# The Leaching of Ground Chrysotile

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## Introduction

Various types of asbestos minerals are known to be somewhat unstable, in that cations contained within the lattice can be removed by mild chemical treatment. Although under normal conditions the effect is small and frequently encountered in other silicate minerals, a freshly ground chrysotile can be persuaded to part with a substantial proportion of its cations other than silicon. This chemical leaching can take place at pH conditions close to neutrality and is very different from the effects in high acid solution when the mineral may be completely decomposed (1).

The authors have examined this phenomenon with especial reference to the bearing which the leaching might have on the occurrence of asbestosis in lung tissue. In previous literature, other workers have published results of leaching experiments but these are often confusing and conflicting (2, 3, 4, 5, 6). In several cases the influence of grinding and sample preparation has been disregarded; in others the leaching conditions have not been standardised. These factors are of vital importance and must be given due regard in studies of this nature.



## Nature of the Release Phenomena.

The crystal structures of asbestos minerals are based on a complex chain or layer lattice-type silica arrangement with

counter-balancing ions principally of magnesium, aluminium, ferrous and ferric iron. The crystal habit of all asbestos minerals is fibrous.

The cations other than those of silicon occupy mainly octahedral lattice sites and are linked by ionic/covalent bonds to the silica conformations (1). Usually in one crystallographic direction the structure is not continuous by ionic bonding so presenting lines of weakness and easy fracture.



The ultimate layers within the lattice are capable of easy distortion and in this way cations may be released from the structure by leaching.

When the asbestos mineral, chrysotile, is subjected to size reduction by grinding, the strain and distortion is greatly aggravated and considerably more release of cations might be anticipated. In addition the total surface area for attack is increased.

## The Magnitude of the Leaching Effect

By and large the amount of cations which can be extracted from the lattice of an asbestos mineral such as chrysotile depends on the pH of the solution. At high acid values, chrysotile even in well-developed fibre form can be decomposed completely although this phenomenon takes place rapidly only at pH values less than 2.

In the course of our investigations several anomalous findings were observed in the leaching with solutions near to neutrality. In particular the presence of an organic buffer such as glycine changed the extraction markedly.

In a series of experiments using chrysotile which had been subjected to various processing operations both the amount of magnesium taken into solution and the changes in pH were measured when the asbestos mineral was stirred in an acid aqueous medium of known initial pH. In all experiments, hydrochloric acid was the sole reactant and the liquid/solid ratio was a constant value, namely 50 : 1 in each experiment. All leaching experiments were carried out at 37°C. and the reaction was allowed to proceed for 1 hour. The total amount of magnesium passing into solution was estimated by the D.C.T.A. method of Pribil and Vesily (7). Some of the results are shown in Table 1.

Table 1: Phenomena Associated with the Leaching of Chrysotile*

| | Initial pH of leach solution | Final pH of leach solution | Magnesium released / total Magnesium x 100% |
|---|---|---|---|
| Hand picked fibre | 2.1 | 4.2 | 3.3% |
| | 5.5 | 7.3 | 0.4 |
| Fibre, ball-milled 24 hours | 2.1 | 9.9 | 3.6 |
| | 4.0 | 10.6 | 1.0 |
| | 5.5 | 10.2 | 0.9 |
| + glycine buffer | 4.1 | 8.9 | 16.0 |
| Fibre, ball-milled 72 hours | 2.1 | 10.1 | 3.1 |
| | 4.0 | 10.6 | 0.6 |
| | 5.5 | 10.5 | 0.7 |
| + glycine buffer | 4.1 | 9.0 | 21.1 |

* The sample used was a chrysotile from Thetford, Canada, containing 21.2% magnesium.
Ball milling conditions were standardised by introducing 5 gm. samples into a 1.25 l. Pascall porcelain unit with the recommended charge of pebbles.

The release of magnesium cations into solution produced a marked change in pH conditions but less so when glycine was present. Much more magnesium was extracted when the buffer was used.

The results of treating chrysotile after grinding for 24 hours and 72 hours showed little significant difference, except when glycine was present; if anything, less magnesium was removed from the sample subjected to the long grinding exercise under normal leaching conditions but the pH change was more pronounced.

An analysis of those results revealed that chemical factors other than simple leaching of free surface cations were involved and that these were causing apparently anomalous observations. Published chemical data shows that magnesium in solution becomes unstable at alkaline pH conditions when insoluble magnesium hydroxide precipitates. This occurs in the pH range 9.5 - 10.5. In the experiment under investigation the release of magnesium from the chrysotile produced an ever-increasing alkaline condition until pH conditions favoured the precipitation of magnesium hydroxide. Further release then either did not occur or the magnesium was instantaneously precipitated as an insoluble form. The presence of glycine as a buffering agent prevented excess alkaline development, so that considerably more magnesium could be released.

This conclusion was confirmed and an accurate indication of the true magnesium release from chrysotile was established by radically altering the conditions of experiment.

The problem of the change to alkaline pH was solved by observing the release of magnesium in a neutral solution and maintaining the neutrality at pH 7 by adding hydrochloric acid solution until no further change in pH took place on standing. This has proved to be a reliable and reproducible technique which gives an accurate assessment of the cations which would pass into solution from a chrysotile under the mildest but prolonged aqueous conditions.

Under these test conditions, the amount of magnesium released was appreciably higher and was proportional to the intensity of crushing and grinding to which the sample had been subjected, as shown in Table II.

Table II: Release of Magnesium from Chrysotile under Maintained Neutral pH Conditions

| | % Total Magnesium extracted at observed equilibrium |
|---|---|
| Hand picked Fibre | 2.4 |
| Fibre, Ball-Milled 24 hours | 58.7 |
| Fibre, Ball-Milled 72 hours | 79.4 |

In control tests with glycine buffer addition, the amount of magnesium liberation was unchanged and the results were of the same order as those presented in Table II.

The time required to reach completion was prolonged. About 90% of the leachable magnesium was removed in about 1 hour, but at least 24 hours were required to obtain a sensibly constant value. In these experiments the solid/liquid ratio varied throughout the experiments, but this had no significant effect. The amount of magnesium passing into solution was virtually independent of the concentration of acid used to restore neutrality, and hence of the final volume of liquid to amount of solid.

Effect of Particle Size on the Leaching of Chrysotile

The grinding of chrysotile produced a material of obvious wide particle size range. In order to assess the leachability as a function of size, the product was firstly leached and then separated into fractions by dispersing a known weight of sample in redistilled ethanol and washing it through 64 μ and 15.6 μ sieves. (The method is adapted from Zwicker (8) and Kupel et al (9)). The samples so obtained were then analysed for residual magnesium.

The results are shown in Table III.

Table III: Residual Magnesium in Leached Fractions of Chrysotile

| | Sieve size (Microns) | % in fraction | % $Mg^+$ in residue |
|---|---|---|---|
| Hand Picked Fibre | + 64 | 95.0 | 22.3 |
| | -64 + 15.6 | 1.3 | * |
| | -15.6 | 4.7 | * |
| Fibre, Ball-Milled | + 64 | 46.6 | 14.2 |
| for 24 hours | -64 + 15.6 | 35.9 | 14.7 |
| | -15.6 | 17.2 | 12.1 |
| Fibre, Ball-Milled | + 64 | 1.0 | 7.5 |
| for 72 hours | -64 + 15.6 | 39.9 | 3.3 |
| | -15.6 | 59.1 | 3.6 |

* Samples small in amount; the material was largely non-fibrous and it probably was mainly non-asbestos impurities mostly rich in iron.

+ Total magnesium content of original chrysotile 22.5%.

Several interesting features are revealed in these results.

Prolonged ball milling caused a greater release of magnesium from particles of comparable size. The surface layers of the chrysotile crystallites were presumably strained and distorted by this treatment and the lattice magnesium converted to a highly reactive state.

Although there was a tendency for a greater release of magnesium from small particled materials, the effect was not related to the increased surface area which might be anticipated. The magnesium release was dependent on the intensity of the comminution process, thus suggesting that distortion of surface layers or the production of strained octahedral sites at depth in the lattice was the main factor involved. In intense grinding the lattice distortion extended virtually throughout the entire crystallites.

Release of Ions Other Than Magnesium

The leaching effect which occurred in ground chrysotile did not represent complete lattice destruction. In many cases the original fibrous form was retained after chemical treatment, although the characteristic X-ray and d.t.a. curves were affected by the grinding process, the major features were restored, at least in part, by the chemical leaching. Of even greater significance was the fact that the amount of free silica which could be leached was extremely small. At alkaline pH values, less than 3%

of the available silica could be removed thus confirming the fact that a stable lattice grouping still existed.

Other ions present in the lattice mostly followed the behaviour pattern of magnesium. Iron, however, could only be taken into solution at pH conditions more acid than 5.5, presumably because insoluble hydroxides would tend to form at more alkaline values. Further work has been carried out on iron-bearing asbestos minerals such as amosite; it has been shown that iron leaching becomes significant only under more acidic conditions than pH 5.5.

The influence of pH is of the greatest importance in measuring the release of trace elements associated with asbestos minerals.. Preliminary observations on this topic indicate that a critical condition is the precipitation of the appropriate hydroxide although the total solubility product must also be taken into account.



## Conclusions

When the asbestos minerals were ground some of the magnesium and other octahedral cations in the layer lattice become more reactive and could be leached by mild acidic reagents although the amount taken into solution was also dependent on the final pH conditions in that insoluble hydroxides may precipitate. Chrysotile which had been ball-milled for 72 hours released nearly 80% of its total magnesium into solution provided that the reacting solution was maintained at neutral pH values by acid additions.

An analysis of sized fractions of ground leached chrysotile showed that the removal of magnesium was probably from distorted lattice layers, rather than from very fine crystal debris and in this fact chrysotile may be compared with silica. Dempster and Ritchie (10) showed that in ground quartz a similar distorted layer of high chemical activity was produced. They further suggested that the active layer was an important factor in inducing silicotic tendencies in lung tissue. This same phenomenon in an asbestos mineral may also have an important bearing on the incidence of asbestosis.

## References


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