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Obtaining Magnesium Chloride from Magnesium-Rich Deposits at the Karmana Serpentinite Site

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ABSTRACT: Magnesium oxides and salts play crucial roles in various industries such as chemical, agricultural, and metallurgical sectors for producing construction and polymer materials. The Republic of Uzbekistan hosts abundant magnesium-containing minerals within its territory, including ultrabasic rocks like dolomite and saponite group minerals. Despite these local resources, Uzbekistan predominantly relies on imports to meet its magnesium needs. Addressing this dependency by locally sourcing magnesium compounds has become a pressing issue in the country's market-driven economy.

Initial serpentinite samples from the Karmana deposit revealed approximately 30% magnesium oxide content. Mineral composition analysis identified various mineral associations such as antigorite, nepuine, franklinite, talc, and magnesite. Study of the mineral's properties focused on solubility dependencies related to particle size distribution and solvent characteristics. Physicochemical analysis highlighted the resilience of magnesium-silicate bonds within the mineral structure, which remain stable even at temperatures up to 800 °C. Research confirmed the feasibility of extracting magnesium oxide and silicon dioxide from serpentinite at the Karmana site.

KEY WORDS: serpentinite of the Karmana deposit, dissolution, hydrochloride, sulfuric acids, chrysotile, serpentine, antigorite, mineral composition, elemental composition, pH, density, ophite.

1. INTRODUCTION

Magnesium compounds play a vital role in the national economy, encompassing essential substances like magnesium oxide, magnesium chloride, magnesium carbonate, magnesium sulfate, and other related salts. These compounds are pivotal in various industrial applications such as binder production, petroleum refining, and as fillers in rubber manufacturing. Their high melting points make them indispensable in industrial cable insulation, as key components in refractory materials, and as raw materials for fired and fused powders and metallurgical fluxes. Magnesium oxide, known for its abrasive properties, finds frequent use in the electronics industry [1-2].

Agriculturally, magnesium oxide holds promise as a soil amendment, preventing fertilizer clumping and enriching soil independently. Addressing magnesium deficiencies in agricultural soils is critical for maximizing crop yields. Magnesium salts, particularly magnesium chloride, are crucial in the production of magnesium chlorate defoliants [4].

Currently, global efforts emphasize advancing technologies for extracting pure salts and magnesium oxides from abundant raw materials such as brines from salt lakes, seawater, and natural deposits [5].

The objective of this study is to explore the composition and fundamental properties of serpentinite minerals from the Karmana deposit, intended as feedstock for producing magnesium chlorate defoliants. A critical focus lies in developing a processing technology for extracting magnesium-containing salts from Karmana's serpentinite in Uzbekistan's Navoi region. This necessitates establishing several scientific approaches: devising an efficient method to

derive purified and concentrated magnesium chloride solutions from serpentinite, and producing chlorate-based defoliants using these solutions [5].

Objectives and methods of research revolve around serpentinite rock samples sourced from the Karmana deposit in the Navoi region, Uzbekistan. Sample preparation involved crushing using JC 6 jaw crushers and an ИBC-4 vibration grinder, achieving a particle size of 45 μm . Material classification utilized a Retsch AS-450 control sieve shaker.

Research methods employed included spectral analysis via CPM 20 and S-115 spectrometers, mass spectrometric analysis using an ICP-MS device, X-ray phase analysis conducted on a DROH-YM1 X-ray diffractometer with $\text{CoK}\alpha$ radiation and a shooting speed of $1^\circ/\text{min}$, and thermogravimetric analysis using a Setaram Lab Sys Evo derivatograph (France) within the temperature range (20-1200) $^\circ\text{C}$. Data processing and calculations were executed using MS Excel software. Semi-quantitative X-ray phase analysis employed the "Profex - Open source XRD and Reitveld Refinement" software, following the Rietveld method.

Results and discussion. To develop an efficient method for extracting purified magnesium chloride, extensive research was conducted on the mineral composition and geological attributes of serpentinite sourced from the Karmana deposit in the Navoi region of the Republic of Uzbekistan. The topographical positioning of the Karmana field is illustrated in Figure 1.

Serpentinite belongs to the serpentine group, comprising various magnesium hydrosilicates that share a similar composition but differ in their structural arrangements, including antigorite, chrysotile, and ophite. Serpentine is a prevalent mineral in many metamorphic rocks and forms the basis of the rock serpentinite. The serpentine group also encompasses nickel hydrosilicates such as garnierite and others. Serpentinite, characterized by its dense and soft nature, exhibits hues ranging from bluish-black to brownish and greenish, often displaying a distinctive flame-like structure. It is interspersed with veins and contains disseminated newly formed minerals.

Serpentinite (serpentine): Composition and origin of the rock Serpentine $(\text{Mg,Fe,Ni})_6\text{Si}_4\text{O}_{10}(\text{OH})_8$ (derived from the Latin *serpens* meaning "snake") is a compact rock formed through serpentinization, distinct from the mineral serpentine. Serpentine refers broadly to a group of hydrated layered magnesium silicates (including antigorite, chrysotile, lizardite, etc.) with the general formula $\text{Mg}_3[\text{Si}_2\text{O}_5](\text{OH})_4$.

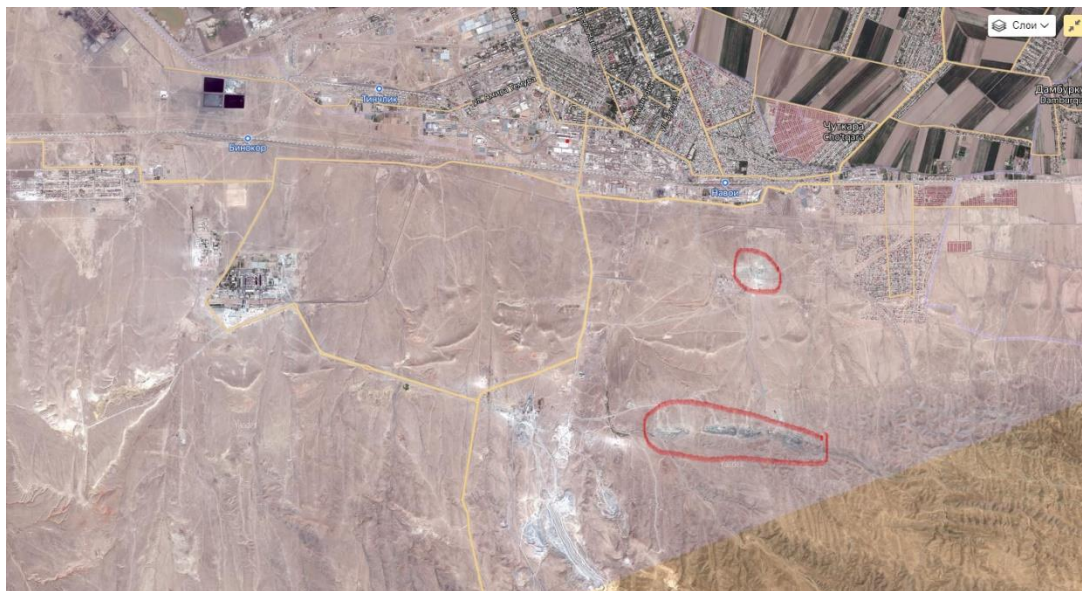


Fig. 1. Topographic map of the Karmana deposit [12].

Samples from the Karmana deposit underwent initial processing at the laboratory of the Navoi State Mining Institute. Following crushing, solid material was fashioned into tablets for subsequent X-ray phase analysis. Figure 2 displays the X-ray diffraction pattern obtained from these samples. The X-ray phase analysis (XRD) of serpentinite from the Karmana deposit encompassed both natural and cation-substituted forms using an X-ray diffractometer. The phase composition was determined in accordance with the ASTM card index.

X-ray investigations (Fig. 2) of Karmana serpentinites revealed a diverse array of minerals including apogarts, burgite serpentinites (with interplanar spacings of 0.375 nm, 0.253 nm, 0.246 nm), serpentinitized harzburgite - olivine

(0.276 nm, 0.247 nm, 0.176 nm), actinolite (0.273 nm, 0.145 nm, 0.844 nm), fine-grained magnetite (0.251 nm, 0.147 nm, 0.296 nm), and serpentinite itself constituting up to 65% (0.368 nm, 0.155 nm, 0.737 nm).

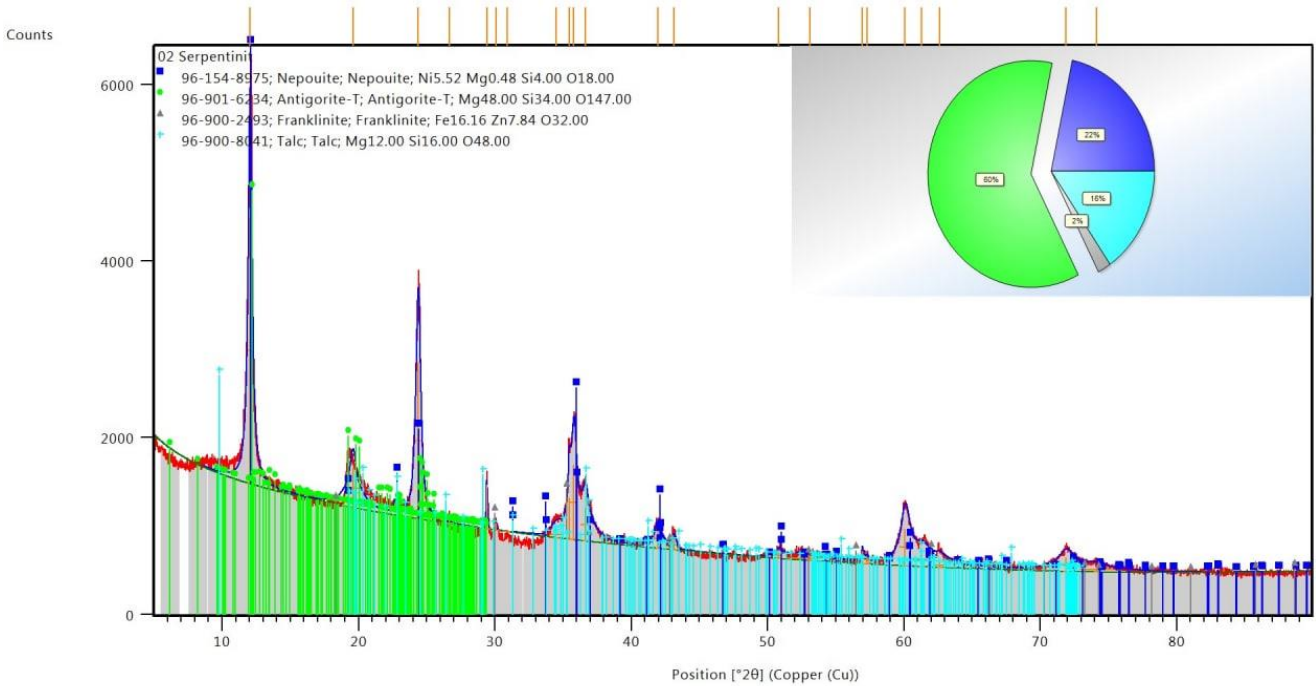


Fig. 2. X-ray diffraction pattern of serpentinite from the Karmana deposit

The findings from semi-quantitative X-ray phase analysis indicated that antigorite, comprising magnesium hydrosilicate, predominated quantitatively among the mineral associations.

Table 1.
Mineral composition of serpentinite, established by X-ray phase analysis

Mineral	Formula	m, % weight
Antigorite	$(Mg_8[Si_2O_3](OH)_4)$	60
Nepuit	$Ni_3(Si_2O_5)(OH)_4$	22
Franklinite	$(Zn, Mn)Fe_2O_4$	2
Talc	$(Mg_3Si_4O_{10}(OH)_2)$	15
Magnesite	$(MgCO_3)$	0,5-1,0

The presence of magnesium in the silicate form within antigorite underscores the challenge posed by heat treatment of serpentinite. Research [4] demonstrates the remarkable strength of magnesium-silicate bonds, which endure temperatures up to 800 °C without decomposition. As a result, a more efficient approach involves acid treatment of unbound raw materials to address magnesium-silicate bonds.

To elucidate the functional relationships among the elemental constituents present in the samples under study, the IR spectrum of serpentinite sourced from the Karmana deposit was analyzed (Fig. 3).

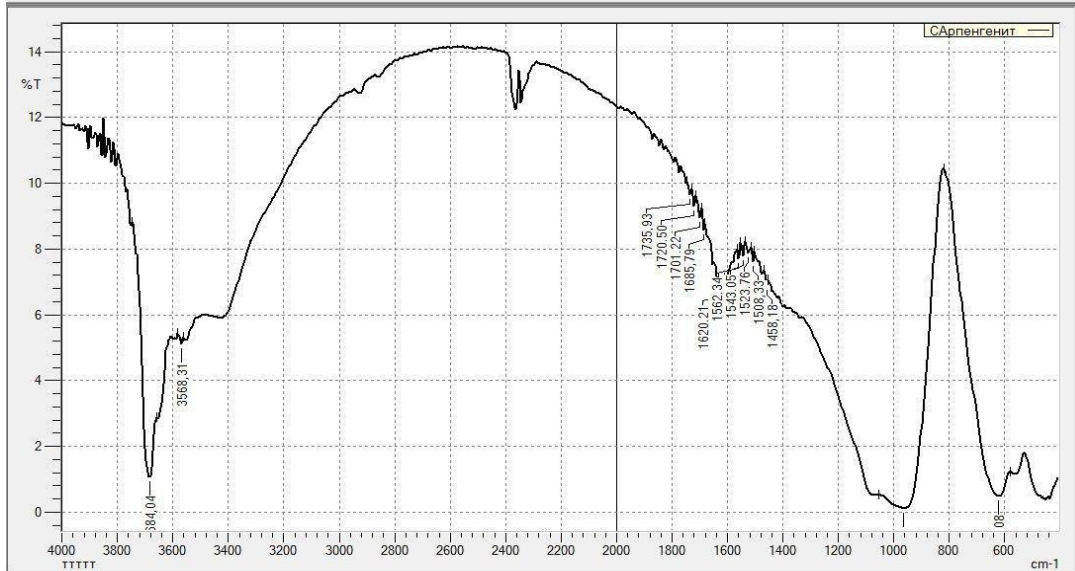


Fig. 3. IR- spectra of serpentinite from Karmana deposit

The initial serpentinite spectrum exhibits absorption bands attributed to SiO_4^{4-} in the wavelength range of 3660, 3640, and 3440 cm^{-1} , corresponding to functional groups $\text{V}(\text{OH}^{-1})$ and $\text{V}(\text{H}_2\text{O})$. Bending vibrations of hydroxide ions were detected at 1410 and 1620 cm^{-1} , respectively. Additionally, an absorption band M-OH appeared at 600 cm^{-1} . The presence of the SiO_4^{4-} functional group is confirmed by the triple degenerate antisymmetric stretching vibration band of SiO_4^{4-} in the 1065-950 cm^{-1} range (V_{ac}^{-2}) and bending vibration at approximately 625 cm^{-1} .

To elucidate the roasting process of serpentinite from the Karmana deposit, a derivatogram was obtained under the following conditions: substance weight of 398 g; DTA - 1/10, DTG - 1/10, TG - 200 mg; $T = 800^\circ\text{C}$, heating rate 10 $^\circ\text{C}/\text{min}$. The DTA curve revealed three endothermic effects at 415, 580, and 695 $^\circ\text{C}$, with one exothermic effect observed at 825 $^\circ\text{C}$. Overall, the total weight loss amounted to 14.6% (Fig. 4).

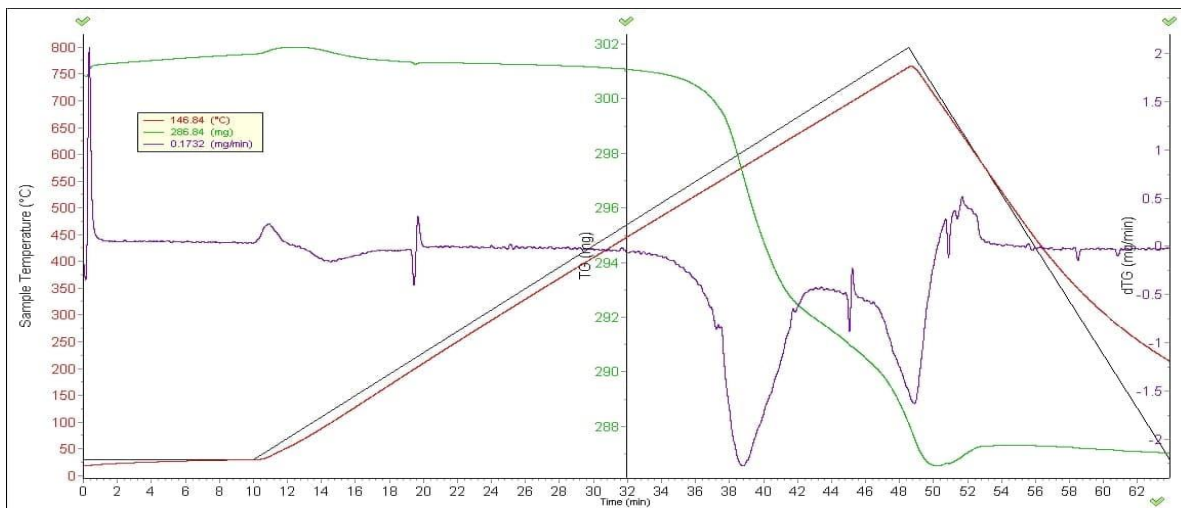


Fig. 4. Differential thermal analysis (DTA) of serpentinite from Karmana deposit

To interpret the derivatogram, the initial material underwent heating from 20 $^\circ\text{C}$ to 800 $^\circ\text{C}$. It was observed that during thermal treatment, the intermediate phases of the serpentinite mineral sample primarily consisted of $\text{Mg}_3[\text{Si}_2\text{O}_5](\text{OH})_4$. At 800 $^\circ\text{C}$, the substance exhibited a brownish color and transformed into magnesium orthosilicate Mg_2SiO_4 . Other accompanying compounds in the mineral composition decomposed under heat, transitioning into an unstable form that eventually became amorphous.

In this experimental setup, the conversion of sodium hypochlorite with a solution of magnesium chloride derived from Karmana serpentinite proceeded as follows: Initially, a 500 cm³ tube equipped with a sensor thermoconductor was connected to a mixer. The flask contained 20 g of magnesium chloride salt mixed with an equal amount of sodium hypochlorite. The tube was placed in a thermostat set at a specific temperature and vigorously stirred.

The chemical reactions involved were:



The resulting magnesium hypochlorite was filtered, and magnesium chlorate was obtained through repeated heating of the solution at 70-90°C for 40-50 minutes.



II. CONCLUSION

The composition and characteristics of serpentinite samples from the Karmaninskoye deposit were investigated using a comprehensive suite of applied physicochemical analytical methods. This study identified the principal rock-forming minerals: antigorite ($\text{Mg}_8[\text{Si}_2\text{O}_3](\text{OH})_4$) comprising 60%, nepuite $\text{Ni}_3(\text{Si}_2\text{O}_5)(\text{OH})_4$ at 22%, franklinite ($\text{Zn}, \text{Mn})\text{Fe}_2\text{O}_4$) at 2%, talc ($\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$) at 15%, and trace amounts of magnesite (MgCO_3) at 0.5-1% or magnetite ($\text{FeO}\cdot\text{Fe}_2\text{O}_3$) with microinclusions of chromite (FeCr_2O_4).

Differential thermal, X-ray, and IR spectroscopic analyses of the serpentinite samples revealed that impurities were separated during calcination through exhaust gases. Analysis indicated that the initial samples contained approximately 30% magnesium oxide. Solubility studies showed variation depending on particle size and solvent properties. Physicochemical analyses demonstrated that acid decomposition is an effective method for breaking down magnesium-silicate bonds, previously considered stable even at 800°C.

Preliminary investigations of serpentinites from the Karmana deposit suggest their potential not only for manufacturing heat-resistant ceramics and insulating building materials in their natural state but also as raw materials for producing magnesium chlorate. Magnesium chlorate, a hygroscopic powder, serves as a defoliant in agricultural practices, specifically for pre-harvest removal of cotton leaves during mechanical cotton harvesting.

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