

TECHNOGENIC RAW MATERIALS FOR THE PRODUCTION OF MAGNESIUM AND SILICON-CONTAINING COMPOUNDS

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Abstract: This work considers technogenic waste from chrysotile asbestos production as a source of magnesium and silicon-containing compounds. The products obtained by hydrochloric acid dissection of chrysotile asbestos wastes were studied by chemical, scanning electron microscopy, thermogravimetric analysis.

KEY WORDS: CHRYSOTILE-ASBESTOS, TECHNOGENIC WASTES, LEACHING, SILICA, MAGNESIUM

1 Introduction

The anti-asbestos campaign launched in the countries of Western Europe and the USA, which is mainly competitive in nature and aimed against the use of amphibolite asbestos, has significantly reduced chrysotile-asbestos export opportunities. For this reason, many asbestos mining and processing plants in the world have created additional capacity for the production of nonmetallic building materials demanded by consumers. Complex processing of chrysotile asbestos raw materials, as well as industrial wastes from their enrichment has become very relevant for many mining and processing enterprises associated with asbestos under market conditions and a crisis situation around asbestos [1-3].

There are various mineral classes of asbestos, including amphiboles and serpentinites. In Kazakhstan and in Russia, the deposits of the latter are widespread.

During the processing of chrysotile asbestos raw materials, only 6-8% is extracted into the commodity fiber, the rest, which is a serpentine raw material $3\text{MgO}\cdot 2\text{SiO}_2\cdot \text{H}_2\text{O}$, is irretrievably lost as waste. With the enrichment of serpentinite the target product - asbestos fiber (Fig. 1a) and waste (Fig. 1b) are obtained. Fibrous type of serpentinite - asbestos has an independent technical value. Waste from the production of the asbestos industry is a source of environmental pollution and at the same time represents a mineral reserve of mineral raw materials practically prepared for processing for metallurgy and the construction industry [4].



Fig. 1 – Products of serpentinite enrichment

The total reserves of the main useful components contained in industrial wastes are comparable to the reserves of a fairly large polymetallic deposit.

2 Results and discussion

The subject of the research was the sand fraction -1.25 + 0.25 mm technogenic wastes from the serpentinite enrichment of the Zhitikara deposit.

Every year thousands of tons of high magnesium content waste are generated at Kostanay Minerals JSC, which occupy a huge area and carry an environmental hazard to the region (Fig. 1b). The question of the need to recycle the enterprise's waste with the release of new products that are in demand, competitive with high

value-added products is relevant for Kazakhstan, as well as for countries producing asbestos fiber.

Chemical, scanning electron microscopy, thermogravimetric analysis methods were used to perform the studies.

Thermal analysis of the samples was carried out on a Q-1000/D derivatograph of the F.Paulik, J.Paulik and L.Erdey systems from MOM (Budapest) company. The survey was carried out in air, in the temperature range of 20–1000 °C, the heating mode was dynamic ($dT/dt = 10$), the reference substance was calcined with Al_2O_3 , and the sample weight was 500 mg. X-ray phase analysis on a DRON-4 diffractometer, micro-X-ray fluorescence analysis on an EDAX tsl ametek instrument. Chemical analysis data obtained using certified methods.

The mineral base of chrysotile asbestos production wastes, according to X-ray phase analysis, is serpentine- $3\text{MgO}\cdot 2\text{SiO}_2\cdot 2\text{H}_2\text{O}$, containing silica in crystalline and amorphous states (Table 3). Of the other components, up to 5-7 % of iron oxides in the form of hematite and magnetite are present in the feedstock.

Table 3 – X-ray phase composition of asbestos waste

| Component | Formula | Mass composition, % |
|-----------------|---|---------------------|
| Serpentine | $3\text{MgO}\cdot 2\text{SiO}_2\cdot 2\text{H}_2\text{O}$ | 61 |
| Talcum | $3\text{MgO}\cdot 4\text{SiO}_2\cdot \text{H}_2\text{O}$ | 19 |
| Brucite | $\text{Mg}(\text{OH})_2$ | 5 |
| Forsterite | Mg_2SiO_4 | 4 |
| Magnesium oxide | MgO | 3 |

Figure 2 shows the results of the analysis of the initial waste obtained on a scanning electron microscope.

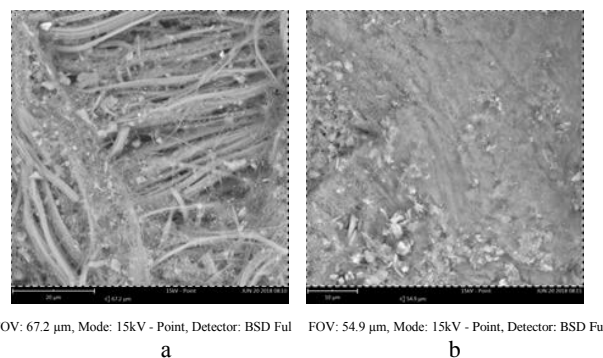


Figure 2 – Electron microphotograph of chrysotile asbestos waste

In electron microphotographs, chrysotile asbestos wastes are represented by particles of different sizes with inclusions of asbestos filamentous fibers (Fig. 2).

Table 1 – The average composition of chrysotile asbestos waste

| Element Symbol | Atomic. % | Oxide Symbol | Stoich. wt % |
|----------------|-----------|--------------|--------------|
| O | 66,17 | | |
| Mg | 19,87 | Mg | 41,25 |
| Si | 9,29 | Si | 33,43 |
| Fe | 0,35 | Fe | 2,75 |
| Ca | 0,46 | Ca | 1,35 |
| C | 0,25 | C | 0,38 |
| Al | 0,13 | Al | 0,23 |

Table 2 – Chemical composition of technogenic wastes

| Fraction size, mm | MgO | SiO ₂ | Al ₂ O ₃ | CaO | Fe ₂ O ₃ | NiO |
|-------------------|------|------------------|--------------------------------|------|--------------------------------|------|
| -1,25 +0,25 | 39,0 | 36,5 | 0,79 | 0,46 | 4,87 | 0,22 |

As can be seen from the data of Tables 1 and 2, the main components of chrysotile asbestos waste are (in %): MgO – 39.0-41.3; SiO₂ – 33.4-36.5; CaO – 0.5-1.4; Fe₂O₃ – 2.7, Fe₃O₄ – 4.9. According to chemical analysis Nickel is present in small amounts..

Sulfuric acid and hydrochloric acid methods of processing waste of this type are known [5-10]. The low level of the market consumption of magnesium sulfate in Kazakhstan should be attributed to the risk factors for the development of sulfuric acid technology [5, 6]. The hydrochloric acid opening of asbestos wastes allows obtaining the marketable products of magnesium and silicon [7-10].

The technology of hydrochloric acid dissection of chrysotile asbestos technogenic raw materials consists in transferring magnesium into solution, two-stage purification of productive solutions from impurities, crystallization of bischofite.

As a result of this work, bischofite was obtained from chrysotile asbestos wastes. Thermograms of the sample MgCl₂·nH₂O at a heating rate of 10 °C/min are presented in Figure 3.

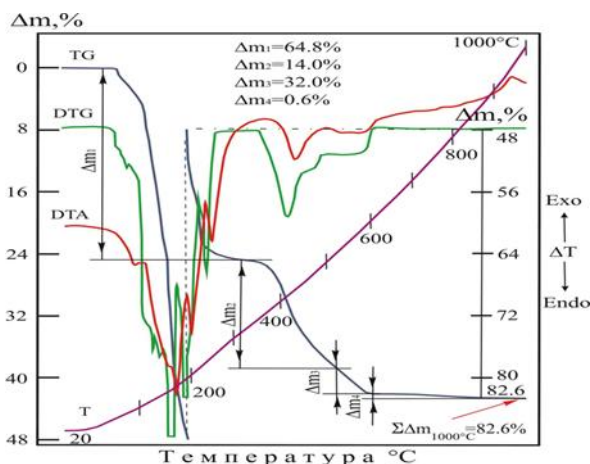


Fig. 3 – Derivatogram of sample MgCl₂·nH₂O

The DTA curve captures a number of endothermic effects associated with the dehydration of the system. According to the literature, the first endoeffect (at T = 132 °C) corresponds to the melting of MgCl₂·6H₂O with water splitting. The second thermal development (at T~213 °C) according to the change in mass characterizes the removal of 3.03 mol of water, the third effect (246 °C) corresponds to the removal of 1.55 mol of water from the system, and the next stage of dehydration (291 °C) is associated with loss 1.18 mole of water. In our case, these endothermic effects are caused by a 64.8 % decrease in sample mass, which corresponds to a loss of ~ 9.7 moles of water.

The endoeffect at 480 °C corresponds to the decomposition of the products of hydrolysis of magnesium chloride and the formation of anhydrous magnesium oxide MgO. The decomposition of magnesium hydroxochloride is accompanied by a change in mass of 14.0 % in the first sample and 15.7 % in the second. This process ends at 635 °C and leads to a loss of 3.2 % by weight.

The endoeffect at 720 °C corresponds to the beginning of the melting of anhydrous MgCl₂ and weight loss of 0.6 % and 0.5 %, which can also be explained by evaporation or decomposition of magnesium chloride.

The chemical composition of the resulting product is, wt. %: MgCl₂·6H₂O 97.5; Mg²⁺ 11.8; sulfate ions SO₄ 0.8; alkali metal ions (Na⁺, K⁺) 0.1; water insoluble residue 0.15.

Electron micrographs of the silicon-containing residue obtained in the process of hydrochloric acid leaching of chrysotile asbestos wastes with the following process parameters: the concentration of acid used is 18–20 %, S:L 1: 3, the process temperature is 85–90 °C, time is 120 min and four-stage washing is shown in Figure 4. The average composition of the silicon-containing residue is shown in Tables 3 and 4.

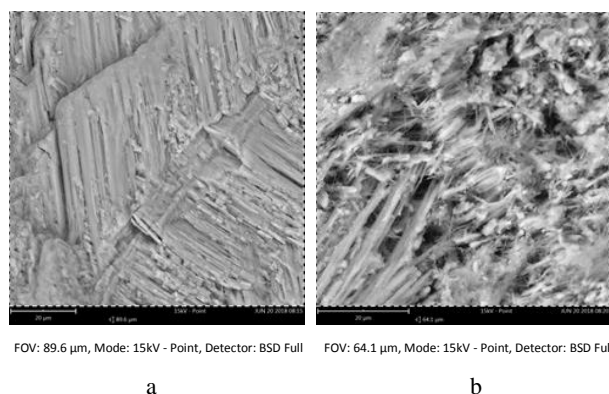


Fig. 4 – Electron microphotograph of silicon-containing residue

Table 3 – The average composition of the silicon-containing residue after leaching

| Element Symbol | Atomic. % | Oxide Symbol | Stoich. wt% |
|----------------|-----------|--------------|-------------|
| O | 74,69 | | |
| Si | 17,46 | Si | 75,29 |
| Mg | 4,88 | Mg | 13,02 |
| Al | 0,51 | Al | 1,98 |
| Fe | 0,55 | Fe | 3,88 |
| C | 0,67 | C | 2,03 |
| Cl | 0,35 | Cl | 1,56 |

Table 4 – The results of chemical analysis of silicon-containing cake after leaching

| Content, wt. % | | | | | | |
|--------------------------------|------|------|-------|------------------|----|------|
| Cr ₂ O ₃ | MgO | FeO | MnO | SiO ₂ | Ni | Cl |
| 0,52 | 7,58 | 3,41 | 0,044 | 75-78 | - | 0,35 |

Silica cake after processing contains up to 13 % of magnesium oxide contaminated with impurities of iron, aluminum, chromium, manganese. This product will be of limited use.

In order to reduce the loss of magnesium, complete its transfer into the solution and obtain pure silica, the second stage of leaching with 18% hydrochloric acid at S:L rate 1: 3, temperature 85-90°C.

Electron microphotograph of the silicon-containing residue after the second stage of acid treatment and two-stage washing with water is shown in Figure 5. The average composition of the silicon-containing residue is shown in Tables 5 and 6.

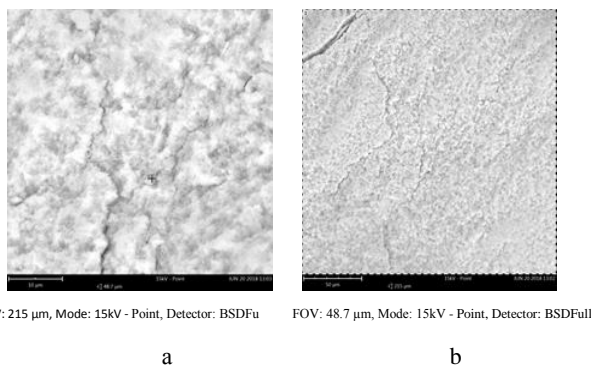


Figure 5 – Electron microphotograph of the silicon-containing residue after the second stage of acid treatment at different magnifications

Table 5 – The average composition of the silicon-containing residue after the second stage of acid treatment

| Element Symbol | Atomic. % | Oxide Symbol | Stoich., wt% |
|----------------|-----------|--------------|--------------|
| O | 75,39 | | |
| Si | 19,39 | Si | 98,11 |
| Mg | 0,33 | Mg | 1,20 |
| Fe | 0,06 | Fe | 0,13 |
| Cl | 0,11 | Cl | 0,59 |

Table 6 – The results of chemical analysis of the silicon-containing residue after the second stage of acid treatment

| Content, wt. % | | | | |
|----------------|------|-------|------------------|------|
| MgO | FeO | MnO | SiO ₂ | Cl |
| 1,92 | 0,08 | 0,046 | 90-95 | 0,33 |

From the presented results it can be seen that the resulting amorphous silica contains almost no iron and other impurities, the magnesium content has decreased by 4 times.

3 Conclusion

Thus, according to the results of an electronic scanning microscope and chemical analysis data, it follows that with complex processing of chrysotile-asbestos wastes using hydrochloric acid technology, in addition to bischofite, amorphous silica with an SiO₂ content of 97-98%, which is recommended for use in as a filler in the rubber industry, in the production of paints, varnishes, silicate adhesives, the starting material for the production of high-purity silicon.

4 References:

- Ivanov V.A. Anti-asbestos company and the situation with the use of chrysotile in the world // Source book of the Fifth Intern. scientific and practical conf. "Geologists 2010: Problems and ways of industrial-innovative development of mining industries" Zhitikara. – 2010. – p.83-91.
- Yizmerov N.F., Kovalevsky E.V. A brief overview of the documents of international organizations on chrysotile // Source book of the Fifth Intern. scientific and practical conf. "Geologists 2010: Problems and ways of industrial-innovative development of mining industries" Zhitikara. – 2010. – p.143-146.
- Dzhafarov F.N., Dzhafarov N.N. Complex utilization of waste from the Dzhetygara deposit of chrysotile asbestos as a source of increasing production efficiency // Mining and Geological Journal – 2003. – № 3. – p. 3-7.
- Ratsen V.Z., Strelnikova V.Ya., Kolomiytsev V.V. Waste from the processing of asbestos-containing ores and their characteristics as a mineral material for road construction / Uralasbest: Asbestos. – 2005.
- Bedelova Zh.D., Tabylganova A.N., Homyakov A.P., Dagubaeva A.T. Developing the technology of waste sulfuric acid leaching of chrysotile asbestos production // International journal for science, technics and innovations for the industry. – 2017. – Issue 7. – p. 350-352.
- Khomyakov A., Tabylganova A., Nurkhodzhaev E., Bedelova J., Dagubaeva A. Obtaining of magnesium sulphate from chrysotile - asbestos waste // Industry of Kazakhstan. – 2015, № 2. – P. 72.
- Figara P., Chin E., Walker T. Magnola. New Industrial Process of Magnesium Production // The Canadian Mining and Metallurgical Bulletin. – 1998. – V. 91, № 1019. – P. 214.
- Shayakhmetova R.A., Nurkhodzhaev E.S., Stepanenko A.S., Baygenzhenov O.S., Osipov P.A., Zhumataev B.A. Obtaining magnesium chloride and carnallite from chrysotile asbestos wastes // Proceedings of the international scientific-practical conference "Mining sciences in the industrial-innovative development of the country", Almaty. – 2015. – p. 423-427.
- Baigenzhenov O.S., Kozlov V.A., Luganov V.A., Mishra V.A., Shayahmetova R.A., Aimbetova I.O. Complex Processing of Wastes Generated in Chrysotile Asbestos Production // Mineral Processing and Extractive Metallurgy Review. – 2015. – № 36. – p. 242-248. DOI: 10.1080/08827508.2014.955610
- Shayakhmetova R., Stepanenko A., Osipov P., Zhumakynbay N. Obtaining carnallite from technogenic chrysotile asbestos wastes // Industry of Kazakhstan. – 2016. – № 4. – p. 83-85.