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CONTENTS

PHYSICS

U.A. Ualikhanova, Y.Y. Kurban, A.M. Syzdykova, A.B. Altaibayeva, G.S. Altayeva
 Dynamical systems analysis of the Starobinsky cosmological model.....11

M.B. Zhassybayeva, Z. Myrzakulova, M. Abeuova
 Darboux transformation for the two-layer M-LXXII equation.....24

G.K. Beketova, N.N. Zhanturina, Z.K. Aimaganbetova
 Cs₂AgBiBr₆ double halide perovskites as advanced materials for high-efficiency solar cells.....38

L.I. Shestakova, R.R. Spassyuk
 Spectral studies of the k–f corona interface at 5000–6000 Å.....52

A.Khazhidinova, A. Khazhidinov
 On the issue of fuel consumption of a thermal power plant.....66

T.B. Koshtybayev, K.K. Zhantleuov, M.E. Aliyeva
 Greens function in the theory of quantum fluids.....77

A.V. Serebryanskiy, Ch.B. Akniyazov, Ch.T. Omarov, S. Sittykova, D. Kadyrova
 Analysis of lunar impact flashes statistics.....91

G.T. Omarova, Zh.T. Omarova
 The Lagrange - Jacobi equation and its application to the N - body problem.....105

Zh. Muratkhan, M. Khassanov
 Methods for estimation of stellar wind parameters in high-mass X-ray binary systems with neutron stars.....113

V. Mukamedenkyzy, A. Izbasar, A. Aqikat
 Investigation of structured flows induced by concentration-driven convection in ternary gases systems.....127

K. Saurova, S. Nysanbaeva, G. Turlybekova
 Modeling of the optical system of a star tracker for accurate spacecraft attitude determination.....140

CHEMISTRY

- B.S. Serikbayeva, M.S. Satayev, N.K. Sarypbekova**
Study of the electroplating process on polypropylene using a conductive layer.....157
- A.P. Auyeshov, Ch.Z. Yeskibayeva, A.K. Dikanbayeva**
Resource-efficient utilization of serpentinite waste for magnesium sulfate production.....172
- A.K. Kozybaev, Zh.D. Alimkulova, S.O. Abilkasova**
Kinetic and thermodynamic studies of heavy metal adsorption onto water-washed Ca-montmorillonite clay.....184
- A.Abdрахmanova, V. Krivchenko, A. Sabitova1, B. Kuderina**
DOL-enhanced electrolytes as a route to stable anodes in Li–V₂O₅ systems.....196
- B.K. Massalimova, A.S. Shayakhmetova, A.S.Darmenbayeva**
Water resources of Northern Kazakhstan: environmental monitoring and sustainable anagement.....208
- A. Rakhimov, N. Zhanikulov, B. Taimasov, E. Potapova, A.K. Sviderskiy**
Investigation of lead slag processing waste as raw material for cement industry.....227
- L.M. Kalimoldina, K.Zh. Zhalgasbayev, A.S. Dauletbayev**
Comparative study of industrial wastewater treatment methods.....241
- A. Nurlan, S.R. Konuspayev, T.S. Abildin, K. Toshtay**
Transformations of hydrocarbons during the hydrogenation of gasoline containing benzene.....256
- G.J. Baisalova, B.K. Yertay, A.A. Taltenov, P. Kuzhatova, G. Saspugayeva**
A quantitative determination of the phenol compounds sum in the thallus of *Parmelia sulcata*.....274
- B.E. Myrzabekov, A.B. Makhanbetov, T.E. Gaipov, B.S. Abzhalov, N.N. Nurgaliyev**
Electrochemical reduction of manganese (II) ions on titanium and lead electrodes.....286
- A.S. Darmenbayeva, G.M. Zhussipnazarova, R. Reshmy, Zh.B. Mukazhanova, V.A. Rube**
Biocoatings based on flax stem cellulose and their properties.....298

МАЗМҰНЫ

ФИЗИКА

У.А. Уалиханова, Е.Е. Құрбан, А.М. Сыздыкова, А.Б. Алтайбаева, Г.С. Алтаева Старобинскийдің космологиялық моделін динамикалық жүйелер арқылы талдау.....	11
М.Б. Жасыбаева, Ж. Мырзақұлова, М. Абеуова Қос қабатты М-LXXII теңдеуі үшін дарбу түрлендіруі.....	24
Г.К. Бекетова, Н.Н. Жантурина, З.К. Аймағанбетова Cs ₂ AgBiBr ₆ қос галоидты перовскиттер: күн батареяларына арналған тиімділігі жоғары жаңа озық материалдары.....	38
Л.И. Шестакова, Р.Р. Спасюк 5000–6000 Å диапазонында k- және f-короналар арасындағы өтпелі аймақты спектрлік зерттеу.....	52
А. Хажидинова, А. Хажидинов Жылу электр станциясының отын тұтыну мәселесі.....	66
Т.Б. Қоштыбаев, К.Қ. Жантлеуов, М.Е. Алиева Кванттық сұйықтар теориясындағы Грин функциялары.....	77
А.В. Серебрянский, Ч.Б. Акниязов, Ч.Т. Омаров, С. Ситтыкова, Д. Кадырова Айдың беткі қабатына метеоридтардың соқтығысуын статистикалық тұрғыдазерттеу.....	91
Г.Т. Омарова, Ж.Т. Омарова Лагранж – Якоби тундеуі және оны N -денелі есепке қолдану.....	105
Ж. Мұратхан, М. Хасанов Нейтрон жұлдыздары бар массивті рентгендік екілік жүйелердегі жұлдыздық жел параметрлерін бағалау әдістері.....	113
В. Мукамеденқызы, А. Избасар, А. Ақиқат Үшкомпонентті газ жүйелеріндегі концентрациялық конвекцияның әсерінен құрылымдық ағындардың пайда болуын зерттеу.....	127
К. Саурова, С. Нысанбаева, Г. Турлыбекова Ғарыш аппараттарының ориентациясын нақты анықтау үшін жұлдыз сенсорының оптикалық жүйесін модельдеу.....	140

ХИМИЯ

Б.С. Серикбаева, М.С. Сагаев, Н.К. Сарыпбекова

Электрөткізгіш қабатты қолданып, полипропиленге гальваникалық қаптама алу процесін зерттеу.....157

А.П. Ауешов, Ч.З. Ескибаева, А.К. Диканбаева

Серпентинит қалдығынан магний сульфатын алудың техникалық-экономикалық зерттеуі.....172

А.К. Қозыбаев, Ж.Д. Әлімқұлова, С.О. Әбілқасова

Сумен жуылған са-монтмориллонит сазында ауыр металдардың сорбциясының кинетикасы мен термодинамикасы.....184

А. Абдрахманова, В. Кривченко, А. Сабитова, Б. КудеринаLi–V₂O₅ жүйесіндегі тұрақты анодтарға қол жеткізуге арналған DOL-мен модификацияланған электролиттер.....196**Б.К. Масалимова, А.С. Шаяхметова, А.С. Дарменбаева**

Солтүстік Қазақстанның су ресурстары: экологиялық мониторинг және ұтымды басқару.....208

А. Рахимов, Н. Жаникулов, Б. Таймасов, Е. Потапова, А.К. Свидерский

Цемент өнеркәсібі үшін шикізат ретінде қорғасын қожын өндеу қалдықтарын зерттеу.....227

Л.М. Калимолдина, Қ.Ж. Жалғасбаев, А.С. Даулетбаев

Өнеркәсіптік сарқынды суларды тазартудың әдістерін салыстырмалы түрде зерттеу.....241

Ә. Нұрлан, С.Р. Конуспаев, Т.С. Абильдин, К. Тоштай

Құрамында бензол бар бензинді гидрлеу кезінде көмірсутектердің өзгеруі.....256

Г.Ж. Байсалова, Б.К. Ертай, А.А.Талтенов, П. Кужатова, Г.Е. Саспугаева*PARMELIA SULCATA* талломындағы фенолды қосылыстардың жиынтық мөлшерін сандық анықтау.....274**Б.Э. Мырзабеков, А.Б. Маханбетов, Т.Э. Гаипов, Б.С. Абжалов, Н.Н. Нұрғалиев**

Марганец (II) ионының титан және қорғасын электродында электрохимиялық тотықсыздануы.....286

А.С. Дарменбаева, Г.М. Жусипназарова, Р. Решми, Ж.Б. Мукажанова, В.А. Рубе

Зығыр сабағынан алынған целлюлоза негізіндегі биожабындар және олардың қасиеттері.....298



СОДЕРЖАНИЕ

ФИЗИКА

У.А. Уалиханова, Е.Е. Курбан, А.М. Сыздыкова, А.Б. Алтайбаева, Г.С. Алтаева Анализ космологической модели старобинского с помощью динамических систем.....	11
М.Б. Жасыбаева, Ж. Мырзакулова, М. Абеуова Преобразование Дарбу для двухслойного уравнения M-LXXII.....	24
Г.К. Бекетова, Н.Н. Жантурина, З.К. Аймаганбетова Cs ₂ AgBiVg ₆ : двойные галоидные перовскиты как передовые материалы для высокоэффективных солнечных элементов	38
Л.И. Шестакова, Р.Р. Спасюк Спектральные исследования области перехода между К и F короной в диапазоне 5000–6000Å.....	52
А. Хажидинова, А. Хажидинов К вопросу о расходе топлива на тепловой электростанции.....	66
Т.Б. Коштыбаев, К.К. Жантлеуов, М.Е. Алиева Функции Грина в теории квантовых жидкостей	77
А.В. Серебрянский, Ч.Б. Акниязов, Ч.Т. Омаров, С. Ситтыкова, Д. Кадырова Исследование статистики ударов метеороидов о поверхность луны	91
Г.Т. Омарова, Ж.Т. Омарова Уравнение Лагранжа – Якоби и его применение к задаче N -тел.....	105
Ж. Муратхан, М. Хасанов Методы оценки параметров звездного ветра в массивных двойных рентгеновских системах с нейтронными звездами.....	113
В. Мукамеденкызы, А. Избасар, А. Акикат Исследование возникновения структурированных течений, обусловленных концентрационной конвекцией в трёхкомпонентных газовых системах.....	127
К. Саурова, С. Нысанбаева, Г. Турлыбекова Моделирование оптической системы звёздного датчика для точного определения ориентации космических аппаратов.....	140

ХИМИЯ

Б.С. Серикбаева, М.С. Сатаев, Н.К. Сарыпбекова

Исследование процесса гальванопокрытия на полипропилене с использованием электропроводного слоя.....157

А.П. Ауешов, Ч.З. Ескибаева, А.К. Диканбаева

Технико-экономическое исследование получения сульфата магния из серпентинитового отхода.....172

А.К. Козыбаев, Ж.Д. Алимкулова, С.О. Абилкасова

Кинетика и термодинамика сорбции тяжелых металлов на промытой водой кальциево-монтмориллонитовой глине.....184

А. Абдрахманова, В. Кривченко, А. Сабитова, Б. КудеринаDOL – модифицированные электролиты как путь к стабильным анодам в системах $Li-V_2O_5$196**Б.К. Масалимова, А.С. Шаяхметова, А.С. Дарменбаева**

Водные ресурсы Северного Казахстана: экологический мониторинг и устойчивое управление.....208

А. Рахимов, Н. Жаникулов, Б. Таймасов, Е. Потапова, А.К. Свицерский

Исследование отходов переработки свинцового шлака в качестве сырья для цементной промышленности.....227

Л.М. Калимолдина, К.Ж. Жалгасбаев, А.С. Дәулетбаев

Сравнительное исследование методов очистки промышленных сточных вод.....241

А. Нурлан, С.Р. Коңуспаев, Т.С. Абильдин, К. Тоштай

Превращения углеводов при гидрировании бензина, содержащего бензол.....256

Г.Ж. Байсалова, Б.К. Ертай, А.А.Талтенов, П. Кужатова, Г.Е. СаспугаеваКоличественное определение суммы фенольных соединений в талломе *PARMELIA SULCATA*.....274**Б.Э. Мырзабеков, А.Б. Маханбетов, Т.Э. Гайпов, Б.С. Абжалов, Н.Н. Нургалиев**

Электрохимическое восстановление ионов марганца (II) на титановом и свинцовом электродах.....286

А.С. Дарменбаева, Г.М. Жусипназарова, Р. Решми, Ж.Б. Мукажанова, В.А. Рубе

Биопокрытия на основе целлюлозы из стебля льна и их свойства.....298



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RESOURCE-EFFICIENT UTILIZATION OF SERPENTINITE WASTE FOR MAGNESIUM SULFATE PRODUCTION

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Abstract. This study presents a techno-economic assessment of technologies for producing magnesium sulfate from serpentinite waste generated during the mining and processing of chrysotile asbestos, which poses an environmental hazard. The investigation focuses on a new alternative method for processing powdered serpentinite waste (PTW), including stages of low-concentration sulfuric acid leaching and subsequent neutralization of the resulting sulfate solution using serpentinite waste thermally activated at 750 °C. The approach aims to evaluate the efficiency of magnesium sulfate production, the quality of the final product, and the potential profitability of the technology. It was demonstrated that the combined leaching and neutralization of serpentinite waste enables the production of magnesium sulfate with a total yield of 46%, yielding a high-quality commercial product — $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$. Preliminary techno-economic indicators, calculated based on material and energy inputs (excluding fixed costs) and average market prices of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, indicate the economic feasibility of the proposed technology. A comparative analysis with conventional magnesium sulfate production methods showed that the use of local serpentinite waste and its thermally activated form for neutralization significantly reduces raw material costs and enhances profitability. The study establishes that the proposed processing scheme has high technological efficiency and can be integrated into existing chrysotile waste



processing facilities. Overall, the findings confirm the feasibility of industrial-scale magnesium sulfate production based on Kazakhstan's local mineral resources, offering an environmentally responsible and resource-efficient approach while generating a valuable chemical product for agricultural and industrial applications.

Keywords: magnesium sulfate, serpentinite waste, sulfuric acid leaching, thermally activated serpentinite

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СЕРПЕНТИНИТ ҚАЛДЫҒЫНАН МАГНИЙ СУЛЬФАТЫН АЛУДЫҢ ТЕХНИКАЛЫҚ-ЭКОНОМИКАЛЫҚ ЗЕРТТЕУІ

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Аннотация. Бұл мақалада хризотил асбестті өндіру және байыту кезінде пайда болатын серпентинит қалдықтарынан магний сульфатын алу технологиясының технико-экономикалық зерттеулері ұсынылған. Зерттеу барысында ұнтақталған технологиялық қалдықтарды төмен концентрациялы күкірт қышқылы ерітіндісімен өңдеу және алынған сульфат ерітіндісін 750 °С-та термоактивтенген серпентинит қалдығымен бейтараптау және тазарту кезеңдері жан-жақты қарастырылған. Бұл тәсіл магнийдің тиімді шығуын қамтамасыз етіп, қосымша иондармен ластануды азайтуға мүмкіндік береді. Бұл тәсіл магний сульфатын $MgSO_4 \cdot 7H_2O$ 46% өнімділікпен және тазалығы жоғары сапада алуға мүмкіндік береді. Элементтік талдау барысында магний сульфатының құрамында кальций мен темірдің мөлшері өте аз екені анықталды, бұл өнімнің коммерциялық тұрғыдан тартымдылығын арттырады. Материалдық және энергетикалық шығындар, сондай-ақ өнімнің орташа нарықтық бағалары негізінде, магний сульфатын өндірудің технико-экономикалық көрсеткіштері анықталып, технологияның экономикалық тиімділігін бағалауға мүмкіндік берді. Салыстырмалы талдау көрсеткендей, жергілікті серпентинит қалдықтарын магний сульфатын алу өндірісінде пайдалану және оның термоактивтенген формаларын қышқыл

ерітіндісін бейтараптауда қолдану шығындарды айтарлықтай азайтып, өндірістің рентабельділігін арттырады. Сонымен қатар, ұсынылған технология экологиялық тұрғыдан қауіпсіз, тұрақты өндіріс процессін қамтамасыз етеді және ресурстарды тиімді пайдалануға мүмкіндік береді. Бұл технология қайта өңдеу арқылы техногендік қалдықтардың қоршаған ортаға тигізетін зиянды әсерін азайтады. Жаңа өңдеу технологиялық сұлбасы жоғары тиімділікке ие болып, хризотил қалдықтарын қайта өңдейтін кәсіпорындарға енгізілуі мүмкін. Зерттеу нәтижелері Қазақстандағы жергілікті минералдық-шикізат базасына сүйене отырып, магний сульфатының өнеркәсіптік өндірісін ұйымдастырудың перспективтілігін нақты дәлелдейді.

Түйін сөздер: магний сульфаты, серпентинит қалдықтары, күкіртқышқылды сілтісіздендіру, термобелсендірілген серпентинит

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ТЕХНИКО-ЭКОНОМИЧЕСКОЕ ИССЛЕДОВАНИЕ ПОЛУЧЕНИЯ СУЛЬФАТА МАГНИЯ ИЗ СЕРПЕНТИНИТОВОГО ОТХОДА

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Аннотация. В статье представлено технико-экономическое исследование технологии получения сульфата магния из серпентинитового отхода, образующегося при добыче и обогащении хризотил-асбеста и представляющего экологическую опасность. Рассмотрены основные аспекты новой альтернативной технологии переработки порошкообразного отхода хризотилового сырья, включающей стадии сернокислотного выщелачивания растворами серной кислоты низкой концентрации и последующей нейтрализации продуктивного сульфатного раствора с использованием термоактивированного при 750 °С серпентинита. Проведена оценка эффективности получения сульфата магния, качества конечного продукта и потенциальной рентабельности предложенной технологии. Показано, что сочетание процессов выщелачивания и нейтрализации позволяет получить сульфат магния с общим выходом 46% и высокими качественными характеристиками товарного продукта $MgSO_4 \cdot 7H_2O$. На основе расчетов материальных и энергетических затрат (без учета постоянных расходов) и средней рыночной стоимости $MgSO_4 \cdot 7H_2O$ определены предварительные



техничко-экономические показатели, позволяющие прогнозировать экономическую эффективность технологии. Проведен сравнительный анализ с известными методами получения сульфата магния. Установлено, что использование местных серпентинитовых отходов и их термоактивированных форм для нейтрализации кислых растворов выщелачивания позволяет существенно снизить затраты на сырьё и повысить рентабельность производства. Показано, что новая технологическая схема обладает высокой эффективностью и может быть интегрирована в действующие предприятия по переработке хризотилловых отходов. Результаты исследования подтверждают перспективность организации промышленного производства сульфата магния на основе минерально-сырьевой базы Казахстана.

Ключевые слова: сульфат магния, серпентинитовые отходы, сернокислотное выщелачивание, термоактивированный серпентинит

Introduction. Serpentinites are magnesium-rich silicate rocks containing significant amounts of silica and have been widely investigated as raw materials for producing magnesium and its compounds. These rocks, including industrial waste generated during the processing of chrysotile-asbestos ores, represent a valuable source of magnesium (Kalichenko et al. 2007; Sagarunyan et al. 2014; Shevko et al. 2022; Kozlov et al. 2015; Gabdullin et al. 2012; Fedorôcková et al. 2016; Sierra et al. 2018). Various processing methods for serpentinites have been proposed, each with specific technological and economic limitations (Auyeshov et al. 2024).

The serpentinite ores from the Zhitikara deposit, located on the eastern slope of the Southern Urals in Kazakhstan, belong to the Bazhenov geological-industrial type and consist primarily of serpentinized peridotites, dunites, and serpentinites (Dzhafarov 2013).

The average chrysotile content in these ores is approximately 4.5–5.5%. The mineralogical composition includes chrysotile, lizardite, and antigorite ($\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$), along with brucite ($\text{Mg}(\text{OH})_2$) and magnetite (Fe_3O_4). The processing plant, JSC "Kostanay Minerals," has an annual production capacity of approximately 500,000 tons of chrysotile, and over 65 years of operation, it has generated substantial volumes of waste. This waste, which may still contain residual chrysotile fibers, poses environmental and health risks due to airborne dispersion (Punenkov et al. 2022).

To mitigate these issues, several approaches for valorizing the tailings have been proposed, with particular attention to extracting magnesium from serpentinite waste. Compared to dolomite, which contains 20–22 wt.% Mg, serpentinite can have a higher magnesium content of 25–26 wt.%, making it a promising alternative raw material. Previous studies have investigated its leaching behavior using various acids, including sulfuric (Błońska et al. 2016) and hydrochloric acid (Mpouras et al. 2017; Fouda et al. 1996; Shaban et al. 2018; Huang et al. 2017; Teixeira et al. 2012). However, despite extensive research, there is still limited practical implementation of technologies for producing specific industrial-grade magnesium compounds from serpentinite, especially those supported by techno-economic analyses.

In response to this gap, the present study proposes a novel process scheme for the production of magnesium sulfate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) from serpentinite waste generated during chrysotile processing at the Zhitikara deposit. The process involves sulfuric acid leaching followed by neutralization using thermally activated serpentinite, combined with a preliminary economic evaluation of the key process stages. The aim is to assess the resource and economic efficiency of this technology and the feasibility of utilizing industrial waste for the production of high-purity magnesium compounds.

Materials and Methods. *Sample preparation.* Powdered process waste (PTW) from the chrysotile beneficiation plant at JSC "Kostanay Minerals" was used as the main raw material. The chemical and mineralogical composition of this waste closely resembles that of the original chrysotile ore. The material appears as a bluish-gray fibrous powder without lumps or solid inclusions, collected using bag-type dust collection systems used during the crushing and fractionation of chrysotile raw materials. The elemental composition of the PTW is presented in Table 1.

Table 1. Elemental composition of PTW

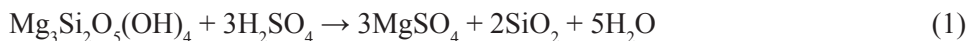
Element	C	O	Mg	Al	Si	S	Ca	Fe	Total
Elemental composition of PTW, wt.%	2.58	51.00	25.00	0.54	17.45	–	0.50	2.93	100.00

Thermal activation. Thermal treatment of the PTW was carried out at 750°C for one hour in order to prepare it for use as a neutralizing and purifying reagent for the sulfate solution. The treatment significantly altered the particle size distribution, eliminating fractions smaller than 0.9mm. The dominant particle size fraction after calcination was in the range of 0.14—0.08—0.07mm, representing approximately 94% of the material. The thermally activated PTW was used without any further grinding.

Analytical instrumentation. Analytical measurements were performed using a JSM-6490LV scanning electron microscope (JEOL, Japan) equipped with an INCA Energy 350 EDS system, and an iCAP-Q mass spectrometer (Thermo Scientific, Germany). All analyses were conducted in accordance with established laboratory protocols to ensure the accuracy and reproducibility of results.

Results and discussion. *Leaching of process tailings (PTW) with sulfuric acid*

Leaching of powdered PTW with sulfuric acid was carried out according to the following stoichiometric reaction:



To ensure complete reaction of magnesium with sulfuric acid and account for the presence of trace metal impurities, a slight excess of acid was introduced. The leaching process also follows the simplified ionic reaction:



A molar ratio of 1.0:1.046 (Mg^{2+} : H_2SO_4) was selected. The stoichiometric amount of sulfuric acid was calculated based on the total magnesium content in PTW.

Leaching was performed in a round-bottom flask equipped with a thermometer, reflux condenser, sampler, and a propeller stirrer. A mixture of 500 g of PTW and 1000 cm^3 of distilled water was placed into the flask. Under continuous stirring at 200–300 rpm, 415 cm^3 of 92% sulfuric acid (density = 1.824 g/cm^3) was added dropwise in three portions of 150–200 cm^3 using a dropping funnel. The total mass of the reaction mixture was 2256 g, resulting in a liquid-to-solid (L:S) ratio of 4.51.

Upon acid addition, the suspension rapidly heated to 100–105°C within 2–3 minutes, accompanied by intense foaming and boiling. To avoid overheating, acid was added in intervals. After the final portion, gentle boiling was maintained throughout the remainder of the 3-hour leaching period.

The resulting mixture appeared as a dense bluish-gray suspension with a measured pH of 0.57. Aliquots (10 mL) were taken at 30, 60, 120, and 180 minutes. Samples were filtered, and the residues were washed, dried at 105°C, and analyzed chemically. Magnesium concentration was determined both instrumentally and by classical chemical titration, with a relative error not exceeding 2–3%, confirming the consistency of results. The elemental compositions of both filtrates and residues for the different leaching durations are summarized in Table 2.

Table 2. Elemental composition of the filtrate and insoluble residue at different leaching durations (30, 60, 120, and 180 min, $t = 100\text{--}105^\circ\text{C}$)

Element	Leaching time, min							
	30	60	120	180	30	60	120	180
	Filtrate, wt. %				Residue, wt. %			
C	—	—	—	—	4.85	4.36	5.19	4.43
O	5.09	57.10	53.65	57.41	54.17	53.53	53.79	53.98
Mg	10.36	10.71	11.11	11.69	3.31	2.99	2.42	2.39
Al	0.48	0.42	0.37	0.30	0.33	—	—	—
Si	4.10	3.82	4.25	3.86	34.53	36.06	36.36	36.45
S	28.99	28.02	28.46	28.42	1.50	1.31	1.19	1.56
Ca	—	0.27	—	—	0.22	0.28	—	—
Fe	1.98	2.66	2.16	2.32	1.10	1.46	1.06	1.19
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
m, g (MgSO_4)	168.65	168.90	171.60	167.68	—	—	—	—

Note: “—” indicates values below the detection limit or not determined.

Analysis of the data in Table 2 shows that within 30 minutes from the start of PTW leaching with sulfuric acid, nearly all elements present in the waste are transferred into the sulfate solution, with the exception of calcium, which appears in the solution only after 60 minutes. However, a significant change in the concentrations of the main elements in the sulfate solution and insoluble residue is not observed in the time interval from 30 to 180 minutes. Specifically, the magnesium content in the solution increases by only 12.8%, iron by 17%, and silicon decreases by 5.8%. In the insoluble residue, the concentrations of these elements also change accordingly: magnesium decreases

by 27%, silicon increases by 5.5%, and iron by 17%. These results confirm that the maximum rate of PTW dissolution during acid leaching occurs within the first 30 minutes of contact with sulfuric acid.

The mass of magnesium sulfate formed during the leaching of 100 g of PTW with sulfuric acid at 98 °C after 30 minutes was 168.65 g (containing 10.36% Mg, equivalent to 16.90 g), which corresponds to 70% of the theoretical yield. It is also notable that the yield of magnesium sulfate in the solution does not increase significantly beyond the 30–180-minute range (168.65, 168.90, 171.60, and 167.68 g).

Neutralization and purification of the productive sulfate solution using thermally activated PTW at 750°C. Under the same conditions, the leaching of PTW with sulfuric acid was conducted, but the leaching time was limited to 30 minutes. Upon completion of this step, 1.0 dm³ of distilled water was added to the acidic suspension. Thermally activated PTW (TA-PTW), previously heated at 750°C for one hour, was used as the neutralizing agent. At this temperature, the alkaline reactivity of the material is significantly enhanced due to internal structural transformations of the serpentinite, including the formation of periclase (Dikanbayeva et al. 2021; Yeskibayeva et al. 2024). Neutralization was carried out until the suspension reached a pH of 8.3. The resulting mixture was then filtered, and the solid residue was washed twice with 0.5 L of distilled water. It is noteworthy that at pH = 8.3, both filtration and washing were completed efficiently. The obtained filtrate was almost completely free of impurity metal ions, with the exception of trace amounts of calcium.

Table 3 presents the results of elemental analysis of both the filtrate and the solid residue after neutralization of the acidic suspension using thermally activated PTW (TA-PTW). The data reflect the composition of the purified productive magnesium sulfate solution and the remaining solid phase.

Table 3. Elemental analysis of the neutralized sulfate suspension at pH = 8.3: initial materials, filtrates after phase separation, and solid residue (OS)

Element	Initial materials		Neutral suspension		
	PTW	TA-PTW	Filtrate I	Filtrate II	Residue (OS)
C	2.58	2.54	—	—	9.35
O	51.00	45.22	59.90	61.90	48.55
Mg	25.00	27.89	16.60	15.64	11.91
Al	0.54	0.46	—	—	0.56
Si	17.45	19.17	—	—	23.60
S	—	—	23.50	22.21	0.43
Ca	0.50	0.53	—	0.25	0.30
Fe	2.93	4.19	—	—	5.30
Total	100.00	100.00	100.00	100.00	100.00

Note: “—” indicates values below the detection limit or not determined.

The yield of magnesium sulfate during the neutralization of the acidic PTW suspension using TA-750 reaches 46% of the total magnesium content in the initial materials (PTW and TA-PTW), while magnesium recovery relative to the amount of sulfuric acid used was approximately 100%.

The concentration of magnesium sulfate in the filtrate obtained after leaching the first portion of PTW (Filtrate I) was 243 g/L (24.3%). When a second, fresh portion of PTW was leached using this magnesium sulfate solution (with sulfuric acid concentration adjusted for repeated leaching), the concentration of magnesium sulfate in Filtrate II increases to 47—48%. Calcium remained in the final product at a concentration of 0.014—0.016% (see Table 3, residue—OS).

The solid residue obtained after neutralization of the acidic PTW suspension using TA-PTW contained the following elements: Mg = 11.91%, Al = 0.56%, Si = 23.56%, S = 0.43%, Ca = 0.30%, and Fe = 5.30%. These values suggest the potential reuse of the residue as a magnesium- and silicon-containing fertilizer for agricultural applications.

The use of TA-PTW as a neutralizing reagent offers several advantages over conventional reagents such as NaOH:

1. It additionally enriches the productive sulfate solution with magnesium due to acid—base interactions between TA-PTW and the acidic suspension;
2. It does not introduce any foreign elements into the sulfate system from external sources;
3. Owing to its specific structural and adsorptive properties, it ensures more efficient purification of the magnesium sulfate solution from impurity metal ions, except for a minor amount of calcium.

The production of magnesium sulfate heptahydrate using the described leaching (Figure 1), neutralization, and purification processes with TA-PTW enables the formation of high-purity $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$.

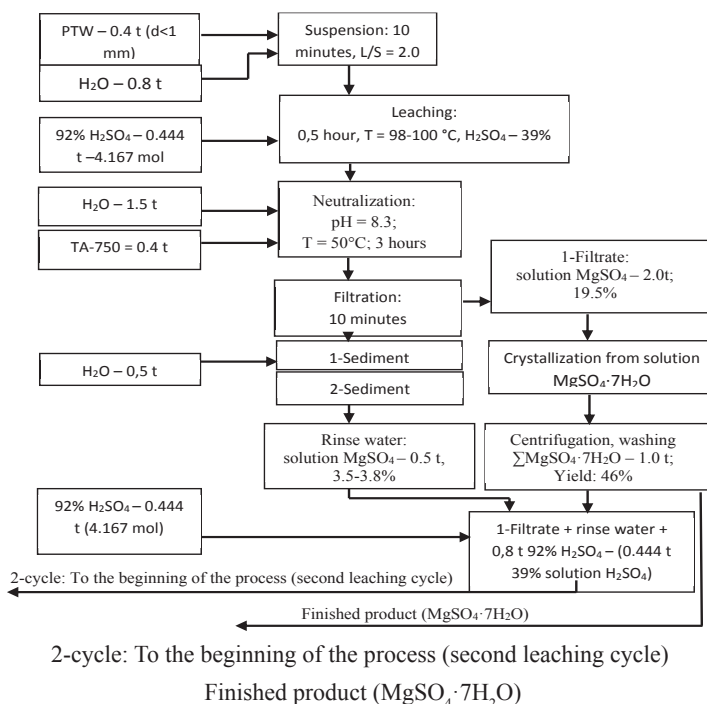


Figure 1 - Technological scheme for the production of magnesium sulfate heptahydrate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) from chrysotile processing waste (PTW)

Comparative analysis (Table 4) demonstrates that the purity characteristics of the synthesized magnesium sulfate comply with the requirements of GOST 4523-77, confirming its classification as a marketable product with established commercial value.

Table 4. Comparison of magnesium sulfate heptahydrate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) quality indicators with GOST 4523-77

No	Indicator	Norm		Experimentally obtained $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}^*$
		Chemically pure	Pure for analysis (h.d.a.)	
1	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (magnesium sulfate heptahydrate), %	99.5	99.5	99.5
2	Water-insoluble substances, %	0.00200	0.00200	0.00100
3	H_2SO_4 (acidity), %	0.00200	0.00200	–
4	MgO (alkalinity), %	0.00100	0.00100	0.00100
5	Cl (chlorides), %	0.00050	0.00200	–
6	NH_4 (ammonium salts), %	0.00100	0.00200	–
7	Fe (iron), %	0.00020	0.00030	0,00024
8	Ca (calcium), %	0.01000	0.02000	0.01400-0.01600
9	Mn (manganese), %	0.00050	0.00100	0.00070
10	As (arsenic), %	0.00004	0.00004	–
11	Pb (heavy metals), %	0.00010	0.00010	–
12	Zn (zinc), %	0.00100	0.00500	0.00020

Note: * — Analysis performed using Thermo Scientific iCAP-Q Mass Spectrometer.
 “–” indicates values below the detection limit or not determined.
 h.d.a., highly defined analytical.

Based on the scaled data from Table 3, the resource and energy efficiency of the proposed technology for producing 1.0 t of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ from PTW was assessed, considering only material and energy inputs and excluding capital and operational costs. The calculations were performed using average market prices for sulfuric acid and electricity tariffs in Kazakhstan in 2024 (0.065 \$/kWh) (Table 5).

Table 5. Resource and energy efficiency of the technology for producing commercial-grade magnesium sulfate heptahydrate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) from PTW (serpentine waste)

1) Specific consumption of raw materials and energy required to produce 1 ton of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$			
Resource type	Unit	Consumption per product	Role
PTW	tons	0.40	Raw material
TA-PTW		0.40	Raw material
Sulfuric acid (density = 1.824 g/cm ³)	tons	0.44	Reagent 1
Technical water	tons	2.80	Reagent 2
2) Specific consumption of raw materials and energy resources to produce 0.400 tons of TA- PTW			
Resource type	Unit	Consumption per product	Role
PTW	tons	0.46	Raw material
Electricity	kWh	92.40	Energy input
3) Resource and energy efficiency $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$			

Articles	Unit	Quantity	Price, \$/t	Price, \$
Income part				175.00
MgSO ₄ ·7H ₂ O	tons	1.00	175.00	175.00
Expenditure part				60.00
PTW	tons	0.46	3.00	1.40
TA- PTW	tons	0.40	3.00	1.20
Sulfuric acid (density=1.824 g/cm ³)	tons	0.44	100.00	44.40
Water (technical)	tons	2.80	1.00	2.80
Electricity (firing)	kWh	92.40	0.07	6.00

Note: Estimated based on average market prices for 2024 in Kazakhstan: sulfuric acid — \$100/t; technical water — \$1/t; electricity — \$0.07/kWh. Labor, depreciation, and overhead costs are not included.

Thus, the gross profit, excluding fixed costs, for the production of magnesium sulfate (MgSO₄·7H₂O) is \$115/t. The break-even price (P_{\min}) is \$60/t, and since $P_{\min} < \$175/t$, this indicates that magnesium sulfate production by this method is economically viable. From an economic perspective, the process demonstrates a sufficiently positive balance. Industrial production of magnesium sulfate heptahydrate (MgSO₄·7H₂O) is carried out using several technological routes, which differ both in terms of the raw materials employed and the associated cost structures. The most common approaches include: 1) extraction from natural kieserite/epsomite; 2) processing of magnesite/dolomite using sulfuric acid. Under typical prices for industrial H₂SO₄ and energy resources, the production costs via these conventional routes generally exceed those of direct processing of serpentinite waste, reaching approximately from 150 to 220 USD/t. Therefore, reducing the costs of raw materials (PTW) and the neutralizing agent (TA-PTW) represents a critical factor in enhancing the economic efficiency of the proposed technology.

Conclusions. The techno-economic study of the processes of sulfuric acid leaching of PTW using low-concentration sulfuric acid solutions and the neutralization of the resulting sulfate solution with thermally activated serpentinite waste (TA-PTW) demonstrates that this technology can achieve a total magnesium sulfate yield of 46% relative to the theoretical magnesium content in the raw serpentinite involved in the extraction processes, producing a commercial-quality product — MgSO₄·7H₂O.

The techno-economic indicators, determined based on calculations of material and energy consumption and the average market price of the product, show promisingly high values, confirming the resource and economic efficiency of the proposed magnesium sulfate production technology from PTW, as well as the feasibility of the repeated utilization of chrysotile-based technogenic waste.

Simple calculations show that 1.0 ton of PTW can yield magnesium sulfate (MgSO₄·7H₂O) products valued at \$175-200. At the same time, success from both technological and economic standpoints is ensured by the use of thermally activated PTW for the neutralizing and purifying the sulfate leaching solution. The rational use of sulfuric acid, which is the only consumable reagent, is an additional advantage in the process of producing magnesium sulfate from serpentinite waste.

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