Kinetic Study of Dissolution of Asbestos Fibers in Water

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Kinetics of dissolution of asbestos minerals in water were studied over a temperature range of 5 to 45°C. A parallelism was noted between the rate of dissolution of magnesium from magnesium silicates and the rate of pH drift. The rate of dissolution reaction was directly proportional to the specific surface area of the asbestos minerals.

Both magnesium ion and hydroxyl ion concentrations were temperature-sensitive only in the initial stage of the contact between chrysotile mineral and water.

The mechanism of dissolution of dissolved species from chrysotile was discussed in terms of the energy of activation. The activation enthalpies were calculated to be 5.5 and 6.5 kcal/mol for dissolution of magnesium and increasing of hydroxyl ion concentration, respectively. These results indicate that the rate controlling mechanism for both magnesium and hydroxyl ion dissolution is diffusion from the surface into water.

INTRODUCTION

Asbestos is a broad term embracing a number of fibrous silicate minerals. These minerals look extremely fragile, yet their fibers have a tensile strength equal to that of piano wire. Chrysotile asbestos is the only mineral that can be woven into cloth, and its fibrous structure is, if anything, even more amazing than its remarkable ability to withstand heat.

Because of its unique physical properties asbestos has achieved great industrial importance, and more than 3,000 current uses are known, ranging from use in the kitchen to use in space missiles. Because their minuscule fibers are eminently respirable, asbestos minerals have also found their way into the lungs of humans, where they apparently produce serious biological effects such as asbestosis and lung cancers (1–3).

Because of both their usefulness and their hazardous properties, these minerals have attracted a good deal of attention from research workers during recent years. For example, the surface properties of asbestos minerals have been studied by many investigators (4–9). However, even for the important mineral chrysotile, the literature data are more or less conflicting. Pundsack (4) measured a PZC (point of zero charge) of 10.1; Martinez and Zucker (5) measured 11.8; Chwastiak (6) reports 10.8–11.0; and Riddick (7) measured three separate apparent PZC's at about pH 8.3, 10.0 and 10.9. More recently Trivedi (8) reports 10.1. Naumann and Dresher (9) have studied surface charge enhancement of chrysotile by metal ions, and describe how the mineral reacts with contaminant ions.

In the present paper, the mode of dissolution of magnesium and hydroxyl ion from asbestos minerals placed in water was studied by kinetic experiments involving the rate at which these items leave the minerals. Also, some study was made of the interaction between dissolved species.

EXPERIMENTAL

Chrysotile asbestos from Quebec, Canada was obtained from Ward's Natural Science Establishment, Inc., Rochester, N. Y. The sample was received in block form. The mineral is a hydrated magnesium orthosilicate containing a high percentage of magnesia and water. Its chemical formula may be expressed as either $Mg_3Si_2O_5(OH)_4$ or $3MgO \cdot 2SiO_2 \cdot 2H_2O$. The sample was cut by scissors into lengths of less than about one-half inch. Fine particles of chrysotile were prepared with a mortar and pestle and by dry grinding with a pebble mill. The product of grinding was sized by sieving. The minus–325–mesh fraction was kept for subsequent experimentation. Fabricated fibers of chrysotile were also prepared in a motor-driven commercial blender.

A known amount of deionized distilled water was added to a known amount of chrysotile contained in a beaker. The initial pH of the distilled water was pH 5.9–6.1. The pH of the chrysotile-containing suspension was measured immediately after water was added. The continuous change of pH was recorded as a function of time, using an electrometer connected to a strip-chart recorder. Dissolved magnesium ion from the chrysotile sample was measured by means of a specific divalent cation electrode as a function of time. Measurements of hydrogen and magnesium ion concentration were repeated at temperatures both lower and higher than room temperature.

Minus–325–mesh fractions of the asbestos minerals amosite and crocidolite were prepared as was chrysotile. In addition, similar quartz, magnesium oxide, iron oxide, and alumina samples were prepared. The pH measurements of these materials were recorded as a function of time at room temperature only. A constant temperature bath was used for high temperature experiments. For below-room temperature, an Eberbach immersion cooler was used.

RESULTS AND DISCUSSION

Chrysotile asbestos dissolves incongruently in the short-term and congruently in the long-term according to following reaction (10, 11);

$$Mg_3Si_2O_5(OH)_4 + 5H_2O = 3Mg^{2+} + 6OH^- + 2H_4SiO_4 \quad (1)$$

The experimental results show that magnesium ion and hydroxyl ion concentrations from chrysotile suspension increase in the initial stage of aging time.

The interaction between chrysotile asbestos and in terms of change in pH of the solution is shown in Fig. 1. Even a small amount of chrysotile asbestos significantly increases hydroxyl ion concentration in solution. The rate of hydroxyl ion in solution increases logarithmically with reaction time at room temperature. As the sample size of fine-ground chrysotile is increased, the time required to reach equilibrium pH decreases. In each sample the pH change levels off after a certain time elapses.

However, if sufficient time is allowed, the pH drops again. This phenomenon is shown in Fig. 2. As one can see from this figure, the equilibrium pH ultimately starts decreasing at long aging times, indicating that chrysotile dissolves congruently in water. This decrease in pH is probably due to either the formation of $MgOH^+$ or readsorption of $Mg(H_2O)_6^{2+}$ and $MgOH^+$ ions on the negative silica surface sites exposed as the chrysotile fibers dissolve.

Figure 3 shows the change of pH with time for various aqueous suspensions of asbestos minerals and the simple oxides that go into the makeup of asbestos minerals. Among these minerals, the pH change of Mg–oxide and Mg–hydroxides are similar to that of the chrysotile asbestos suspension indicating that the surface of chrysotile contains mainly a magnesium hydroxide layer. In other words the chrysotile surface behaves like magnesium oxide or magnesium hydroxide in terms of pH change in water. The values of zero point of charge (ZPC) on chrysotile and magnesium oxide were reported elsewhere (4, 6, 12). Figure 3 indicates that the ground chrysotile sample exhibits a greater pH change than unground chrysotile fibers. This result also clearly shows that the surface property of chrysotile is a function of exposed surface. The specific surface areas of chrysotile sample of +200–100 mesh, 10 mm original fiber and fabricated fiber were 33.4 mm^2/gm, 16.6 m^2/gr and 26.8 m^2/gm (13), respectively. The ground sample contains a greater metallic content, particularly of magnesium and iron, than the unground fiber, presumably

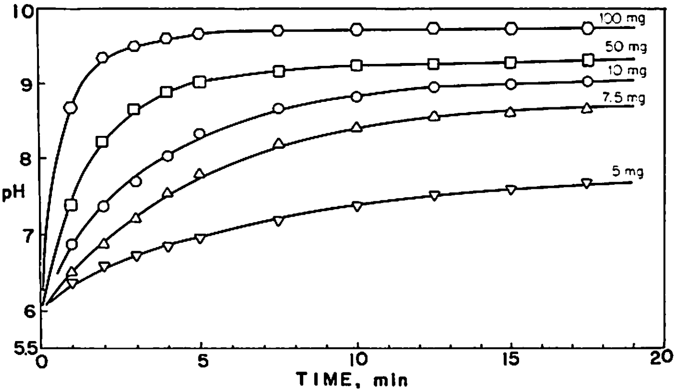


Fig. 1. Sample size effect on pH as a function of time at room temperature. Conditions: sample chrysotile, −325 mesh pH_i = 6.0; volume = 100 cc water.

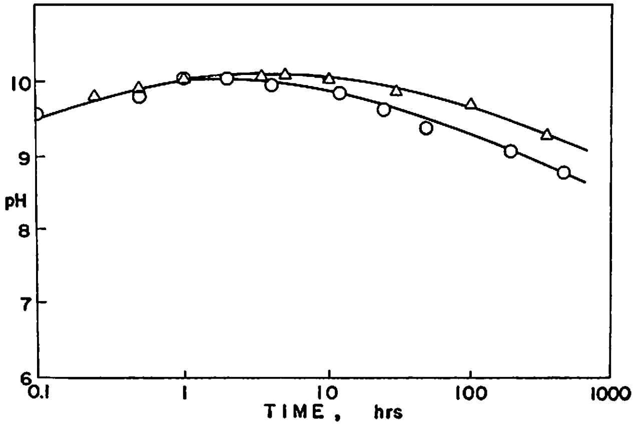


Fig. 2. pH change of chrysotile for long period. ○, 3 gm of −120 mesh serpentine in 500 gm distilled water (Luce, Ref. (*10*)). △, 100 mg of −325 mesh chrysotile in 100 cc distilled water.

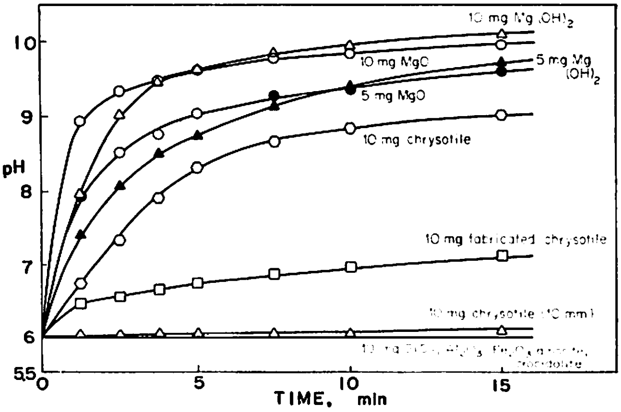


Fig. 3. pH change of various oxide minerals (−325 mesh and 0.01% suspension) as a function of time.

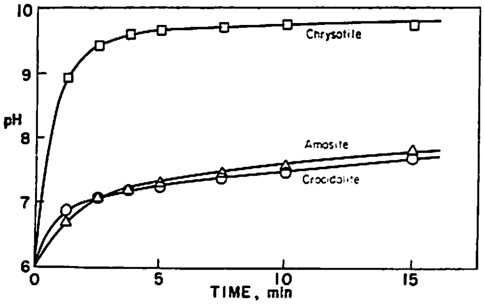


FIG. 4. pH change ofthree asbestos mineral suspensions (0.1%). Conditions: −325 mesh; pH_i = 6.0.

because of destruction of the fiber structure from grinding the physically contained iron oxide and exposing the inner magnesium layer and from contamination of the grinding device. This agrees with other investigators (14). As seen in this figure, 10 mg of 10 mm length fibers of chrysotile, 10 mg of pure quartz, alumina, iron oxide, amosite, and crocidolite show very little pH change in the initial 20-minute aging period.

However, some pH change would be expected if one were to take a large sample size as shown in Fig. 4, where 100 mg of amosite and crocidolite were compared with the equivalent amount of chrysotile. Since amosite and crocidolite contain rather small amounts of magnesium oxide compared with chrysotile, it is not surprising that the pH changes of suspensions of the former two minerals are less than for chrysotile. Also the greater pH change of chrysotile suspension may be partly due to chrysotile's greater surface area (23.0 m^2/gm). The surface areas for amosite and crocidolite were obtained; 6.67 m^2/gm and 6.22 m^2/gm, respectively.

In the surface properties of chrysotile, reported by many investigators (5–17) the properties of the solid-gas interface are especially interesting. They observed that the surface area of the unactivated fibers (evacuated at 10^{-5} mm Hg at 25°C for 24 hr) available to water vapor is nearly twice that available to nitrogen. However, the sample activated at 450°C, showed the same area for both gases. These results have been explained by the hypothesis that chrysotile fibers have an internal capillary structure. It is also proposed that the entrance to these capillaries is blocked by bound water, through which water vapor and ammonia, but not the other gases, can diffuse. Thus, internal and external surfaces in the chrysotile are quite different. The hypothesis of sorbed water plugs in the capillaries in chrysotile fibers was proven by the surface area calculations, by Harkin's absolute method using heats of immersion for the chrysotile and water vapor system at variour relative pressures of the adsorbed film.

The investigation of the surface properties of asbestos fibers after various chemical treatments is in progress. The results will be published in the near future. We have found that the surface area of chrysotile can be increased by a factor of ten with a strong acid leaching. The X-ray diffraction patterns for the acid-leached chrysotile fibers are similar to that of silica gel. The effects of aging at elevated temperatures and leaching with acids on the surface OH groups are also in progress with infrared spectroscopy.

Figure 5 illustrates the variation of pH with reaction time over the temperature change of 5–45°C for chrysotile. Figure 6 shows the hydroxyl ion concentration which was calculated from the data of Fig. 5.

Figure 7 shows the concentration of magnesium ion in chrysotile suspension as a function of aging time. A specific magnesium divalent cation electrode was used for magnesium ion determination. Three different temperatures were studied, 5, 25 and 45°C. Essentially, both hydroxyl and magnesium concentrations increase as reactions proceed, indicating that the surface hydroxide layers and magnesium layer leach out, putting OH^- and Mg^{2+} in solution. This is strong evidence that the hydrated magnesium substantially dissolves as Mg^{2+} and OH^-. And this slow removal of the $Mg(OH)_2$ layer is apparently the rate-controlling step of the dissolution of chrysotile in water. The initial rate of dissolution of chrysotile is faster at a higher temperature. However, the rate decreases as reaction progresses as noticed in Figs. 6 and 7 at constant temperature.

It is well known that chrysotile asbestos fibers in water liberate magnesium ions and

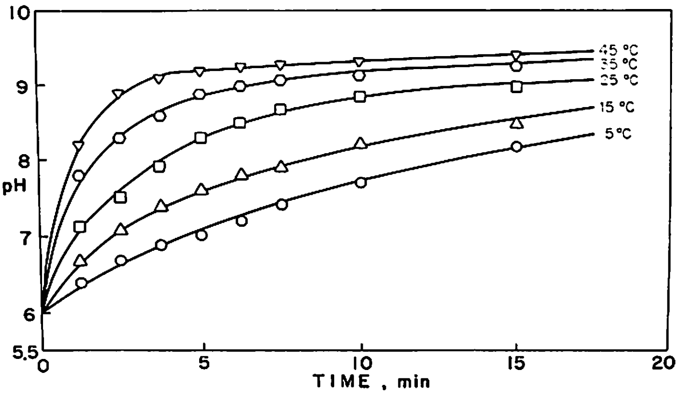


FIG. 5. pH dependence on temperature in chrysotile–water system. Conditions: sample, chrysotile, −325 mesh; $pH_i = 6.0$; suspension, 0.01%.

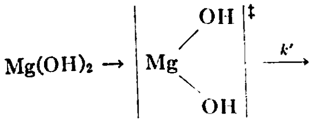
hydroxyl ions. In aqueous systems, the hydrated magnesium ion most likely formed, $Mg(H_2O)_6^{2+}$, binds the water in the first coordination sphere. The initial rate of dissolution of hydroxyl ion and magnesium ion are one pOH unit/min. and $3.06 \times 10^{-2} M$/min., respectively, at 25°C.

Since the brucite layer forms the outer layer of the curved composite structure of chrysotile, the external surfaces of all chrysotile fibers, assuming the cylindrical form (18) to be complete, are composed exclusively of hydroxyl ions. Chrysotile thus possesses strong basic properties, exerts a relatively high surface potential in water, and has a marked hydrophilic nature (19).

For a unit cell of chrysotile asbestos, the following dissolution mechanism may occur, assuming primarily magnesium oxide in the surface;

$$\text{¦}\,MgO + H_2O \rightarrow \text{¦}\,MgO\cdot H_2O \quad \text{rapid adsorption} \qquad [2]$$

$$\text{¦}\,MgO\cdot H_2O \rightarrow Mg(OH)_2 \quad \text{rapid hydration} \qquad [3]$$



$$Mg(OH)_2 \rightarrow \left| Mg\begin{matrix} \diagup OH \\ \diagdown OH \end{matrix} \right|^{\ddagger} \xrightarrow{k'} Mg^{2+} + 2OH^- \quad \text{slow dissociation} \qquad [4]$$

$$Mg^{2+} + OH^- \rightarrow MgOH^+ \quad \text{slow complex formation} \qquad [5]$$

where k' is a specific rate constant.

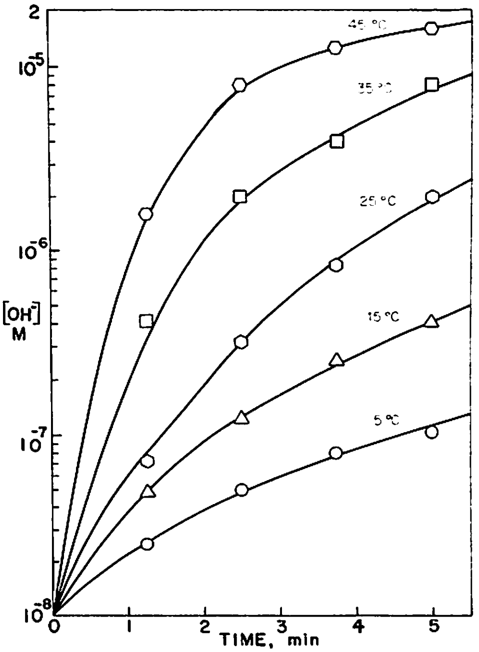


FIG. 6. Replot from Fig. 5 in terms of $[OH^-]$ *vs.* time at various temperatures.

The general kinetic equation for a solution reaction may be written:

$$\text{Rate} = (dC)/(dt) = -k'\,C^n \qquad (6)$$

where

C concentration
k' rate constant in minutes, (this includes

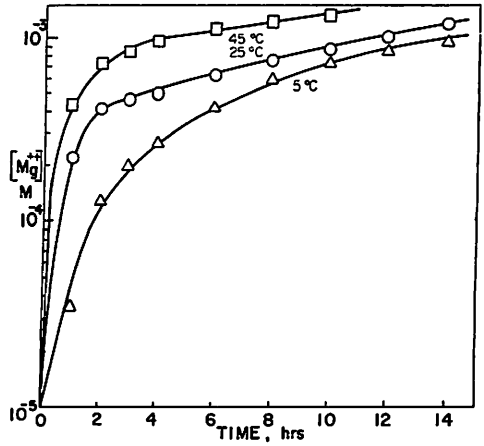


FIG. 7. Rate curves for $[Mg^{2+}]$ in the chrysotile–water system. Conditions: sample; chrysotile, −325 mesh; $pH_i = 6.0$; $Mg_i^{2+} = 10^{-5}$ moles/liter; suspension, 1%.

a surface roughness factor and a reactive site factor)
t is time in minutes, and
n is constant.

According to the theory of absolute reaction rate (20), the rate constant may be expressed as

$$k' = \frac{kT}{h} e^{-\Delta F^\ddagger/RT} = \frac{kT}{h} e^{-\Delta H^\ddagger/RT} e^{\Delta S^\ddagger/R} \quad [7]$$

where k is Boltzmann's constant, h is Plank's constant, T is absolute temperature, $\Delta F^\ddagger$ is the free energy of activation, $\Delta H^\ddagger$ is the heat of activation, $\Delta S^\ddagger$ is the entropy of activation, and R is the gas constant.

In the case of hydroxyl ion

$$\text{Rate} = (d[OH^-])/(dt) = k'[OH^-]^n. \quad [8]$$

If one measures the maximum slopes from Fig. 6, these data provide the rate = $(\text{slope})_{max}$ in which one assumes a first order reaction, so that n is equal to unity.

Therefore equation [8] can be written as:

$$\text{Rate} = \frac{kT}{h} e^{\Delta S^\ddagger/R} [OH^-] e^{-\Delta H^\ddagger/RT}. \quad [9]$$

Rearranging equation [9] and taking logarithms:

$$\log \frac{\text{Rate}}{T} = \log \frac{k}{h} + \frac{\Delta S^\ddagger}{2.3R} + \log [OH^-] - \frac{\Delta H^\ddagger}{2.3R}\left(\frac{1}{T}\right). \quad [10]$$

From equation [10] one can calculate the heat of activation $\Delta H^\ddagger$ by plotting log (Rate/T) against $1/T$.

Figure 8 illustrates the results obtained by making this plot. From the slope of the straight line obtained, the energy of activation was calculated to be 6.5 kcal/mole. Similarly in the case of dissolution of magnesium ion in water from the surface of chrysotile, the rate equation could be represented:

$$\text{Rate} = \frac{d[Mg^{2+}]}{dt} = k' [Mg^{2+}] \quad [11]$$

and

$$\log \frac{\text{Rate}}{T} = \log \frac{k}{h} + \frac{\Delta S^\ddagger}{2.3} + \log [Mg^{2+}] - \frac{\Delta H^\ddagger}{2.3R}\left(\frac{1}{T}\right) \quad [12]$$

By plotting log Rate/T *vs.* $1/T$ as is shown in Fig. 9, the energy of activation for magnesium ion into the water solution turns out to be 5.48 kcal/mole.

The energy of activation of dissolution for both hydroxyl ion and magnesium ion from the surface of chrysotile asbestos appears to be of the order of magnitude of solution diffusion. Thus, it appears that the rate-determining step for these dissolution reactions is diffusion away from the chrysotile surface.

It is interesting to note that the activation energy of self-diffusion of water molecules in water has been reported to be 5.3 kcal/mole (21). In the present study, the hydroxyl ion diffusion through water has an activation energy of 6.5 kcal/mole, which is a good agreement with the above value.

Generally speaking, diffusion in a liquid may be treated as a rate process requiring a definite activation enthalpy of the order of 5 kcal. The picture for diffusion in liquids does not differ essentially from that for solids, the only difference being a lower

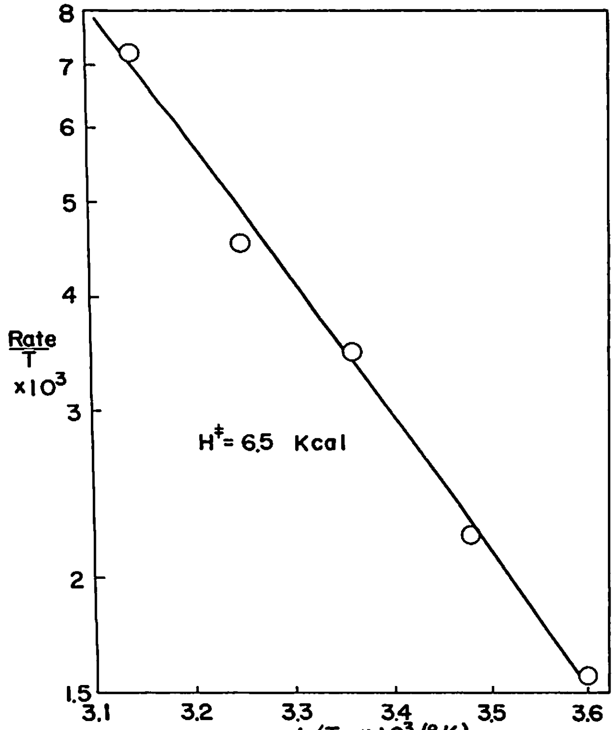


FIG. 8. Activation enthalpy plot for hydroxyl ions.

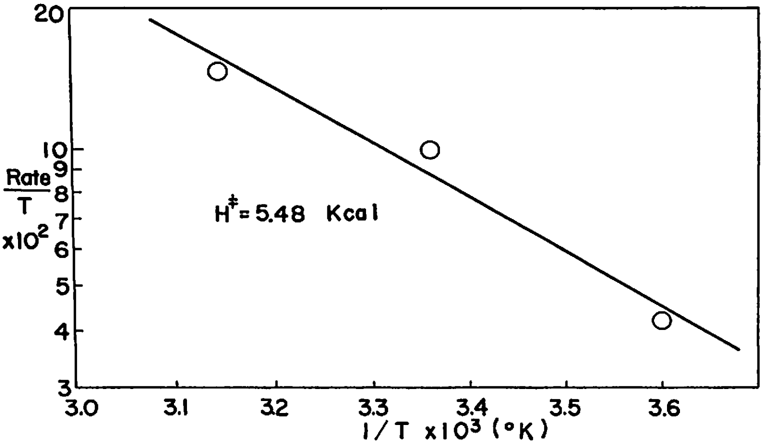


FIG. 9. Activation enthalpy plot for Mg dissolution.

energy of activation in the case of liquids (22). Recently, many kinetic studies have been carried out in aqueous media, such as cementation of copper by iron (23, 24) and dissolution of metals (25) or minerals (10, 26) in aqueous solutions, fast reactions of hydrogen and hydroxide ions (27), and reactions of main group metal ions with biological carriers (28). In the last reference mentioned, the kinetics and mechanism of

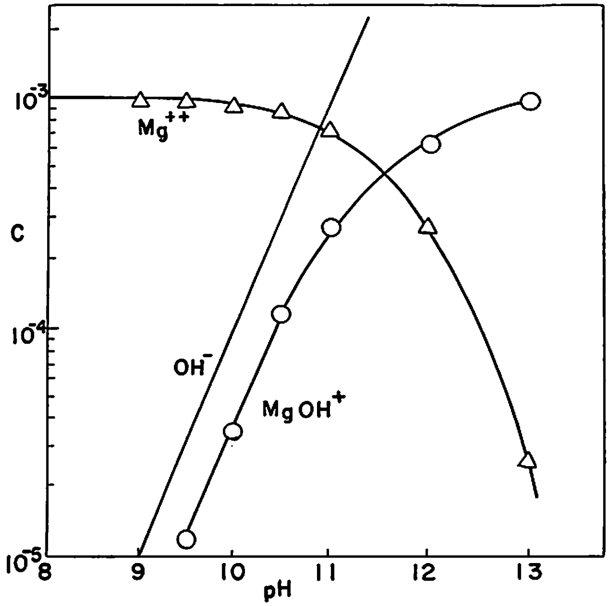


FIG. 10. Concentration diagram of magnesium–water system; assumed a total concentration of magnesium 1×10^{-3} *M*.

formation of metal complexes were surveyed, and many of the main group metal complexes which are of biological importance were noted. Most striking is the highly specific behavior of metal complexes in enzyme activation and in bioelectrical phenomena.

Two mechanisms may account for the dissolution of chrysotile in water. First, hydroxyl ions diffuse into solution, and second, magnesium cations are extracted from the surface, leaving behind a silica layer as described earlier. It is also probable that the dissolution mechanism could be a surface renewal process, since magnesium cations are continuously leached out from the layer structure of chrysotile. Based on electron microscope studies, even the ground sample (−325 mesh) shows clear rod- or cylinder-like shapes which may keep their layer structure as dissolution proceeds.

Experimental data on rates and stability constants of alkaline earth complexes are scarce in the literature; studies are difficult for three reasons (28):

(1) Such complexes usually are weak and the study has to be made at high solution concentrations.

(2) Rate constants are very rapid (10^{-5}–10^{-9} sec).

(3) Reactions cannot usually be followed spectrophotometrically; there are only few indicators which can be used.

Actually, a considerably increased sensitivity and time resolution of relaxation methods may be required such as can be measured with a temperature-jump device and by electric field-pulse method (28).

Essentially all of the dissolved magnesium is present as Mg^{2+}; the concentrations of dissolved carbonate and bicarbonate are far too low to allow significant formation of magnesium complexes. Likewise in the present system, the concentration of OH^- is too low to permit significant formation of $MgOH^+$. According to dissociation constants of Butler (29) and Sillen (30), neglecting activity coefficients:

$$Mg^{2+} + OH^- = MgOH^+ \qquad K = 10^{2.58} \qquad [13]$$

$$Mg(OH)_2 = Mg^{2+} + 2OH^-$$
$$K_{Mg(OH)_2} = 1.82 \times 10^{-11} \qquad [14]$$

$$H_2O = H^+ + OH^- \qquad K_w = 10^{-14}. \qquad [15]$$

The concentration of Mg^{2+} and $MgOH^+$ are presented as a function of pH in Fig. 10, assuming total dissolved magnesium concentration of 1×10^{-3} M. Since the pH is below 10, the concentration of $MgOH^+$ is less than 3.5% of the total concentration of dissolved magnesium and the formation of $MgOH^+$ at early stages of the reactions can be neglected. However, after a long period of time, it is probable that Mg-complexes may be formed due to hydroxyl ion decrease as noted in Fig. 2. The $MgOH^+$ complex formed may readsorb back into the silica surface, since the surface of exposed silica of chrysotile must be negatively charged. This hypothesis is supported by many flotation studies in which adsorption of cations by quartz has been observed (28, 29).

It should be mentioned that the dissolution of magnesium from ground chrysotile suspension is a temperature-sensitive reaction. On the contrary, in the case of unground chrysotile fiber suspensions, the ultimate magnesium concentration in solution at high temperature (33, 34) is essentially the same as at room temperature. This may be due to the high metal content found in ground samples, as described previously (14). It was found that fabricated chrysotile which has an initial, white color turns partly dark-gray after fine grinding. This color change, and an increase in free metallic oxide content, may be due to destruction of the fiber structure.

Future refinements in the continuous recording of rates of dissolution of other types of cations such as ferrous and ferric ions, and including those present in trace amounts such as nickel, copper, aluminum, cobalt, chromium and also soluble silica, may make it possible to provide some further light on the surface chemistry of asbestos minerals. It is possible that some of these metals may be involved in asbestos carcinogenesis. Of particular importance may be total iron and the ratio of ferric to ferrous ion (35). In addition, it has been suggested that alkaline earths are bound in significant amounts by proteins, but in general only when the protein is negatively charged (36). The binding of the metal to the protein is very tight, so that no dissociation of the complex is detectable. Also, the local rise in pH accompanying in asbestos fiber lodged in the lung may be important considering the recent work on the pH dependent changes in surfactants of lung substances (37).

CONCLUSIONS

(1) The rate of dissolution of asbestos minerals in water is a function of the specific surface area of the minerals.
(2) Magnesium cations may be continuously liberated from chrysotile fibers leaving behind a silica skeleton that has the elements of the original structure.
(3) Chrysotile dissolves congruently in water.
(4) Experimental evidence suggests that the rate-controlling step is the removal of brucite layer from the fiber surface of chrysotile.
(5) The smaller the particle size, the more magnesium liberated from chrysotile-water suspension.

ACKNOWLEDGMENT

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