ABSTRACT

of dissertation of Dikanbayeva Aizhan Kossybayevna on the theme
"Development of technology of obtaining magnesium sulphate based on recycling of chrysotile-asbestos production waste"
for the degree of Doctor of Philosophy (PhD) in the specialty
6D0720000 – "Chemical technology of inorganic substances"

The relevance of the theme. Technogenic wastes of chrysotile-asbestos industries have long been of interest to scientists as magnesium raw materials, since they contain up to 45.0% of MgO and up to 45% of SiO_2. These technogenic wastes are formed in the process of enrichment of rocks, i.e., the production of chrysotile-asbestos from them. They are mainly composed of magnesium hydrosilicates, which have a layered structure. The rocks are dominated by these types belonging to the group of serpentinites (chrysotile, antigorite, liserdite).

The problem of disposal of chrysotile-asbestos production wastes in Kazakhstan belongs to the group of important issues that have not been resolved to date. Over the past 65 years of chrysotile-asbestos production at Zhitikara mine, the local concentrating mill (Kostanay Minerals JSC) has processed 310 million tons of asbestos ore. The output of commercial asbestos in it is 6-7%, the rest (about 300 million tons) is sent to special landfills with an area of hundreds of hectares as a waste product. The studies showed that these wastes have a harmful effect on the environment. The geological and commercial field of Zhitikara mainly consists of serpentinized periodites, dunites and serpentinites. In addition to chrysotile, these rocks are known for their high content of magnesium, iron, chromium, nickel and cobalt.

Currently, there are several methods and recommendations for technological processing of technogenic wastes from chrysotile-asbestos production. Most of the proposed methods are aimed at extracting the magnesium part from the acid treatment residue. Available data from the literature on acid waste treatment technologies differ from each other only in the types of acids used or in the technological regimes of the process. In addition, in research works aimed at processing serpentinite wastes, the main purpose is to maximize the complete extraction of magnesium from them. However, despite numerous and multidisciplinary studies, there is still no industrially developed technology for processing these technogenic wastes. There are the following reasons preventing the use of the proposed methods and technological schemes in industry: the need for heat treatment of wastes for processing; the duration of the magnesium extraction process and the multi-stage purification of the resulting products from metal ions (Fe, Al, Ni, Co, Ca, etc.) and silicon. In the proposed technologies, to extract the maximum amount of magnesium, an excess of acids is used in excess of the required amount.

Another reason for the relevance of the research theme is that technogenic wastes from chrysotile-asbestos production are environmentally hazardous at an average level. The safety of these wastes is currently limited by their accumulation

in special waste storage facilities in the form of a technogenic massif. This situation has also developed at Zhitikara deposit of chrysotile-asbestos (Kostanay region). The main reason is the lack of an optimal and cost-effective technology for their processing. Besides, magnesium and its compounds (magnesium oxide, magnesium hydroxide and its salts – magnesium sulfate, magnesium nitrate, magnesium chloride, etc.) are substances widely used in various industries. They are used in the production of steel, refractory, rubber, technical and polymer products, as well as in the leather, chemical, food, pharmaceutical, oil and gas and other industries. It should be noted that there are no high-quality deposits of magnesium ores in Kazakhstan. Therefore, the creation of physicochemical foundations for new innovative processing technologies and their manufacturing application is a matter of great importance and relevance. One of the valuable salts with many useful properties is magnesium sulfate.

The purpose of the work is to study the patterns of interaction between dusty serpentinite wastes and sulfuric acid, to develop the physicochemical foundations of technologies for producing magnesium sulfate from technogenic chrysotile enrichment wastes.

The research objectives. To achieve the purpose of the research, the following scientific objectives were solved:

- determination of chemical, mineral and granulometric composition of dusty technogenic wastes generated during technological chrysotile enrichment processes at Kostanay Minerals JSC;
- thermodynamic and experimental study of regularities of stoichiometric interaction of technogenic wastes with sulfuric acid, determination of kinetic parameters of their dissolution in acid;
- development of physicochemical foundations and parameters of a cost-effective technology for producing magnesium sulfate from serpentinite wastes that meets the quality requirements of regulatory documents (State standard);
- development of a schematic diagram of an integrated technology for processing serpentinite wastes from chrysotile production, suitable for obtaining magnesium sulfate and road-building material – stabilizing additive, as well as assessment of the technical and economic efficiency of the technology;
- testing prototypes of magnesium sulfate in road-building material (stabilizing additive) for compliance with the requirements of regulatory documents in the field of their application in specialized accredited laboratories.

The research methods. When performing the work, methods of modern physicochemical research and analysis of initial and final products were applied: IR-Fourier spectroscopy (Shimadzu JR Prestige-21); X-ray phase analysis (DRON-3 and D8ENDEAVOR “Bruker”); differential analysis (Q-DERIVATOGRAPH) and electron microscopy with energy dispersive analysis. The study of the processes of interaction of prototype waste samples with acid was carried out in a glass reactor equipped with a stirrer, a thermometer, and pH control devices. When processing the experimental study results, methods of mathematical modeling and statistical data processing were used.

The research objects. Dusty serpentinite wastes of chrysotile-asbestos production of Kostanay Minerals JSC, obtained magnesium sulfate and silicon residue after leaching.

The research subject is the interaction processes between dusty wastes from chrysotile and sulfuric acid production, the physicochemical bases of the technology for producing magnesium sulfate from serpentine-containing materials.

The main provisions for the defense:

- physicochemical properties of chrysotile-asbestos industrial dusty serpentine waste and patterns of its interaction with sulfuric acid solutions;
- influence of temperature of preliminary heat treatment of the industrial waste on the process of its dissolution in sulfuric acid solutions;
- physicochemical bases and features of the proposed technology for obtaining magnesium sulfate from industrial serpentine wastes;
- technology for complex processing of technogenic wastes, which allows the production of magnesium sulfate and road-building construction material that meets the requirements of current regulatory documents;
- feasibility study for the technology of obtaining magnesium sulfate based on chrysotile-asbestos waste.

The main research results:

- it is shown that serpentines, which are the basis of dusty waste from chrysotile production, can be used in various industries and technologies, including as a source for magnesium compounds' production.
- it is shown that the use of solutions containing 0.4-0.5 stoichiometric quantity needed of sulfuric acid makes it possible to extract 40-50% of magnesium from its total amount in waste with a sulfuric acid utilization rate of up to 98%.
- fundamental IR spectroscopic and X-ray data were obtained to study the process of transformation of the silicate component of serpentinite into silica in the "serpentinite-sulfuric acid" system.
- the apparent activation energy of the interaction between serpentinite waste and sulfuric acid was determined to be about 45.0 kJ/mol, which means that the interaction process occurs with diffusion control.
- the main physicochemical parameters of the technology for producing magnesium sulfate based on serpentinite waste were determined:
- granulometric composition of the waste – 0.104-0.074 mm;
- solutions containing – 0.4-0.5 stoichiometric quantity needed of H_2SO_4 in relation to the amount of magnesium in the waste, with a liquid/solid ratio, S:L = 4:1; temperature, t^o – 80^o-90^oC; duration – 25-30 minutes.
- the possibility of using insoluble acid residue to obtain the stabilizing additive for crushed stone-mastic asphalt concrete mixture is shown. A patent of the Republic of Kazakhstan was received for the method of producing the stabilizing additive.
- a conceptual scheme was developed for the complex processing of dusty serpentinite waste from chrysotile production to produce magnesium sulfate and the stabilizing additive for crushed stone-mastic asphalt concrete.

- the quality of the resulting products ($MgSO_4$ and stabilizing additive) was tested in specialized accredited laboratories for compliance with the requirements of regulatory documents (State standards).

- it is shown that the amount of magnesium sulfate obtained from the annually generated (3000 t/g) dusty serpentinite waste at Kostanay Minerals JSC allows consumers of this product in Kazakhstan to save 68 668 750 KZT a year.

Justification of the novelty and importance of the results obtained:

- on the basis of the research, a new concept of processing technology was proposed, allowing the use of 50% of the stoichiometrically required amount of sulfuric acid, the acid utilization rate was increased to 95-98%;

- freely and hardly soluble components and structural fragments of magnesium-containing minerals in technogenic wastes were determined. It was established that brucite layer in serpentinite structure with $Mg(OH)_2$ and MgO components (50% of the amount) belongs to the freely soluble ones, the hardly soluble magnesium was found in $Mg(OH)_2Si_2O_5$ fragment in serpentinite structure (50% of the total);

- it was established that the rate of dissolution of technogenic waste in sulfuric acid solutions depends both on the resulting layer of silica, which diffusely prevents the movement of hydrogen ions, and on the structural (layered) features of serpentinite molecule;

- a method was found for obtaining a road-building material from an acid-insoluble residue, after the isolation of magnesium sulfate. The obtained stabilizing additive for crushed-stone-mastic asphalt concrete was tested in the accredited laboratory “KazDorNII”, it was shown that, according to physical and mechanical parameters, the additive meets the requirements of State standard 3105-2002 – stabilizing additive. The patent № 35566 of the Republic of Kazakhstan was obtained for the developed method for obtaining a stabilizing additive from crysotile-asbestos production waste;

- the possibility of creating a new technology for complex processing of technogenic wastes is shown, which can be implemented by obtaining magnesium sulfate and road-building material from silica acid-insoluble residue.

The theoretical significance of the work lies in the establishment of patterns of quantitative interaction between serpentinite and sulfuric acid, the mechanism of transformation of the silicate component of magnesium hydrosilicate into silica when treated with sulfuric acid solutions. The practical significance lies in the fact that the possibility of obtaining magnesium sulfate and road-building material based on the complex processing of serpentinite waste from chrysotile production is shown.

Compliance with directions of scientific development or government programs. The work was carried out within the framework of the theme of the plan No. B-16-02-03 for 2016-2020 of “Chemical technology of inorganic substances” chair, M. Auezov SKSU, in the direction of research work “Development of innovative technologies for producing mineral fertilizers and salts from natural raw materials and technogenic wastes from various industries”.

The principle of reliability. The scientific data of the dissertation are based on the results obtained by conducting experimental works and physicochemical studies using modern research equipment and instruments. Works related to thermodynamic calculations, mathematical modeling and data processing were performed using computer technologies.

Publications on the dissertation theme. 10 scientific papers were published on the dissertation theme, including 2 articles in international scientific editions included in the Scopus database, 2 articles in journals recommended by the Committee for Quality Assurance in Science and Higher Education, 4 articles in collected works of international and national conferences, 1 patent of the Republic of Kazakhstan was received for an invention.

Personal contribution of the doctoral student to the preparation of each publication:

1. Article "Influence of structural and molecular features of chrysotile on interaction within acid-chrysotile system" in the journal "RASAYAN Journal of Chemistry" – preparation of review and data analysis, obtaining and processing of results.

2. Article "Researching of sulfuric acid leaching of magnesium from serpentines" in the journal "News of the Academy of Sciences of the Republic of Kazakhstan. Series of geology and technical sciences" – preparation of review and analysis of literature data, obtaining and processing of results.

3. Article "Study of structural changes in mechanically thermally activated serpentinite" in the journal "Bulletin of EKTU" – obtaining and discussing experimental data.

4. Article "Recycling of chrysotile-asbestos production wastes as a factor in the ecological safety of the environment" in the journal "Bulletin of EKTU" – preparation of review and analysis of literary sources.

5. Article "Physicochemical characteristics of production wastes of chrisotile asbestos from the Zhitikara deposit" in Proceedings of International Conference of Industrial Technologies and Engineering (ICITE 2018), M. Auezov SKSU – obtaining and discussing experimental data.

6. Article "Development of technology for processing chrysotile-asbestos production wastes into industrial magnesium compounds" in "Proceedings of the X International Berimzhanov Congress on Chemistry and Chemical Technology" – obtaining and discussing experimental data, preparing literature sources' review.

7. Article "IR spectroscopic studies of structural changes occurring in chrysotile-asbestos wastes during heat treatment" in "Proceedings of KarSTU" – preparation of review of literature data.

8. Article "Environmental and technological aspects of acid treatment of serpentinite wastes from chrysotile-asbestos mining and processing" in the journal "International Journal of Engineering Research and Technology" – obtaining and discussing experimental data, preparing literature sources' review.

9. Thesis "The nature of the quantitative interaction of chrysotile asbestos and sulfuric acid" in international youth scientific forum "Lomonosov – 2020" of

Moscow State University – description and presentation of experimental data and analysis results.

10. Patent “Method of obtaining a stabilizing additive for crushed stone-mastic and asphalt-concrete mixture” – search and analysis of analogues and prototypes, obtaining experimental data.

The structure and scope of the dissertation. The dissertation consists of introduction, four chapters, conclusion, references and appendices. The work is presented on 103 pages, contains 18 tables, 24 figures, a bibliographic list of 171 titles.