

INFLUENCE OF STRUCTURAL AND MOLECULAR FEATURES OF CHRYSOTILE ON INTERACTION WITHIN ACID-CHRYSOTILE SYSTEM

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ABSTRACT

Investigation of the quantitative interaction in the chrysotile system, $\text{Mg}_6[\text{Si}_4\text{O}_{10}](\text{OH})_8 - \text{H}_2\text{SO}_4$, taken from the calculation of the stoichiometric required amount (SRA) of sulfuric acid to dissolve the amount of magnesium in the composition of chrysotile CA (Mg, mol) in the range of the ratio $\text{H}_2\text{SO}_4:\text{HA}(\text{Mg, mol}) - (0,1-1,0):1,0$, it is shown that the quantitative extraction of magnesium from chrysotile into the solution in the range of sulfuric acid concentrations taken (0-0.3) SRA occurs proportionally from the quantitative content of sulfuric acid in the solution used, in the range of concentrations (0,3-0,5) SRA, a slowdown in the quantitative transition of magnesium into solution is observed, and in the interval (0.5-0.7) of the SRA, the quantitative extraction of magnesium again acquires an almost proportional character of increase depending on the amount of the SRA of sulfuric acid in the solution, quantitative characteristics of the process of chrysotile dissolution in aqueous solutions of sulfuric acid of various concentrations correlate well with the features of the structural and molecular structure of chrysotile

Keywords: Layered Magnesium Hydrosilicate, Chrysotile Asbestos, Sulfuric Acid, Stoichiometric Required Amount.
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INTRODUCTION

The most well-known and widely used representative of magnesium hydro silicates from the serpentine group is chrysotile - $\text{Mg}_6[\text{Si}_4\text{O}_{10}](\text{OH})_8$. Its main components are silicon dioxide and magnesium oxide (up to 45% and 42%, respectively). The remaining components are represented by oxides of metals, iron, aluminum, chromium, and others.¹⁻³ In order to develop methods for the processing of serpentinites and the disposal of chrysotile asbestos-containing waste from the extraction and enrichment of chrysotile, a number of studies were conducted, which had a diverse nature.² The study was also conducted to determine the possibility of using serpentine minerals to capture industrial carbon dioxide emissions.^{4,5} Kinetic aspects of the dissolution of magnesium from serpentine in sulfuric acid were investigated.⁶ It should be noted that despite the multifaceted nature of the research, there are many unclear questions about the nature of the dissolution of serpentine in mineral acids. The purpose of this work is to study the effect of the structural and molecular structure of chrysotile on the course of the process of dissolution (extraction) of magnesium from the composition of chrysotile when they are treated with aqueous solutions of sulfuric acid. Information about the nature of the quantitative interaction of chrysotile and sulfuric acid may be of practical importance in the development of methods for processing serpentine group minerals and industrial waste containing chrysotile asbestos.

EXPERIMENTAL

A 20g sample of chrysotile-asbestos (CA) (grade A-4-20, Kustanay mineral JSC, Kazakhstan) was milled and sieved, a fraction of particles with a mesh size of less than 0.14 mm, weighing 10.0 g and containing 26.6 wt.% of Mg, 18.8 wt.% of Si, and 2.7 wt.% of Fe was used for experimental purposes. The amount of

magnesium and iron in 10.0 g (CA) is 0.11 moles and 0.005 moles, respectively. The stoichiometrically required amount (SRA) of sulfuric acid for interaction in the Mg(CA) - H₂SO₄ system was calculated on the basis of the reaction equations:



The mass and volume of sulfuric acid required for the preparation of 200 cm³ of a solution containing the required SRA of sulfuric acid (from 92% H₂SO₄ of chemically pure grade) were calculated by the following formulas:

$$M = C \cdot Mr \cdot V \cdot \frac{100}{92} = C \cdot 21,30 \quad (2)$$

$$V = \frac{m}{d} = C \cdot \frac{21,30}{d} \quad (3)$$

Where, m – the mass of required H₂SO₄ (92%); C – molar concentration; Mr – molar mass, V – volume, d – density of H₂SO₄ (92%).

Samples of CA were prepared (10 g each) to study the interaction of CA and sulfuric acid, each sample was separately mixed with 118 cm³ of an aqueous solution of sulfuric acid containing sulfuric acid varying from 0 to 0.1 mole/dm³ with an increment of 0.01 mole/dm³ of H₂SO₄. The process of interaction of each individual sample of CA (10 g) with the aqueous solution of sulfuric acid containing the required amount of SRA of sulfuric acid was carried out in a sealed Erlenmeyer flask at a CA suspension temperature of 95 °C, while stirring (350 rpm) during 10 minutes. The CA suspension was then separated by filtration (blue paper filter). The filtrate and insoluble residue, after being preliminary treated (drying at 100°C), were chemically analyzed to determine magnesium. The analysis was carried out using JSM-6490LV, JEOL (Japan), complete with systems of INCA Energy 350 energy-dispersive micro analyzer. The acidity of the reaction medium (pH) was measured using an I-16 MI ion meter.

RESULTS AND DISCUSSION

The ideal structure of chrysotile according to J. Whittaker¹¹ consists of folded kaolin-like layers (Fig.-1).

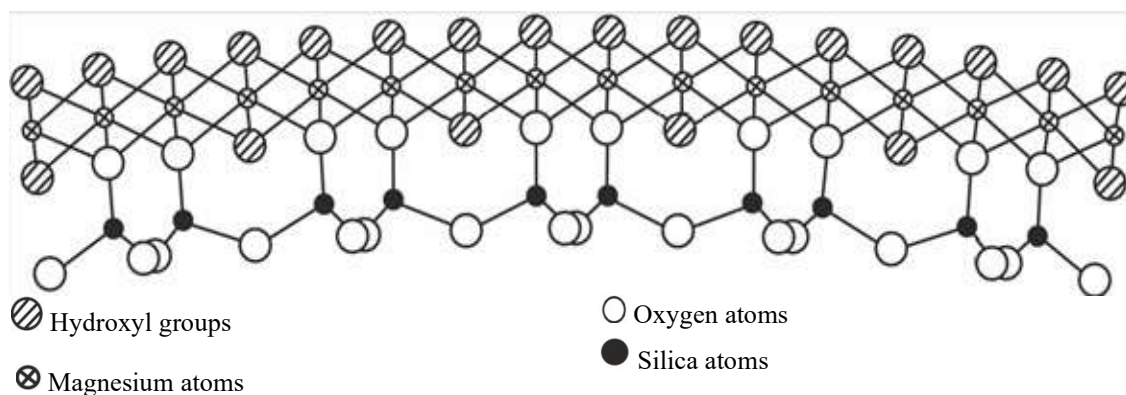


Fig.-1: Ideal Pattern of Crystalline Grid of Chrysotile-Asbestos¹¹

Each of these layers, in its turn, consists of two elementary networks - one is a network of connected silicon-oxygen tetrahedra, and the second is a brucite-like octahedral. There are atoms of magnesium at the peaks of the second grid. The structural and molecular features of chrysotile include 1) the incommensurability of the two-component parts of the layer, which causes the stress between the layers leading to bending of the tetrahedral-octahedral pair, 2) each elementary fiber of chrysotile represents a tube¹², its thickness is limited by the number of packets, the number of double-layer packets twisted into a tube is more than nine, which is energetically very disadvantageous. This results formation of structural and molecular features of

minerals representing a series of folded layers superimposed on each other in a certain way. The study of the quantitative interaction of fibrous magnesium – chrysotile hydrosilicate and aqueous solutions of sulfuric acid taken in quantitative ratio CA (Mg, mol): H₂SO₄ (mol), that is, according to the SRA, shows that the nature of the interaction and the quantitative extraction of magnesium into a solution from chrysotile correlate fairly well with the features of the structural and molecular structure of fibrous magnesium hydrosilicate. Figure-2 (Curve 1) shows the effect of the amount of sulfuric acid (mol) contained in the solution on the amount of actually extracted magnesium (mol) from chrysotile. The theoretical proportional dependence of the amount of extracted magnesium on the amount of H₂SO₄ in the solution calculated by level (1) is shown by a dotted line. It is obvious that during the interaction of CA and H₂SO₄, from chrysotile with a 1:1 structure (tetrahedral magnesium and octahedral brucite layer (Fig.-1) joined into sheets), first of all, the brucite layer should be exposed to H₃O⁺, where the quantitative fraction of magnesium in the molecular structure of chrysotile is about 1/3 of its the total amount. A proportional amount of extracted magnesium in the solution from the amount of H₂SO₄ and a change in the pH of the solution (Fig.-2, curve 2) is observed up to concentrations of 0.03 mol /cm³ (or 0.3 SRA) of sulfuric acid in the solution. In this case, as can be seen from Fig.-2 (curve 1), an equivalent amount of magnesium ions and hydrogen ions is released into the solution. In this interval, elementary brucite meshes of octahedral layer reactions are apparently exposed to the effect:



With a further increase of quantitative content of sulfuric acid (up to 0.05 mole/dm³) in solution, the proportional rate of the amount of magnesium extracted into solution is interrupted, and within the concentration range of 0.05-0.07 mole/l (H₂SO₄) the amount of extracted magnesium again becomes proportional depending on the amount of H₂SO₄ in the solution used. In the event of a further increase of the amount of acid to 0.1 mole/cm³, the quantitative content of sulfuric acid in the solution has little effect on the amount of magnesium extracted from the hydrosilicate into the solution. It should be noted that the slope angles of the lines of proportional change of the quantitative extraction of magnesium into solution on the quantitative concentration of sulfuric acid in the solutions used within the intervals (0.01-0.03 mole/cm³) and (0.05-0.07 mole/cm³) have very close values (Fig.-2a and 2b), which may evidence a similar identity of the processes occurring on the surface layer of chrysotile fibers.

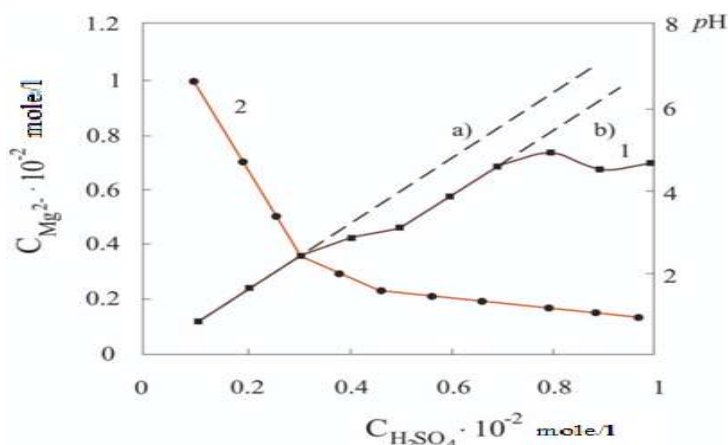


Fig.- 2: Dependence Of Extracted Amount of Magnesium from CA (1) and Medium pH (2) on the Amount of H₂SO₄ in Solution, m (CA) = 10 g, τ = 10 min, t = 96°C

Analysis of the curves of the dependence of the amount of dissolved magnesium and the pH of the medium on the quantitative content of sulfuric acid in the solution taken for interaction suggests that during the interactions of CA and H₂SO₄, initially only external packages (each of which consists of a tetrahedral-octahedral layered pair) from the series are exposed to the effects of H₃O⁺ ions rolled sheets superimposed on each other, an elementary tube of chrysotile fiber. A formal calculation of the distribution of magnesium, based on Figure 1, shows that the octahedral layer (brucite) contains about 30% (Mg), and the tetrahedral

layer contains 70% (Mg). It is obvious that at the beginning of interactions in the chrysotile–H₂SO₄ system, the chemical interaction of H₃O⁺ ions and the brucite component of the octahedral-tetrahedral layered pair occurs first of all. At the same time, the interaction of acid and chrysotile at the initial stage is apparently limited to the brucite layer, that is, 0.3 SRA of sulfuric acid (from the SRA calculated by equation (1)). In the range of acid concentrations taken by SRA (0.3-0.7 mol/L), the efficiency of magnesium extraction from chrysotile is noticeably reduced, which is also most likely due to a change in the texture of the structure of the tetrahedral-octahedral layered pair with a 1:1 structure. Magnesium dissolution from the octahedral (brucite) layer is accompanied by the enrichment of the surface layer with silica, which is poorly soluble in acidic solution. The form of silica existence is very sensitive to medium pH; it is difficult to determine its state. It is obvious that even with the preservation of pair structure, an excessive amount of brucite network of silica in the layer formed as a result of dissolution (destruction) creates a certain diffusion barrier for the penetration of reagent (H₃O⁺) deeper into the surface layer of fiber to react with OH⁻ groups and magnesium, which are in the tetrahedral layer of the package, which leads to a slowdown in the transition of magnesium into solution in the range of SRA concentrations within 0.3-0.5. Thus, when using sulfuric acid solutions containing (0.5-0.7) SRA, the efficiency of magnesium dissolution increases again. The dissolution of magnesium in this range of concentrations of SRA is interesting because the quantitative change of magnesium in solution occurs almost identically as in the range of concentrations of H₂SO₄ taken by (0-0.3) SRA. This experimental fact, discovered, may be related to the fact that the following packets with whole tetrahedral-octahedral layered pairs are subjected to interaction. At the concentration range of sulfuric acid (0.7-1.0) SRA, the degree of the extracted amount of magnesium in the solution does not exceed 70% of its total amount in the composition of the CA. Apparently, at these concentrations of SRA (H₂SO₄) in solution, as a result of interactions, a sufficiently dense layer of polysilicic acid is formed on the surface. At the same time, however, behind a dense layer, chrysotile retains its elementary chrysotile structure on the following inner layers. This assumption is indicated by the results of an X-ray graphical analysis of chrysotile asbestos (CA), which was treated three times sequentially with solutions of sulfuric acid and sodium hydroxide (Figure 3). In the event of the range of concentration of sulfuric acid with 0.7-1.0SRA, the degree of magnesium extracted into the solution does not exceed 70% of its total amount in CA. Apparently, at these concentrations of SRA (H₂SO₄) in solution; a rather dense layer of polysilicic acid is formed on the fiber surfaces as a result of interactions. However, behind the dense layer, the hydrosilicate retains its elementary chrysotile fiber structure. This assumption is also confirmed by the results of X-ray analysis of chrysotile-asbestos (CA), which was treated three times successively with solutions of sulfuric acid and sodium hydroxide (Fig.-3).

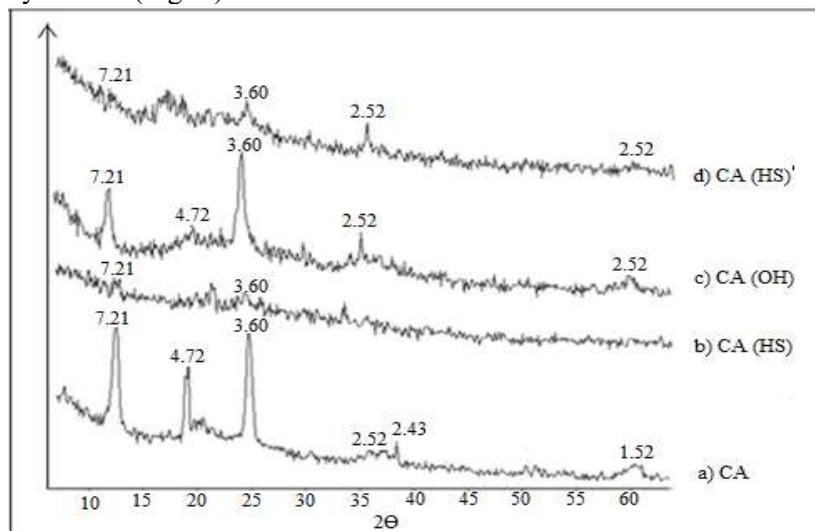


Fig.-3: X-Ray Diffraction Patterns of Chrysotile-Asbestos (CA) Samples Successively Treated With H₂SO₄ (0.7M) And NaOH (0.1M) Solutions: A) CA–Initial Chrysotile-Asbestos; B) CA – After Treatment With 0.7M H₂SO₄; C) CA (OH⁻) – After Treatment With 0.1M NaOH; D) CA (HS) – After Treatment With 0.7M H₂SO₄ Treated With 0.1 M NaOH - CA (OH), Then, The Same Sample Was Again Treated With a Solution of 0.7 M H₂SO₄ - CA (HS)'.

As you can see, after acid treatment, the surface of chrysotile-asbestos (b) is being amorphized, thus, the characteristic intense peaks of the chrysotile mineral, reflexes d/n (I/I_0) are 7.21 (100), 4.72, 3.60 (80), and 2.43 (32) are strongly weakened (b), then, after the acid-treated sample being treated with sodium hydroxide solution to dissolve the amorphous layer, the characteristic main peaks of the chrysotile mineral (c) reappear in the X-ray diffraction pattern. There is a strong weakening of the peak 4.72 associated with brucite ($Mg(OH)_2$). In the event of repeated acid treatment of the same sample, the chrysotile surface is again amorphized (d), which is explained by the dissolution of the brucite layer of the next tetrahedral-octahedral layered pair of sheet-pack on the chrysotile surface.

CONCLUSION

The set of facts discovered experimentally when studying interaction in the chrysotile- H_2SO_4 system made it possible to conclude that peculiarities of the structural and molecular structure of magnesium hydrosilicate play an important role in determining the nature of the interaction in magnesium hydrosilicate-sulfuric acid systems. By studying the quantitative interaction in the chrysotile-sulfuric acid system it is shown that the processes of interaction of an acid and layered magnesium hydrosilicate are of a stage-by-stage-layer nature, external packets from the series of tube-rolled magnesium hydrosilicate sheets are exposed to acid, while the inner layer-packets retain the elementary structural and molecular structure of chrysotile.

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