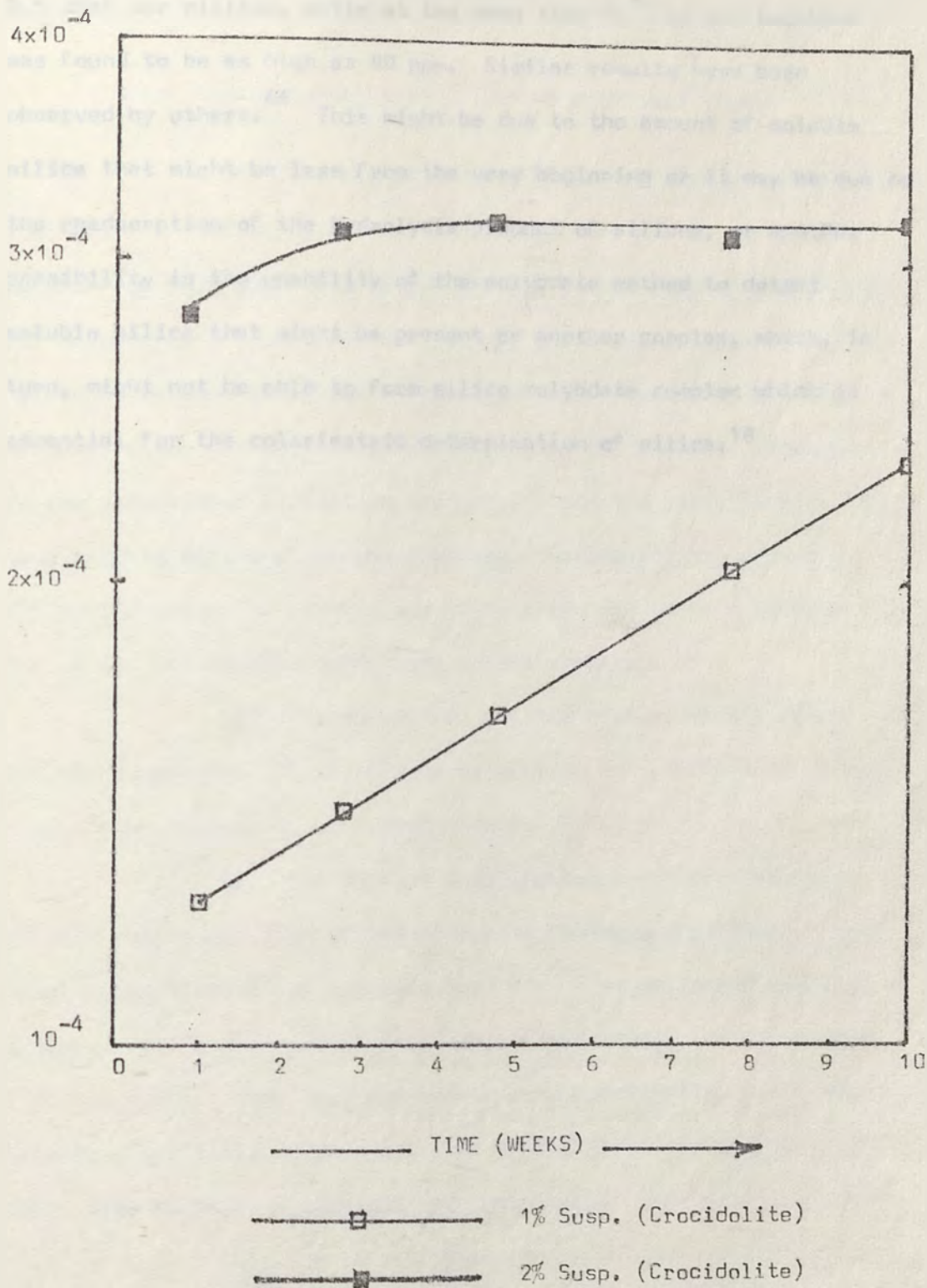


Figure 13-8 Plot of Conc. of Mg^{++} (moles/litre) versus Aging Time (weeks)
1% and 2% Suspensions of Untreated Crocidolite



This can be seen in table IV-9 again. The amount of silicon that was extracted out of the mineral surface was at no time more than 0.5 part per million, while at the same time Mg^{++} in the leachant was found to be as high as 80 ppm. Similar results have been observed by others.⁴⁴ This might be due to the amount of soluble silica that might be less from the very beginning or it may be due to the readsorption of the hydrolysis product of silicon, or another possibility is the inability of the molybdate method to detect soluble silica that might be present as another complex, which, in turn, might not be able to form silico molybdate complex which is essential for the colorimetric determination of silica.¹⁸

CONCLUSIONS

From this investigation it can be concluded that:

(1) The points of zero charge of magnesium silicates are variable quantities and not constants. The pzc of chrysotile varies from 10.1 initially to 8.7 after a ten week aging time. That for serpentine changes from 8.4 to 5.8, while crocidolite shows the points of zero charge at 4.4 initially which decreases to 3.1 after a ten week aging period. This variability of the pzc's is primarily due to the dissolution of surface magnesium hydroxide sites leaving behind less soluble silica sites thus changing the initial proportion of their sites with one another and causing the pzc to move towards the pzc of the new complex oxide site on the surface.

(2) The suspension pH, the history of the mineral and the suspension density of the mineral in water affect the dissolution of the mineral in water and also its pzc.

(3) The surface area and hence the particle size effects the dissolution of the minerals. Because the fibers have a total outer diameter of not more than 600 \AA , which is too small to be compared with the length of an average sized fiber, it can be said that the surface area does not change very drastically. This might lead to the situation where the plot of change of surface area versus aging time might be a straight line parallel to the horizontal axis.

(4) The rate of dissolution of some species is

SUGGESTIONS FOR FURTHER RESEARCH

It is suggested that an extensive experimental research be devoted to carry on additional exploration of the topic investigated in the present project.

A completely new approach should be made to the variable pzc 's of the minerals. For an easy interpretation and generalization of the data, at least four different suspension densities should be studied and if possible, a different size fraction of the minerals should be used. Similar dissolution studies could be carried out at different temperatures and in various atmospheres. The electrokinetic behaviour of these minerals should also be studied under various environments, e.g. inert atmosphere like nitrogen or an active atmosphere like carbon dioxide. An attempt should also be made to correlate change in the surface area with aging and dissolution.

Dissolution should also be studied in a greater detail during the first stage of leaching. Taking more frequent measurements of the concentrations of the dissolved species should throw more light on that stage of dissolution which has been labelled earlier as being the reverse of "nucleation and growth". The dissolution study should be carried out at different temperatures and use should be made of the isotherms thus obtained to determine whether or not the reaction is diffusion controlled.

Development of some type of theoretical formula that might correlate the concentrations of dissolved species with aging time should help decide the structure of the minerals in question.

Looking from the point of view of a medico-engineer, it might prove to be of great importance if pzc, pH, structure and size of the fibrous minerals are correlated with coagulation, dispersion or flocculation of the fibers. This might lead to further knowledge in the direction of carcinogenic properties of fibrous asbestos.

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APPENDIX I

ZETA POTENTIAL, ELECTROPHORESIS AND ZETA METER

At the solid-liquid interface, two types of potentials are developed. They are called pi and zeta potentials. Electrokinetic behaviour of a mineral depends on the potential at the slipping plane between the charged surface and the electrolyte solution. This potential is called the electrokinetic or zeta potential. A layer of water of about one molecule thickness is supposed to be bound to the surface by charge-dipole interaction. Therefore, the surface of shear is generally supposed to be located just outside the Stern layer. (See figure 1, page 5.)

If an electric field is applied tangentially along a charged surface in contact with water or an aqueous electrolyte, a force is exerted on both parts of the double layer. The charged surface and the attached material tend to move in the appropriate direction, while the ions in the diffuse layer alongwith associated water of hydration, show a net migration in the opposite direction. As a result, if the charged surface and the mobile part of the double layer are made to move relative to one another, a potential gradient is created. The movement of charged mineral particles relative to a stationary liquid by an applied potential difference is called electrophoresis. If the material being investigated is a stable suspension or an emulsion containing microscopically visible particles or droplets, then electro-

phoretic behaviour can be observed and measured directly.

The zeta meter is a commercially available apparatus for the measurement of the electrophoretic mobilities of various particles by microelectrophoresis technique. The electrophoretic mobility can be expressed as the zeta potential of the mineral particles by a simple relationship known as Helmholtz - Smoluchowski equation. It is often found that there is a slight extent of error in the conversion of electrophoretic mobility to zeta potential by this formula. This is the reason why attempt is not made to convert the mobilities to zeta potentials, but the data have been interpreted in the form of the mobilities only. Theoretical details in this direction could be found in literature.^{45,46,47,48}

Although the zeta meter is only one of many other commercially available apparatus for surface charge measurements by many methods like the Tiselius moving boundary method, zone electrophoresis, electroosmosis, streaming potential and sedimentation potential, its relative ease in handling and accuracy of results are two main factors that attract the attention of researchers in this field. There are, however, some drawbacks of this apparatus, which should be made note of.

Firstly, the cylindrical nature of the connecting tube of the zeta meter cell (or Riddick cell) requires an optical correction for the focussing action of the cell walls and is unsatisfactory if any sedimentation takes place during the measurement.

Secondly, microelectrophoresis measurements are complicated by simultaneous occurrence of electroosmosis. The internal glass surfaces of the cell are generally charged, causing an electroosmotic flow of the liquid near to the tube walls together with a compensating return flow of the liquid with maximum velocity at the centre of the tube. This results in a parabolic distribution of liquid speeds with depth, and the true electrophoretic mobility is only observed at the locations in the tube where the electroosmotic flow and the return flow of the liquid cancel.⁴⁹ It has been calculated that the diameter factor that marks the position of the tracking line in a circular tube type electrophoresis cell is at 14.7% of the tube diameter from either wall of the tube.⁵⁰

Lastly, the thermal overturn in the liquid in the tube, caused by the rise in temperature of the liquid by the applied potential gradient can have an adverse effect on the observed electrophoretic mobility of the particles.

These are only a few of the facts that should be paid attention to when interpreting electrokinetic data obtained by this method.

Appendix II shows the plot of electrophoretic mobility versus pH for a 2% (w/v) suspension of untreated chrysotile.

APPENDIX II

PLOT OF ELECTROPHORETIC MOBILITY (EPM) VERSUS pH

2% Suspension : Chrysotile in Water

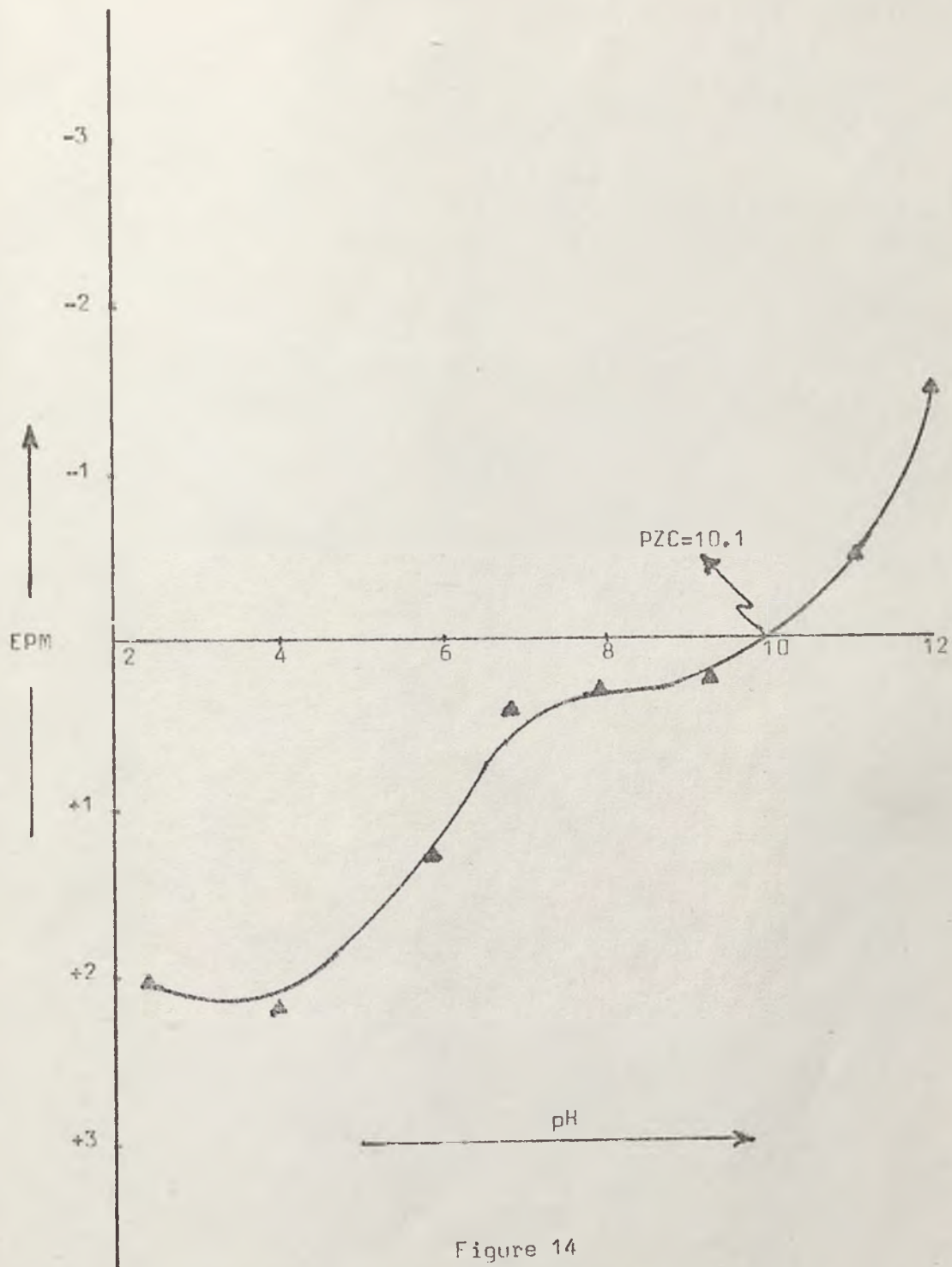


Figure 14