

Environmental and Technological Aspects of Acid Treatment of Serpentinite Waste from Chrysotile Asbestos Mining and Processing

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Abstract

The paper considers the environmental and technological aspects of acid treatment of serpentinite waste from mining and processing of chrysotile asbestos. A study of the quantitative interaction of chrysotile-asbestos and sulfuric acid, taken in molar ratios of sulfuric acid and magnesium, relative to its content in the composition of chrysotile. Based on experimental data, it is shown that when chrysotile-asbestos is dissolved in solutions of sulfuric acid, various stoichiometrically necessary amounts of it are taken in relation to the amount of Mg in chrysotile ratios up to Mg:H₂SO₄=1:0.3, the extracted amount of magnesium in the solution corresponds to the equivalent amount of sulfuric acid in the solution. When the ratio (mol) Mg:H₂SO₄=1:1, the amount of free H⁺ ions in the solution is 30-35%. It is assumed that when interacting, the destruction of the molecular structure of chrysotile by H⁺ ions occurs in stages in a layer-by-layer way. At the same time, a sufficiently dense amorphous layer of polysilic acid is formed on the surface of chrysotile fibers, which leads to changes in its physical and chemical properties, including biological and carcinogenic activity. Maximum dissolution of chrysotile asbestos by mass is achieved when using the concentration of H₂SO₄=0.7 stoichiometrically required amount.

Keywords: Magnesium silicates, Interaction, Chrysotile, Sulfuric acid, Silica, Dissolution.

I. INTRODUCTION

In recent years, the number of works devoted to the study of the interaction of layered silicates (serpentinites) of magnesium with mineral acids has significantly increased. According to the goals pursued, they can be divided into environmental and technological (rational use of natural raw materials).

In terms of relevance, both goals are very important both from the point of view of environmental protection, and for the development of technologies for complex processing of natural chrysotile-asbestos raw materials, taking into account the reduction of harmful effects on the environment of the accompanying asbestos-containing waste from the extraction and enrichment of chrysotile-asbestos.

The idea of using serpentinites to capture CO₂ from emission sources (such as power plants, metallurgical plants, cement plants, etc.) is based on the carbonation reaction of serpentinite suspensions [1,2], which results in the conversion of magnesium ions in the serpentine composition to thermodynamically stable magnesium carbonate. Research in the second direction is also of great importance in terms of developing technologies for the integrated use of chrysotile-asbestos natural raw materials, since the waste from the extraction and enrichment of chrysotile-asbestos usually contains 32-43% MgO and 35-40% SiO₂, as well as some amounts of Fe, Al, Ca, and Ni [3].

Rational use of chrysotile-asbestos raw materials includes not only the production of useful compounds of magnesium and silicon from magnesium silicate waste, but also the environmental content, that is, the disposal of asbestos-containing (~1%) dust-like waste generated at the stage of asbestos enrichment. Most of the research in this area is devoted to the development of acidic methods for processing magnesium silicate waste. It should be noted, although numerous diverse studies of the interaction of H⁺ ions and serpentinites have been conducted. In the applied aspect, the above-mentioned goals have not yet been achieved, which determines the relevance of this research subject.

The interaction of H⁺ ions and layered silicates (serpentinites) occurs in a heterogeneous medium, the mechanism and kinetics of dissolution of magnesium from the structure of layered magnesium silicate is complex. In this regard, the views of various researchers on the chemical processes of dissolution of serpentine in acids are often contradictory [4,5], especially in the question of the degree of leaching of magnesium from serpentine depending on the concentration of acid. This study is aimed at studying the quantitative interaction of the mineral chrysotile-asbestos and sulfuric acid. The influence of the taken molar ratios of the mineral chrysotile-asbestos/H₂SO₄ on the transition of magnesium ions into solution, on the physical and chemical changes in the surface layers and on the completeness of opening the layered molecular structure of chrysotile-asbestos was studied. The found experimental facts indicate that the controversial issues of the process of dissolving serpentine in acids are related to the distinctive features of the construction of layered structures of chrysotile-asbestos molecules.

II. METHOD

Selection of chrysotile asbestos (grade A-4-20– JSC "kustanaysky minerals", Kazakhstan) was due to the fact that the structure of the molecules, it belongs to the layered silicates of magnesium having a serpentinite structure, and atkzhe as the most frequently and widely used among representatives of all groups of asbestos. A sample of chrysotile asbestos (CA) in the amount of 20 g was crushed and sifted, from which a fraction of particles with a size of ≤ 0.14 mm and a weight of 10.0 g was selected for the experiment.

The elemental composition of the used CA (grade A-4-20) is shown in the table (see table). It contains 26.42% of Mg, 18.65% of Si and 2.73% of Fe. The 10 g sample CA contains 2.642 g or 0.11 mole of magnesium and 0.0049 mole of iron. The amount of Mg in CA exceeds the amount of He by 22.45 times; therefore, the amount of He was not taken into account in calculations.

The stoichiometric required amount (SRA) of sulfuric acid for interactions with CA was calculated by the following reaction equation:



The mass and volume required for preparation of 200 ml of solution containing SRA of sulfuric acid was calculated by the following formula:

$$m = C \cdot M_r \cdot V \cdot 100 / 92 = C \cdot 21.304 \quad (2)$$

$$V = m / d = C \cdot 21.304 / d \quad (3)$$

where: m – mass of H_2SO_4 (92%) for preparing a solution of a certain molar concentration; C – molar concentration, M_r – molar mass, V – volume, d – density of H_2SO_4 (92%).

The amount of H_2SO_4 (mol) consumed to dissolve CA was determined by the formula:

$$N_{\text{cons}} = n_{\text{ini}} - n_{\text{fin}} \quad (4)$$

As percentage, by the following formula:

$$\text{H}_2\text{SO}_{4\text{cons}}(\%) = n_{\text{cons}} \cdot 100 / n_{\text{ini}} \quad (5)$$

Samples (10 g of CA) were dissolved in separate 118 ml aqueous solutions of the following concentration: 0-1.0 mole/l of H_2SO_4 in 0.1 mole/l increment at 100°C during 10 minutes in a sealed Erlenmeyer flask with back flow condenser. Experiments were carried out at ratios of Mg (CA):0.1-1.0 SRA (H_2SO_4). The CA suspension in H_2SO_4 solution was stirred at 350 rpm. The suspensions, after a lapse of time, were filtered immediately using blue paper filter. Elemental analysis of filtrate and insoluble residue was carried out using

JSM-6490LV, JEOL (Japan) complete with INCA Energy 350 energy dispersive microanalyzer systems after the target object was preliminary dried (at 100°C). The acidity of the reaction medium (pH) was measured using I-160MI ionomer.

III. RESULT

Chrysotile asbestos, in terms of molecular structure, belongs to sheet silicates, and is the most common and widely used among all groups of asbestos. Chemical composition of chrysotile asbestos has the following crystalline formula: $\text{Mg}_6(\text{OH})_8[\text{Si}_4\text{O}_{10}]$ and has the following minerals (in % by mass): MgO – 43.46; SiO_2 – 43.5; and H_2O – 13.4. In addition to the basic structural elements, commercial CA inevitably contains metal impurities (Table 1).

Table 1. Elemental composition of A-4-20 chrysotile asbestos

Element	Mg	Si	Fe	O
Content, mass %	26.70	18.20	2.63	52.46

Analysis of data [6] on the structure of chrysotile asbestos indicates that this mineral usually forms subparallel aggregates that easily split into tubular fibers with an external diameter of 30-36 nm. According to the results of x ray diffraction analysis CA is a monoclinic variety of serpentine.

It is now generally accepted that the ideal structure of chrysotile consists of folded kaolin-like layers [7]. Each of these layers in turn consists of two elementary grids – one is a grid of linked silicon-oxygen tetrahedra, the second is a brucite-like octahedral. The incongruity of the two component parts of the layer causes the tension between the layers, resulting in the bending of the tetrahedral-octahedral layered pair. As a result, a structure is formed, which is a series of collapsed layers that are superimposed on each other in a certain way. According to [8], each elementary ha fiber represents a tube. Its thickness is limited to nine packages and elementary initial twisting of the nascent crystal, which means that the number of twisting double-layer packages in the tube is more than nine, which is very unprofitable energetically.

It is obvious that the interaction of H_2SO_4 and CA from a silicate mineral with a 1:1 structure (serpentine) of tetrahedral silica and an octahedral layer of brucite [$\text{Mg}(\text{OH})_2$], combined in sheets, primarily dissolves the brucite layer, consuming an equivalent amount of hydrogen ions. Figure 1 shows the effect of the content of the amount of sulfuric acid (mol) in the solution used on the extraction of the amount of Mg^{2+} ions (mol) into the solution, in comparison with the calculated amount of magnesium in accordance with equation (1).

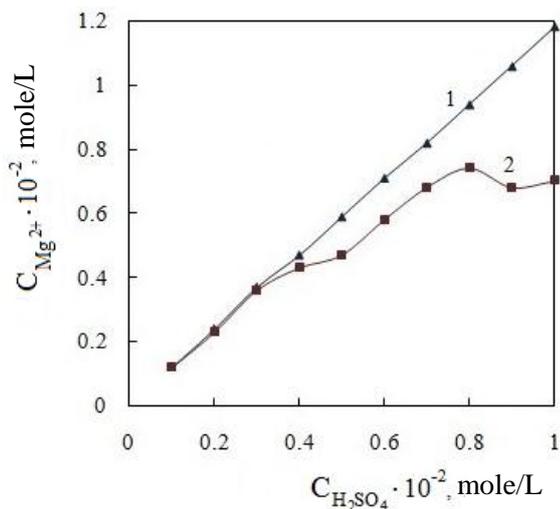
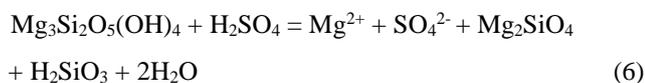


Fig. 1. Correspondence of the theoretical (1) and practical (2) recoverable amount of magnesium from chrysotile asbestos into solution when treating 10 g of chrysotile asbestos (Mg-0.11 M) with sulfuric acid solutions (0.1-1.0 mole/l) of stoichiometric required amount, $\tau = 10$ мин, $t = 100^\circ\text{C}$

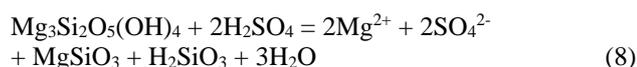
As one can see, when using 0.1-0.3·10⁻² M of H₂SO₄, i.e. up to 0.3 parts of acid SRA, the reaction of interaction of sulfuric acid and CA occurs almost equivalently for magnesium, theoretically calculated according to equation (1). Further, when using solutions containing 0.4-1.0 SRA (H₂SO₄), a gradual deviation of the amount of magnesium recovered from the theoretical value is observed. Within the SRA range (0.5-0.8), the degree of correspondence of the extracted magnesium in solution is approximately 65-70%. At SRA (0.9-1.0), the amount of magnesium recovered drops slightly and makes 60-65% of the theoretically calculated amount contained in CA.

Based on these experimental data and the structural and molecular composition of CA, the nature of the interaction of H⁺ and XA ions is assumed to occur according to the reaction schemes:

1) step by step:



2) total (gross):



Based on the results obtained, it can be assumed that approximately 1/3 of the magnesium in CA crystal lattice is readily available for extraction by H⁺ acids, or the amount released when using up to 1/3 of SRA (H₂SO₄); the concentration layer of silicate ions does not diffusely restricts

the access of H⁺ ions to the following CA molecular layers. When using higher concentrations of H₂SO₄ SRA, on the interfacial near-surface boundary of CA particles, besides transition of magnesium ions into the solution, it is apparent that there is a gradual formation of layer mainly consisting of the destroyed silicate framework of the outer packets of CA fiber tube on the surface of the fibers. Moreover, silicate ions released as the result of destruction of the surface molecular structures of CA in acidic medium can form silicic acid in the form of polysilicic acid – H₂SiO₃ by reaction (9) or H₄SiO₄ by reaction (13). It can be assumed that the former is more likely to form from a tetrahedral and the latter from the octahedral sublayer of the tetrahedral octahedral layered pair. According to changes in the pH of used solutions (0.1-1.0) of SRA (H₂SO₄) before and after the interactions of CA and H₂SO₄ on fig. 2, it can be seen that a certain amount of free H⁺ ions always remains in the solutions after the interaction starting from 0.4 SRA (H₂SO₄). At (0.6-1.0) SRA, the amount of free acid is almost constant. Further, the amount of free acid in the solution was determined by titration with a NaOH solution. The titration results were used to determine the consumption of H₂SO₄ for dissolution of magnesium from CA.

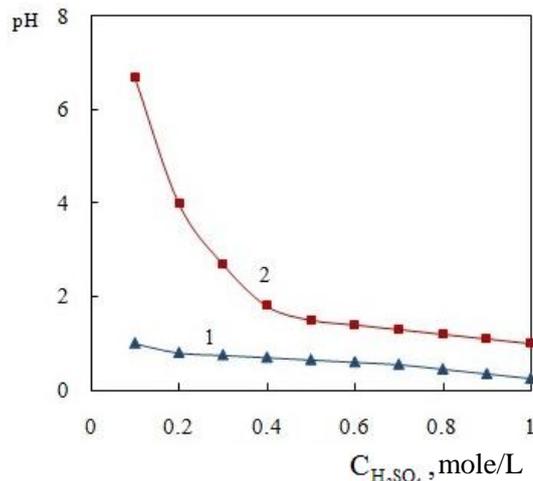


Fig. 2. Change of pH values of solutions of H₂SO₄ (0.1-1.0) mole/L (1) and at the end of interactions of H₂SO₄ and chrysotile asbestos at the ratios: 10 g of chrysotile asbestos (Mg-0.11 M)/H₂SO₄ (0.1-1.0 mole/l) of stoichiometric required amount (2), $\tau = 10$ min, $t = 100^\circ\text{C}$

The discovered fact that about 30-35% of free H⁺ ions remain in the solution indicates the nature of the reaction between CA and sulfuric acid according to the suggested reaction schemes 6-8.

The remainder of 1/3 of free H⁺ ions in the H⁺ - HA system is probably due to the nonequivalent content of Mg²⁺ ions and OH⁻ hydroxyl groups in the molecular structure of HA.

The dissolution of magnesium from the CA crystal framework, as a result of its interaction with H⁺ ions, leads to the formation of silicon dioxide with the complete destruction of the molecular structure of the outer layers of CA fibers, consisting of packages twisted into a tube. The dissolution of the tube layers, in General, seems to have a step-by-step

character. The nature of the change in the amount of Si IMD in insoluble residues after H⁺ and CA interactions at their different mole ratios (relative to Mg²⁺ ions in CA) is shown in Fig. 3. A uniform decrease in the amount of Mg and an increase in the amount of Si in the residue also indicates the step-by-step nature of the interaction of sulfuric acid and CA. Comparative energy dispersion spectra of CA before and after treatment with 1.0 SNC (H₂SO₄) Fig. 4 show that the Mg content in the residue decreases by about 60-65%.

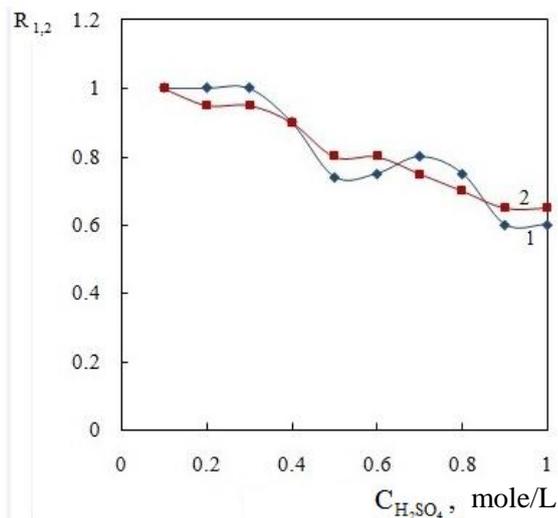


Fig. 3. Change of ratio of amounts (mole), $R_1 = n_{\text{H}_2\text{SO}_4\text{cons}} / n_{\text{H}_2\text{SO}_4\text{ini}}$ (1) and $R_2 = n_{\text{Mg(extr)}} / n_{\text{Mg(ini.form)}}$ (2) when treating 10 g of chrysotile asbestos with sulfuric acid solutions (0.1-1.0 mole/L) of stoichiometric required amount, $\tau = 10$ min, $t = 100^\circ\text{C}$

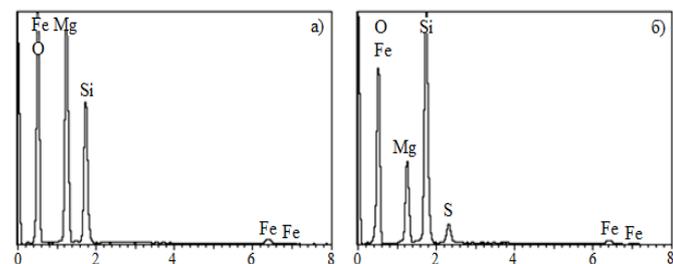


Fig. 4. Energy dispersive spectra of the initial chrysotile asbestos (grade A-4-20) (a), and after its treatment with a solution of chrysotile asbestos: H₂SO₄=1:1 of stoichiometric amount required (b)

The amount of Mg, found as the result of analysis, transmitted into solution at 0.6-1.0 SRA (H₂SO₄) with respect to the amount of magnesium in CA is approx. 65% of its initial content in CA. Therefore, it can be assumed that approximately 60-65% of the layer packets of the initial number comprising tubes of CA fibers were subjected to destruction. Complete destruction of CA fibers does not occur. The remaining undisturbed layer-packets retain their molecular-structural framework, which are protected from further destruction by a more dense hydrated silica surface

layer, which limits further diffusion penetration of H⁺ ions into the depth of the particle fibers.

As can be seen from Fig. 5, the characteristic intense diffraction lines of chrysotile-asbestos with maxima of 7.21 Å, 3.60 Å, etc. (a), after treatment with sulfuric acid, significantly decreases, and the x-ray image (b), in General, characterizes the properties of the amorphized substance.

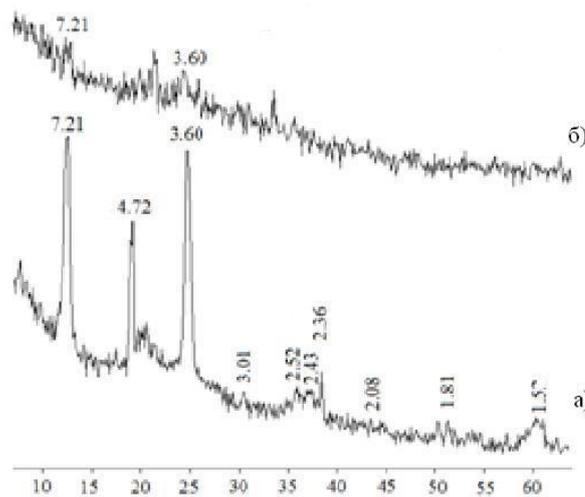


Fig. 5. results of x-ray phase analysis of chrysotile asbestos: a) initial; b) after treatment of chrysotile asbestos with sulfuric acid (CH₂SO₄-0.7 mol/l, 0.7 part of the SRA)

IV. DISCUSSION

Thus, it is determined that the interaction of chrysotile-asbestos and sulfuric acid, the maximum dissolution of CA by mass is achieved when using sulfuric acid 0.7 SRA (Mg²⁺ in CA), while there is a complete destruction of the morphology and structure of the surface layers of CA and the formation of an enriched layer of polysilic acid SiO₂ * nH₂O on the surface. The formed sufficiently dense amorphized layer on the surface of the HA leads to changes in its physical and chemical properties, including biological and carcinogenic activity associated with an increased content of magnesium in the HA, as well as the properties of its surface layers, i.e., it converts them to a more environmentally friendly state. The study of the quantitative interaction of sulfuric acid and serpentine, on the example of CA, showed that the complete extraction of magnesium from serpentine when using an equivalent amount of acid (relative to the content of magnesium in serpentine) does not occur, the maximum degree of leaching does not increase 65-70% of the initial content in CA.

V. CONCLUSION

In case of interaction of chrysotile asbestos and sulfuric acid taken relative to the amount of Mg in chrysotile and the stoichiometric required amount of H₂SO₄ at ratios of Mg:H₂SO₄=1:(0.1-1.0) (mole), the quantitative extraction of magnesium into solution, corresponding to the equivalent

amount of sulfuric acid, occurs only at ratios of $Mg:H_2SO_4=1:(0.1-0.3)$ (mole). Further, when using solutions containing a higher amount of acid, the degree of magnesium extraction into solution deviates from the theoretically calculated amount, which is associated with the gradual formation of an amorphized layer consisting of polysilicic acid $SiO_2 \cdot nH_2O$ on the surface of chrysotile asbestos fibers. Extraction of magnesium from chrysotile asbestos occurs gradually from surface layers of chrysotile pipe fibers. Moreover, complete extraction of magnesium from chrysotile asbestos is not achieved. The maximum amount of magnesium extraction does not exceed 60-65% of its initial content in chrysotile asbestos. The maximum dissolution of chrysotile asbestos by weight is achieved by using a solution of sulfuric acid containing 0.7 stoichiometrically required amount (H_2SO_4), while the molecular structure of chrysotile asbestos fibers does not completely break down, some of the inner layers retain their original magnesium-containing molecular structures.

VI. ACKNOWLEDGMENTS

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VII. CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest that requires disclosure in this article.

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