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Selective extraction of magnesium from asbestos-containing raw materials

In this work, great attention was paid to identifying the reasons for the absence of practically implemented technologies for processing chrysotile asbestos wastes and searching for new methods for treating wastes with the aim of obtaining magnesium and other useful products of commercial interest. A series of experiments with solutions of ammonium chloride of different concentrations was carried out to study the kinetics of magnesium leaching. The concentration of magnesium leached increases with the concentration of the NH_4Cl solution (C_{Mg} = 0.092M; C_{Mg} = 0.1M; C_{Mg} = 0.102M), as well as with the time of the process itself. It was shown that the difference between the leaching rates of magnesium by 3M and 5M NH_4Cl solutions was not significant, and it was rather large for 1M and 3M solutions. The study of the thermodynamics of magnesium leaching was carried out with 3 molar solution of ammonium chloride at various temperatures. Graphs of the concentration of leached magnesium versus the leaching time at different temperatures of the ammonium chloride solution were plotted based on the results obtained. Experiments showed that the degree of magnesium leaching from asbestos increased with increasing temperature. The activation energy was calculated, which was equal to 44 kJ. Sediment identification was carried out using a laser-atomic emission spectrometer apparatus. The results of the experiment showed that a certain amount of magnesium, calcium and a small amount of other metals were contained in the obtained precipitates. Admixture of calcium does not affect the properties of the precipitate obtained. Leaching tests carried out with the help of ammonium chloride solution of various concentrations showed that the fibrous structure of asbestos was not destroyed.

Keywords: selective extraction of magnesium, asbestos-containing raw materials, kinetics, thermodynamics, concentration, magnesium-ammonium phosphate, activation energy, leaching.

Introduction

Asbestos is a valuable mineral that is widely used in industry. Despite the fact that asbestos has certain carcinogenicity, its properties are unique. Processing asbestos and its obtaining from mineral raw materials is accompanied by the formation of waste including non-conforming chrysotile asbestos and amphibole asbestos, as well as its other varieties. During the extraction and enrichment of chrysotile asbestos, large-tonnage industrial waste is formed consisting of overburden and processing components [1, 2].

Magnesium extraction is considered to be one of the traditional types of asbestos processing. All metals are leached out from asbestos in a complex by conventional methods under the action of strong acids. The resulting salts need separation and additional purification. In addition, strong mineral acids are used, which also cause intense corrosion of equipment. The development of selective leaching of magnesium without the use of mineral acids is currently a topical issue. In this regard, we studied the selective extraction of magnesium from asbestos-containing raw materials. To achieve this goal, some tasks such as obtaining thermodynamic and kinetic leaching data, obtaining a magnesium — ammonium phosphate precipitate to convert magnesium into an economically applicable form should be accomplished.

Experimental

An ammonium chloride solution of the concentrations 1M, 3M, 5M was used to study the leaching kinetics of magnesium from asbestos. It is known from the literature [3, 4] that ammonium chloride dissolves magnesium oxide well, while oxides of other metals do not pass into the solution. A solution of ammonium chloride has been proposed for the selective leaching of magnesium from chromate sludge [5]. 20.0 g of asbestos previously dried to constant weight at 200 ºC were added to the solutions obtained. It was kept at room temperature for 2 weeks. The pH was controlled periodically (Table 1) and 5 mL aliquots were taken to determine the concentration of magnesium.

Table 1

pH readings after leaching with ammonium chloride

C	τ								
	0.5	1.5	3	24	72	96	192	288	336
1M	8.569	8.69	8.895	8.9	8.907	8.967	9.04	9.013	9.014
3M	8.246	8.465	8.523	8.652	8.793	8.719	8.676	8.672	8.475
5M	8.18	8.094	8.242	8.245	8.249	8.369	8.45	8.55	8.721

Using concentrated ammonia, the pH of the solutions was adjusted to 11 and solutions were titrated with 0.05M solution of Na_2EDTA (Trilon B) in the presence of an eriochrome black indicator. The magnesium concentration was calculated (Table 2) based on the consumption data of Trilon B using the well-known formula derived from the law of equivalents:

$$C_1V_1 = C_2V_2,$$

where C_1 — is the concentration of Trilon B; V_1 — is the volume of Trilon B consumed during the titration, C_2 — is the concentration of magnesium; V_2 — is the aliquot volume.

Table 2

Results of magnesium leaching in NH_4Cl solution at 20 ºC

$C_{(NH_4Cl)}$	τ								
	0.5	1.5	3	24	72	96	192	288	336
1M	0.021	0.032	0.043	0.057	0.077	0.079	0.081	0.087	0.087
3M	0.024	0.044	0.058	0.071	0.09	0.092	0.096	0.1	0.1
5M	0.032	0.046	0.061	0.079	0.092	0.095	0.098	0.102	0.102

It can be concluded that the concentration of magnesium leached increases with the concentration of the NH_4Cl solution based on the results presented in the Table 2, as well as with the time of the process itself. It is shown that the difference between the leaching rates of magnesium by 3M and 5M NH_4Cl solutions is not significant, and it is rather large for 1M and 3M solutions. The kinetic curves for magnesium leaching from asbestos with ammonium chloride solutions of different concentrations at room temperature are shown in Figure 1.

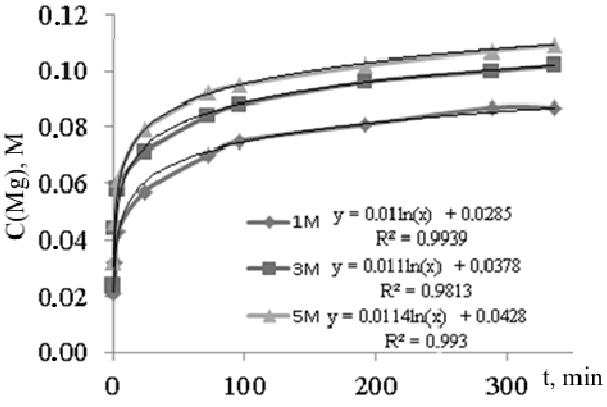

Figure 1. Kinetic curves of magnesium leaching at 20 ºC

After the amount of magnesium leached from asbestos was fixed, the solution was filtered off, so the solution was separated from asbestos. The thick mixture was washed with distilled water and dried in a drying cabinet until moisture was completely removed. According to the formulas of the reaction rate constants [6], they were calculated for 3 orders of reaction (Table 3).

Table 3

Indicators of reaction rate constants

τ	c	c_0	α1	α2	α3
336	0.826	1	0.00057	0.00043	0.00069
336	2.796	3	0.00021	0.00509	2.5E-05
336	4.782	5	0.00013	0.01551	5.6E-06

Comparison of the rate constants calculated shows that the formula for the first order of reaction gives values that are significantly less different from each other than for the second and third orders. It can be concluded that the reaction order for ammonium chloride is first, but the rate is controlled by diffusion. Then, ammonium phosphate was added dropwise to the solutions to convert the leached elements into the sediment. The ammonium phosphate solution was prepared from 85 % phosphoric acid and 25 % ammonia solution. Phosphoric acid was added to ammonia in small portions, each time waiting for the reaction mixture to cool down. The addition of phosphoric acid was continued to adjust pH = 11. The precipitate obtained was dried and samples were prepared for laser spectrometry. Laser spectrometry clearly shows that the sediment contains a sufficiently large amount of magnesium and some calcium (Fig. 2–4). It does not detect the presence of other metals.

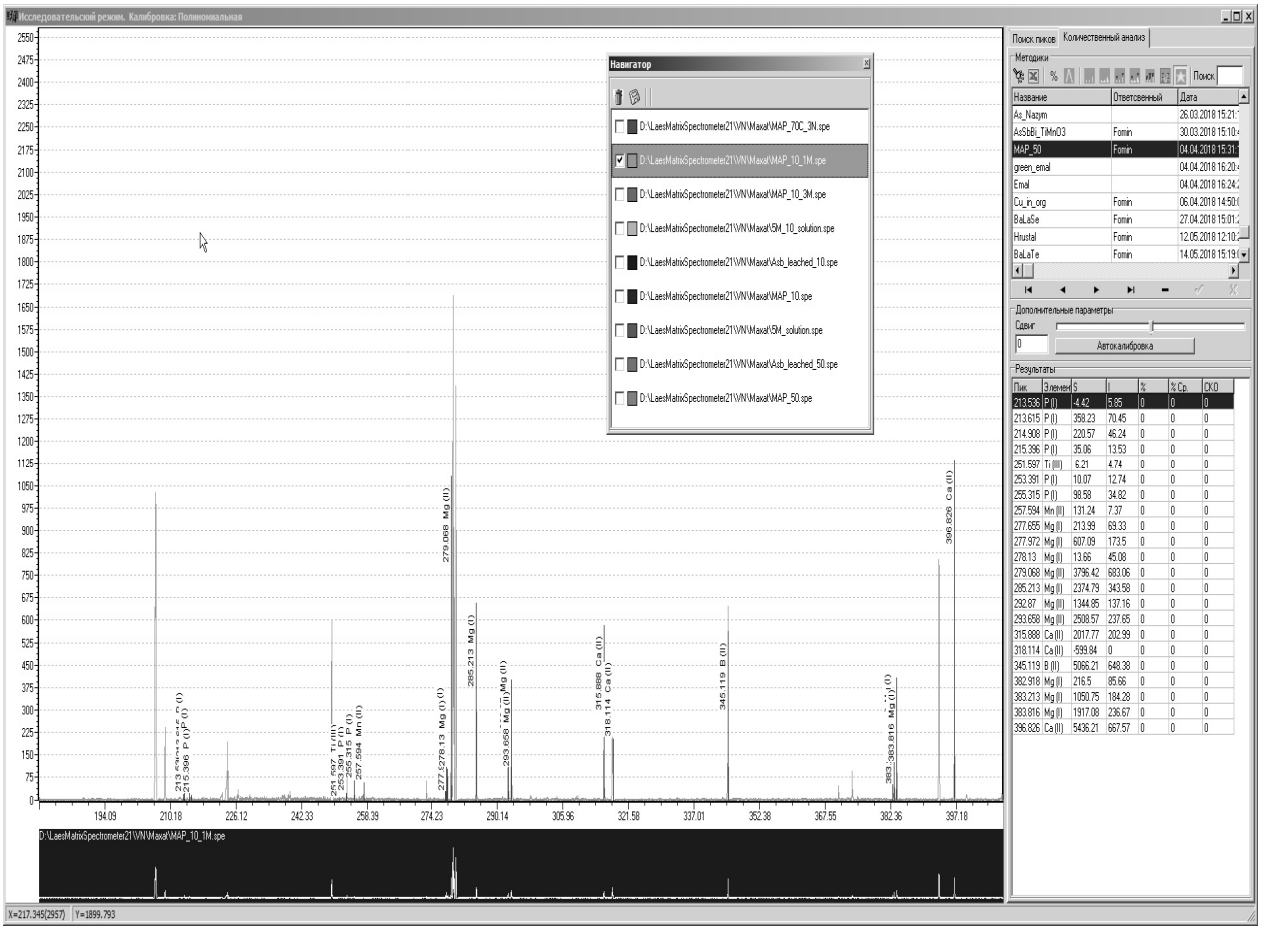

Figure 2. The metal content in the sludge studied during leaching with 1M ammonium chloride solution

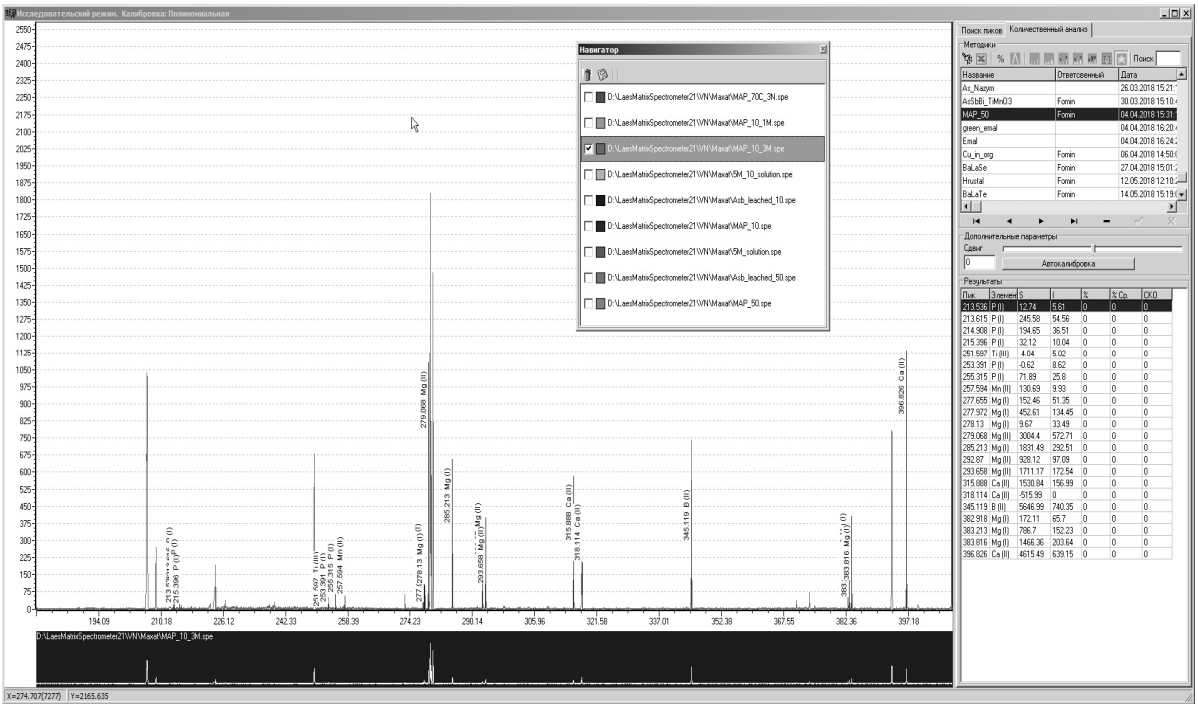

Figure 3. The metal content in the sludge studied during leaching
with 3M ammonium chloride solution

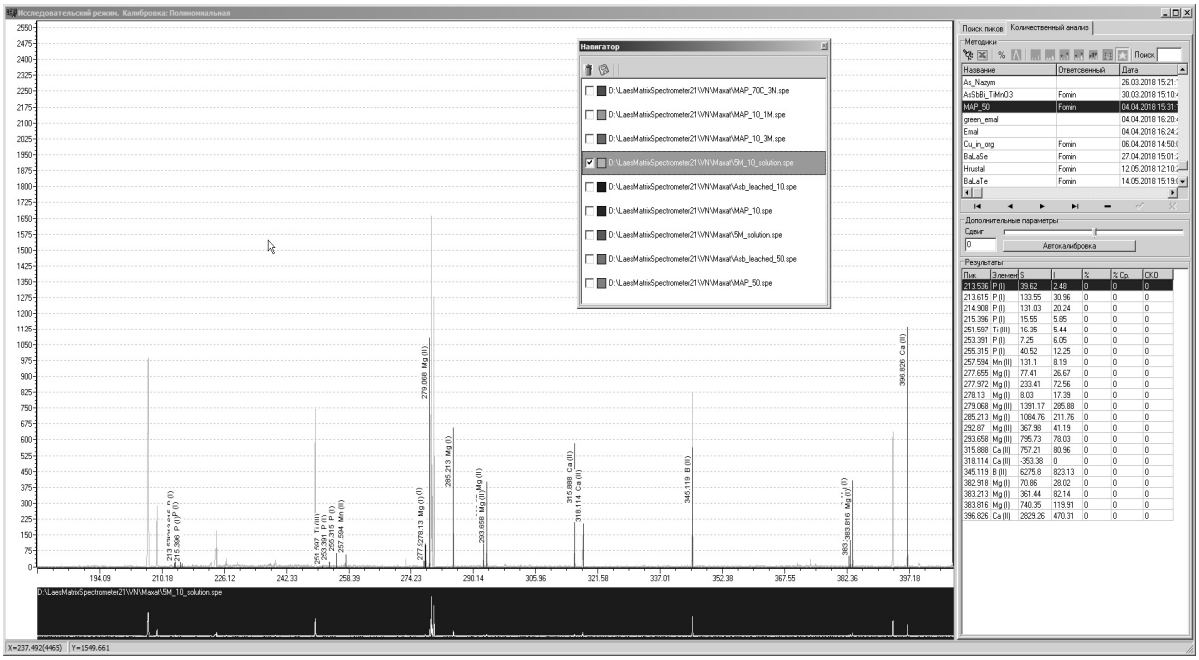

Figure 4. The metal content in the sludge studied during leaching
with 5M ammonium chloride solution

It can be noted that the reaction rate increases with an increase in the concentration of ammonium chloride solution based on the results obtained. In this case, a certain period of time occurs when the saturation peak remains the same regardless of the concentration of the solvent. Thermodynamic parameters of the process are of interest for the production organization on the industrial scale. We carried out a series of experiments on the magnesium leaching with a 3 molar solution of ammonium chloride at different temperatures to study the thermodynamics of leaching. 300 mL of a 3 M solution of ammonium chloride was poured into a flask with 15 g of initial asbestos and thermostated at temperatures of 20, 40, 50, 60, 70 ºC. Samples were

taken and titrated with Trilon B after a certain period of time. The results of the titration are shown in Table 4.

Table 4

The concentration of magnesium in the reaction mixtures, mol/L

T, ºC	τ, h								
	0.5	1.5	3	24	72	96	192	288	366
20	0.024	0.044	0.058	0.071	0.09	0.092	0.096	0.1	0.102
40	0.025	0.054	0.092	0.105	0.106	0.108	0.108	0.109	0.109
50	0.03	0.061	0.1	0.108	0.108	0.109	0.109	0.109	0.11
60	0.036	0.065	0.102	0.109	0.11	0.11	0.12	0.12	0.13
70	0.037	0.069	0.105	0.109	0.11	0.12	0.12	0.14	0.14

As a result of approximation of the experimental points the logarithmic curves are obtained in all cases that are shown in Figure 5. The accuracy of the approximation is 95–98 %.

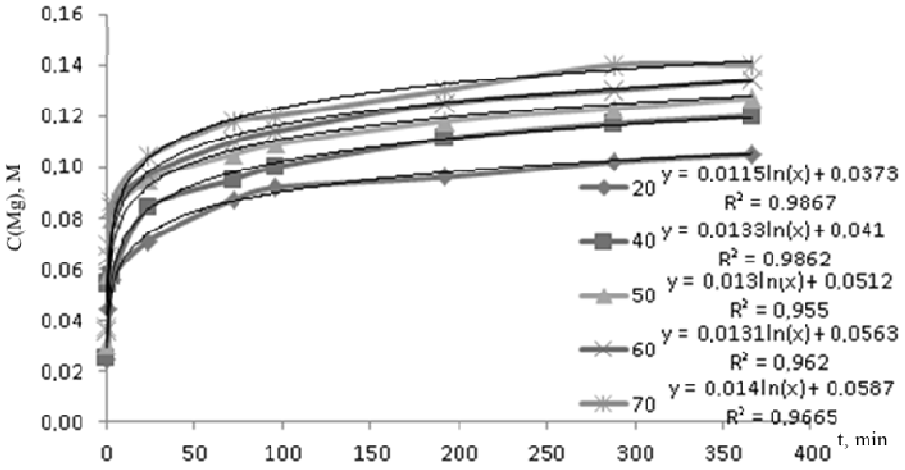

Figure 5. The dependence of the concentration of magnesium leached on the temperature of ammonium chloride solution

The activation energy was calculated with the help of the formula [4]:

$$E_a = R \times \ln \frac{\tau_2 \ln(1-\alpha_1)}{\tau_2 \ln(1-\alpha_2)} \Bigg/ \left(\frac{1}{T_2} - \frac{1}{T_1} \right).$$

The obtained data are given in Table 5. The value of the activation energy after statistical processing was 43.815 ± 8.973 kJ/mol at a significance level of 95 % (p = 0.05).

Table 5

Reaction activation energy

T	τ	α	E_a, J/mol
293.00	360.00	0.21	40941.50299
313.00	123.00	0.21	56236.10255
323.00	63.00	0.21	38413.44866
333.00	41.00	0.21	39668.83503
343.00	27.00	0.21	43814.97231

The obtained value of the activation energy is about 1.1–1.5 times exceeds the value obtained by the authors [7] for the magnesium leaching from calcium-containing magnesite (~30 kJ/mol). Apparently, this difference is due to the different chemical nature of the substrates studied.

Conclusions

The selectivity of the process with respect to calcium is most likely explained by the kinetic parameters of the process and the somewhat higher activation energy of calcium leaching. Apparently, the reaction has the first order in ammonium chloride and a rate constant of ~ $1–5\times10^{-4}$, while the velocity is controlled by diffusion. The experimentally determined value of the activation energy was 43.815 ± 8.973 kJ/mol at a significance level of 95 % (p = 0.05). Magnesium goes into solution, the pH of which is 9. This solution is convenient for precipitating magnesium ammonium phosphate. Magnesium ammonium phosphate is a valuable mineral fertilizer, as well as a profitable, marketable form for pure magnesium. Using ammonium phosphate and bringing the pH to 11, we got magnesium ammonium phosphate. The study of the precipitate obtained with LIBS showed that it contained a minor admixture of calcium and did not contain other metals except magnesium. Thus, the sediment is pure, and the calcium contained in a small amount does not interfere in any way for use it in gardening.

Acknowledgments

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Асбестқұрамды шикізаттан магнийді селективті бөліп алу әдісі

Мақалада хризотилді асбест қалдықтарын өңдеу бойынша іс жүзінде іске асырылған технологиялардың болмау себептерін анықтау және коммерциялық қызығушылық туғызатын магний мен басқа да пайдалы өнімдерді алу мақсатында қалдықтарды өңдеудің жаңа әдістері қарастырылды. Магний шаймалау кинетикасын зерттеу үшін түрлі концентрациядағы аммоний хлориді ерітінділері қатысында бірқатар тәжірибелер жүргізілді. Шаймаланған магнийдің концентрациясы NH_4Cl ерітіндісі концентрациясының (C_{Mg} = 0.092M; C_{Mg} = 0.1M; C_{Mg} = 0.102M) жоғарлауымен сипатталды. 3М және 5М NH_4Cl магний ерітінділерінің шаймалау жылдамдығы арасындағы айырмашылық айтарлықтай емес, ал 1М және 3М шешімдері үшін бұл өте үлкен. Магнийді шаймалаудың термодинамикасын зерттеу әртүрлі температурада аммоний хлоридінің 3 молярлық ерітіндісі қатысында жүргізілді. Алынған нәтижелер негізінде магний концентрациясының аммоний хлориді температурасы бойынша және зерттеуге алынған тұнбаның құрамындағы металл арасындағы тәуелділік графиктері жасалынды. Тәжірибелер нәтижесі асбест құрамынан магнийдің шаймалау дәрежесі температураның жоғарлауымен артатындығын көрсетті. Белсендіру энергиясы 44 кДж-ға тең. Тұнбаны анықтау лазерлік-атомдық эмиссионды спектрометрде жүргізілді. Тәжірибенің нәтижелері бойынша алынған тұнбаның құрамында белгілі бір мөлшерде магний, кальций және басқа да металдар кездесетінін көрсетті және кальций қоспасы алынған тұнбаның қасиеттеріне әсер

етпейтіндігі анықталды. Әртүрлі концентрациядағы аммоний хлоридін шаймалау арқылы жүргізілген тәжірибелер асбестің талшықты құрылымы жойылмағанын көрсетті.

Кілт сөздер: магнийді селективті бөліп алу әдісі, асбесткұрамды шикізат, кинетика, термодинамика, концентрация, магний-аммоний фосфаты, белсендіру энергиясы, шаймалау.

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Селективное извлечение магния из асбестосодержащего сырья

В статье большое внимание уделено выявлению причин отсутствия практически реализуемых технологий переработки хризотил-асбестовых отходов и поиску новых методов обработки отходов с целью получения магния и других полезных продуктов, представляющих коммерческий интерес. Проведены серии опытов с растворами хлорида аммония разной концентрации для изучения кинетики выщелачивания магния. Концентрация выщелачиваемого магния растет с увеличением концентрации раствора NH_4Cl (C_{Mg} = 0.092M; C_{Mg} = 0.1M; C_{Mg} = 0.102M), а также с увеличением времени самого процесса. Показано, что разница между скоростями выщелачивания магния 3М и 5М растворами NH_4Cl незначительна, а для 1М и 3М растворов — довольно велика. Исследование термодинамики выщелачивания магния проводили 3М раствором хлорида аммония при различных значениях температуры. На основании полученных результатов были построены графики зависимости концентрации выщелоченного магния от времени выщелачивания при разных температурах раствора хлорида аммония. Результаты экспериментов показали, что степень выщелачивания магния из асбеста возрастает с увеличением температуры. Вычислена энергия активации, которая составила 44 кДж. Идентификация осадка проводилась на лазерно-атомном эмиссионном спектрометре. Было установлено, что в полученных осадках содержится определенное количество магния, кальция и незначительное количество других металлов. Примесь кальция не влияет на свойства полученного осадка. Испытания, проведённые с применением раствора хлорида аммония различной концентрации, показали, что волокнистая структура асбеста не подвержена разрушению.

Ключевые слова: селективное извлечение магния, асбестосодержащее сырье, кинетика, термодинамика, концентрация, магний-аммоний фосфат, энергия активации, выщелачивание.

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