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Arailym Mukangaliyeva
Satbayev University, Institute of Metallurgy and
Ore Beneficiation JSC, Almaty 050013, Kazakhstan
E-mail: 000316650668-D@stud.satbayev.university
ORCID ID: https://orcid.org/0000-0001-7032-1764

Almagul Ultarakova
Satbayev University, Institute of Metallurgy and
Ore Beneficiation JSC, Almaty 050013, Kazakhstan
E-mail: a.ultarakova@satbayev.university
ORCID ID: https://orcid.org/0000-0001-9428-8508

Azamat Yessengaziyev
Satbayev University, Institute of Metallurgy and
Ore Beneficiation JSC, Almaty, Kazakhstan
E-mail: a.yessengaziyev@satbayev.university
ORCID ID: https://orcid.org/0000-0002-4989-4119

Rinat Abdulvaliyev
Satbayev University, Institute of Metallurgy and
Ore Beneficiation JSC, Almaty 050013, Kazakhstan
E-mail: rin-abd@mail.ru
ORCID ID: https://orcid.org/0000-0001-6747-6984

Nina Lokhova
Satbayev University, Institute of Metallurgy and
Ore Beneficiation JSC, Almaty 050013, Kazakhstan
E-mail: n.lokhova@satbayev.university
ORCID ID: https://orcid.org/0000-0001-9436-5462

Kaisar Kassymzhanov
Satbayev University, Institute of Metallurgy and
Ore Beneficiation JSC, Almaty 050013, Kazakhstan
E-mail: k.kassymzhanov@satbayev.university
ORCID ID: https://orcid.org/0000-0001-8062-8655

Solubility of Alkali Metals in Natural Resources and Industrial Wastes: A Study of Dead Sea Salts and Titanium-Magnesium Byproducts

Abstract: This study investigates the solubility of alkali metal chlorides (KCl, NaCl) and magnesium chloride in a $KCl–NaCl–MgCl_2–H_2O$ system under varying temperatures. Experimental results show a 4% increase in the solubility of potassium and sodium chlorides and a 15% increase in magnesium chloride solubility between 25°C and 65°C. The study also explores the partial separation of magnesium at lower temperatures, contributing to advancements in waste processing technologies in chemical and metallurgical industries.

Keywords: Solubility, alkali metal chlorides, magnesium separation, technogenic waste, $KCl–NaCl–MgCl_2$ system.

Introduction

The extraction and processing of titanium and magnesium production waste have garnered increasing attention due to the potential recovery of valuable metals, particularly rare and rare earth elements. Mamutova et al. (2018) highlighted the pressing need for innovative solutions to manage chloride waste generated during titanium-magnesium production, suggesting various processing techniques to mitigate environmental impacts and recover useful materials. Building on this foundation, Toishybek et al. (2023) conducted a comprehensive review of recovery technologies for rare and rare earth metals derived from the same industrial waste. Their findings emphasized the importance of developing efficient recovery methods to enhance resource sustainability and reduce the ecological footprint of titanium and magnesium production. Moreover, Kenzhaliyev (2019) explored innovative technologies aimed at improving the extraction processes for non-ferrous, precious, and rare metals, underlining that advancements in technology are crucial for maximizing resource recovery. The evolution of these techniques is vital, especially as industries face increasing pressure to minimize waste and enhance the circular economy. In the context of specific metal recovery, Baigenzhenov et al. (2024) focused on scandium extraction from secondary raw materials, providing insights into the methodologies employed and their efficiency. Their overview of extraction technologies reveals the potential for reclaiming valuable materials from waste streams, further supporting the idea that waste can be transformed into a resource. Collectively, these studies underscore the critical need for continued research and development in waste processing and metal recovery technologies, particularly in the titanium and magnesium sectors. By implementing innovative approaches, industries can not only reduce environmental impact but also contribute to a more sustainable future.

In modern industry, a wide range of mineral salts of alkali metals and pure metals, particularly lithium, sodium, and potassium, are extensively utilized, each playing a critically important role in various sectors, including nuclear energy, chemical production, and renewable energy technologies. Lithium, in particular, occupies a central position in nuclear technologies due to its isotope ^{6}Li, which is employed in neutron reactions for tritium production—a key component in thermonuclear reactions:

$$^{6}_{3}Li + ^{1}_{0}n = ^{3}_{1}H + ^{4}_{2}He \qquad (1)$$

This process not only facilitates tritium generation but also underscores lithium's importance in regulating neutron flux and as a coolant in uranium reactors. Beyond the nuclear domain, lithium finds broad application in the production of lithium-ion batteries for electronics and electric vehicles, as well as in the aerospace industry and medicine as a mood stabilizer (Yoo et al., 2023). Sodium is used as a highly efficient coolant in nuclear reactors, both in its pure form and in alloys with potassium. In the chemical industry, sodium is essential for rubber synthesis and is a crucial component in the production of glass, paper, textiles, and cleaning agents. Sodium vapour lamps, employed in street lighting, demonstrate their importance in energy technologies (Sujit et al., 2022) Potassium, as an element, is indispensable in geochemistry for fertilizer production (Ahmed et al., 2023) Industrially, it is used to obtain potassium peroxide (K_2O_2) by Anil et al. (2022), which is applied for oxygen regeneration in closed systems such as submarines and space stations (John et al.,2008). Potassium also serves as an important catalyst in synthetic rubber production and is used in soap manufacturing and as a coolant in nuclear reactors (Jianwei et al., 2022).

Thus, the role of alkali metals in modern industry is undeniably significant, as they serve as key elements in numerous critically important technological processes, ranging from energy production to the manufacture of everyday consumer goods. Research continues in contemporary industry, focusing on the effects of sodium and potassium hydroxides on the properties and technological processes associated with the use of chemical compounds. Special attention is given to the impact of these alkali metals on the technological parameters of mineral extraction and their application in the creation of geopolymer backfills, which facilitate processes in the mining industry by optimizing the properties of the materials used (Noureddine et al., 2020).

Studies demonstrate that alkali metals enhance the catalytic properties of Fe-Co compounds by increasing the dispersion of active sites, thus promoting the transition from disordered carbon to more ordered forms and removing oxygen-containing functional groups such as O-H. This leads to increased CO_2 output and effectively aids in methane splitting and dehydrogenation of organic compounds, thereby boosting hydrogen yield. In this context, the activity of Na surpasses that of K (Deng et al., 2023).

It was also found that the treatment of cellulose with sodium and potassium hydroxides significantly affects its crystallinity, opening new opportunities for its use in fields such as emulsion stabilization (Wang et al., 2023).

The main part of the research

Materials. The studied samples were provided by Ust-Kamenogorsk Titanium and Magnesium Plant JSC (Ultarakova et al., 2013). The above analysis data confirm the content of controlled components in significant concentrations (Table 1).

Table 1. The content of controlled components, %

Products	*Rb	*Li	Na	K	Mg	Cl
Carnallite	н.о	20	1.13	7.86	8.07	35.62
Spent melt of titanium chlorinators (SMTC)	270	48	0.75	11.09	4.38	41.67
Smelter sludge	90	16	0.82	4.18	18.51	21.40

*The contents of Rb and Li are given in ppm

Methods of Analysis. X-ray diffraction (XRD) analysis of the sludge was performed using a D8 Advance diffractometer (BRUKER) with Cu-Kα radiation. The processing of the obtained diffractograms and the calculation of interplanar spacings were conducted using EVA software. Sample interpretation and phase identification were carried out through the Search/Match program, utilizing the ASTM card database. X-ray fluorescence (XRF) analysis was performed on a Venus 200 wavelength-dispersive spectrometer (PANalytical B.V., Netherlands).

Chemical analysis of the samples was conducted using an Optima 2000 DV inductively coupled plasma optical emission spectrometer (USA, Perkin Elmer). Mineralogical analysis was carried out using an OLYMPUS BX51 microscope (Japan).

Results and discussions

According to the mineralogical analysis of samples 114, 117, and 119, the carnallite supplied to JSC "UKTMK" in an anhydrous state gradually transitions into a crystalline hydrate during prolonged storage. The examined sample contains the mineral carnallite, with the chemical formula $KMgCl_3 \cdot 6H_2O$ (Fig. 1). Carnallite is characterized by an orthorhombic crystal system, which defines its crystalline structure.

The crystals of carnallite take the form of hexagonal pyramids, a typical morphological feature of this mineral. Carnallite ($KMgCl_3 \cdot 6H_2O$) crystallizes in the orthorhombic system, indicating its three-axis symmetry with orthogonal axes of varying lengths. This crystal system defines the specific form of the crystals, which, in this case, are represented by hexagonal pyramids. The absence of well-defined cleavage indicates high structural integrity of the carnallite crystals, reducing the likelihood of fracture along certain planes under mechanical stress.

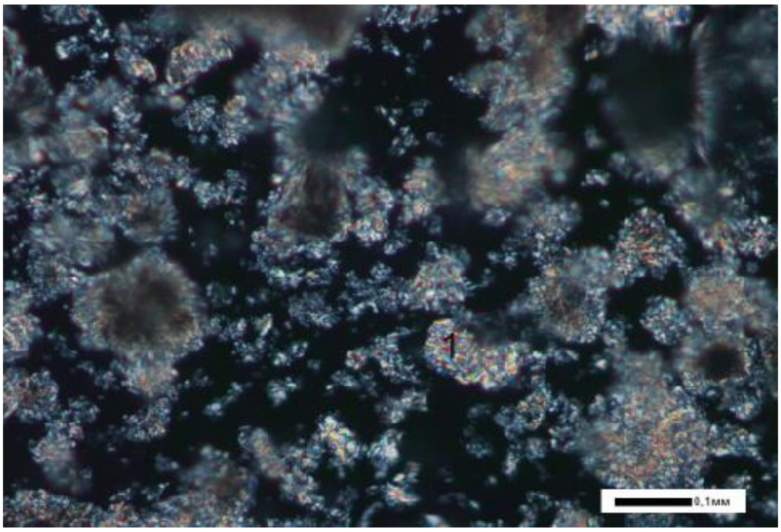

Figure 1. Micrograph of a mineralogical sample of carnallite. Uv.100, nick$^+$

In the analysis of the smelter sludge, two main phases were identified: periclase (MgO) and sylvite (KCl) (Fig. 2). Below are detailed characteristics of these phases, illustrating their crystalline and optical properties.

MgO (Periclase) – Cubic crystal system. Isotropic, colorless. Refractive indices: n=1.7335C, 1.7366D, 1.7475F. Periclase is a mineral with a cubic crystal system and isotropic properties, meaning its optical properties are uniform in all directions, as indicated by its constant refractive index across various wavelengths of light. Periclase is notable for its high refractive indices and absolute isotropy, making it an important material in various technological processes.

KCl (Sylvite) – Cubic crystal system. Cubic crystals with perfect cleavage along the cube. Isotropic, colorless or tinted. Refractive indices: n=1.4872C, 1.4904D, 1.4984F. Sylvite is also characterized by a cubic crystal system and isotropic properties. The cubic crystalline structure provides perfect cleavage along the cube, a key feature for identifying and practically applying this mineral. The refractive indices of sylvite are slightly lower than those of periclase, which is also important to consider in its study and use. Sylvite, with its perfect cleavage and characteristic optical properties, plays a crucial role in industry.

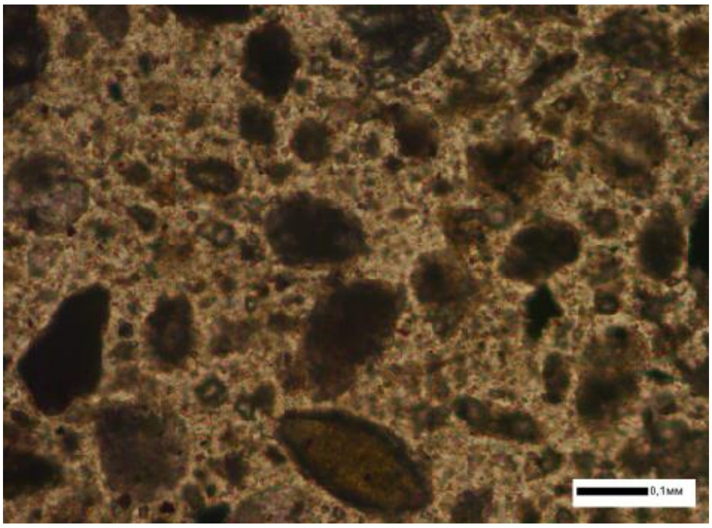

Figure 2. Micrography of a mineralogical sample of the smelter sludge. Uv.100, without analyzer

In the examined sample of (SMTC), two main phases were identified: halite (NaCl) and erythrosiderite ($K_2FeCl_5 \cdot H_2O$) (Fig. 3). These phases differ in their crystalline structure and optical properties, which play an important role in their identification and understanding of their behavior under various conditions.

NaCl (Halite) – Cubic crystal system. Cubic crystals with perfect cleavage along the cube. Isotropic, colorless, or tinted. Refractive indices: n=1.5407C, 1.5443 D, 1.5534F. Halite, also known as rock salt, has a cubic crystal system and isotropic properties, meaning its optical characteristics are the same in all directions. Halite crystals are typically colorless but may be tinted depending on the presence of impurities. The perfect cleavage along the cube is a distinctive feature of halite, making it easily identifiable in both fieldwork and laboratory studies.

$K_2FeCl_5 \cdot H_2O$ (Erythrosiderite) – Orthorhombic crystal system. Perfect cleavage. Refractive indices: Np=1.715, Nm=1.75, Ng=1.8. Color ranges from ruby red to brownish-red. Erythrosiderite is characterized by an orthorhombic crystal system and perfect cleavage. Its optical properties are anisotropic, meaning its refractive indices vary depending on the direction (Np, Nm, Ng). The color of erythrosiderite ranges from ruby red to brownish-red, which is one of the key features for its visual identification.

The phase composition analysis of (SMTC) revealed the presence of halite and erythrosiderite, each possessing unique crystalline and optical properties. Halite is distinguished by its isotropy and perfect cubic cleavage, making it an easily recognizable mineral. Erythrosiderite, with its orthorhombic system and anisotropic optical properties, requires more detailed analysis for precise identification.

These findings are important for understanding the chemical and mineralogical composition of ORTH and can be valuable for further research and application in various technological processes.

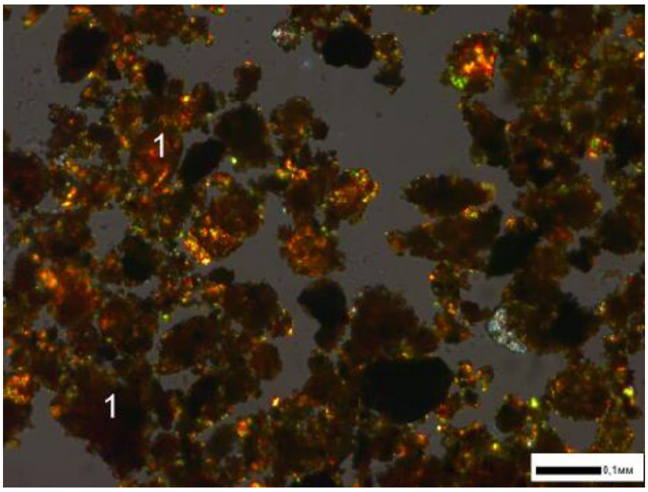

Figure 3. Micrography of a mineralogical sample (SMTC). Erythrosiderite. Uv.100, nick$^+$

To clarify the composition of the studied products, their X-ray phase analysis was carried out (Fig. 4,5,6)

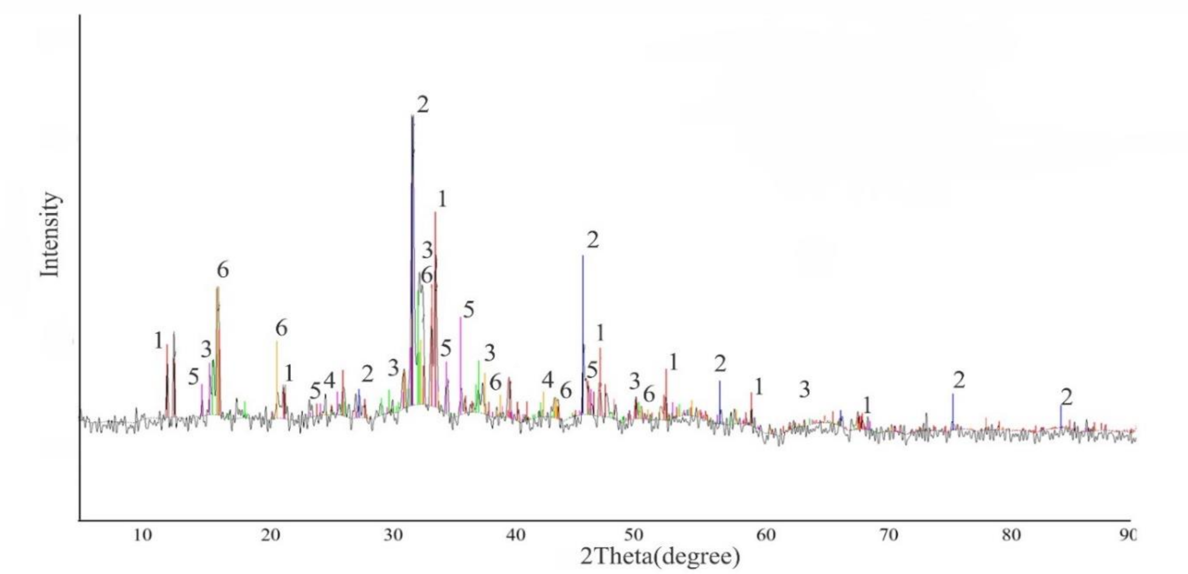

Figure 4. Diffractogram of the carnallite sample

Table 2. Results of X-ray phase analysis of carnallite

Number	Name of the compound	Formula	Content, rel. %
1	Carnallite	$KMgCl_3 \cdot 6H_2O$	45.9
2	Halite, syn	$NaCl$	21.2
3	Sylvite, syn	KCl	19.6
4	Magnesium Oxide	MgO	5.8
5	Magnesium Peroxide	MgO_2	4.1
6	Chlorartinite, syn	$(Mg_2(CO_3)(H_2O)(OH))Cl(H_2O)_2$	3.4

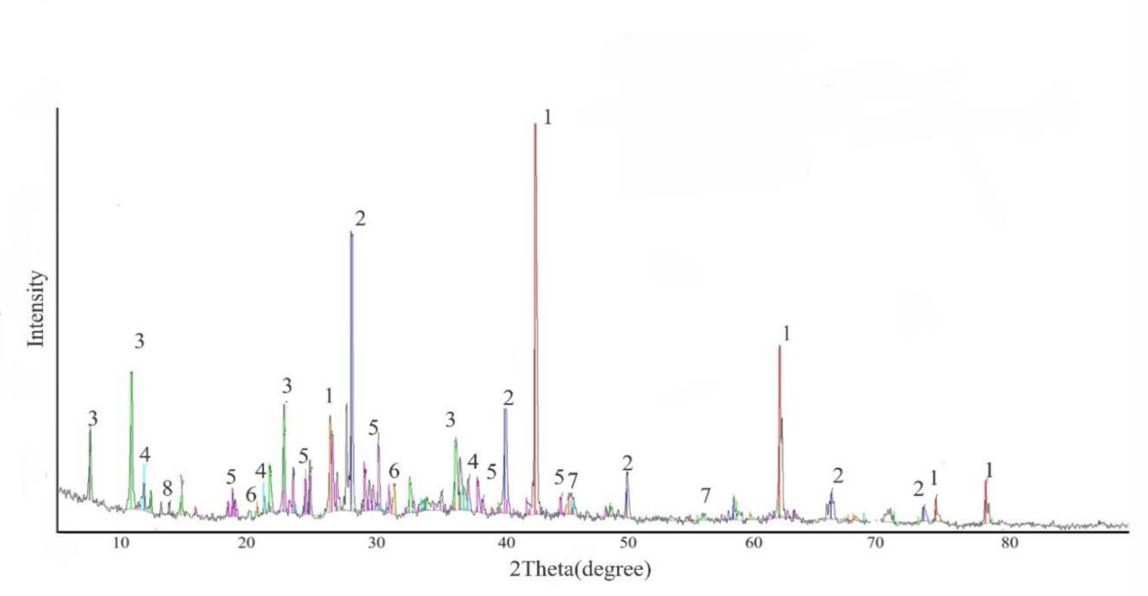

Figure 5. Diffractogram of the smelter sludge sample

Table 3. Results of X-ray phase analysis of the smelter sludge

Phase number	Compound name	Formula	Content, rel. %
1	Periclase, syn	MgO	41.6
2	Sylvite, syn	KCl	27.0
3	Korshunovskite, syn	$Mg_2(OH)_3Cl \cdot 4H_2O$	12.9
4	Carnallite	$KMgCl_3 \cdot 6H_2O$	6.7
5	Magnesium Aqua Chloride Hydroxide Hydrate	$(Mg_3(OH)_5(H_2O)_3Cl)H_2O$	4.3
6	Quartz, syn	SiO_2	2.6
7	Titanium Oxide	TiO_2	2.2
8	Halite, syn	$NaCl$	2.6

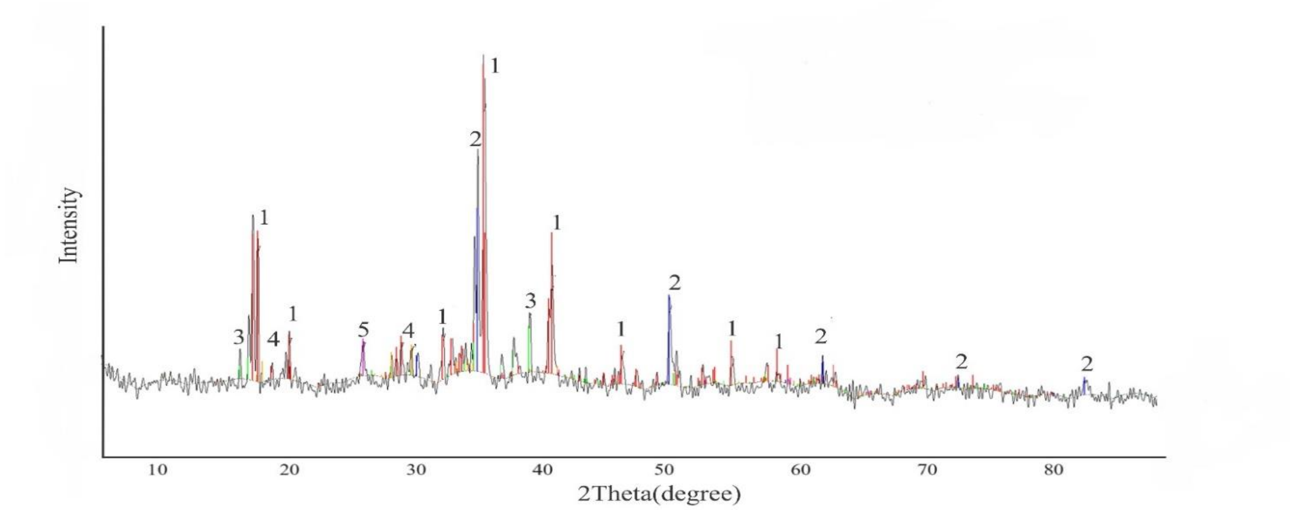

Figure 6. Diffractogram of the (SMTC) sample

According to X-ray phase analysis, the sludge of the smelter includes potassium and sodium chlorides, and potassium is partially bound into carnallite.

The NUT contains highly soluble potassium and sodium chlorides in comparable amounts.

It should be noted that when SMTC is dissolved in water, a certain amount of iron and magnesium will enter the solution.

Table 4. Results of SMTC X-ray phase analysis

Phase number	Compound name	Formula	Content, rel. %
1	Erythrosiderite, syn	$K_2(FeCl_5(H_2O))$	60.0
2	Halite, syn	$NaCl$	15.8
3	Saltonseaite	$K_3NaMnCl_6$	8.9
4	Potassium Iron Silicate	$K(FeSi_2O_6)$	8.1
5	Bernalite	$Fe^{+3}(OH)_3$	7.2

Conclusions

This study on the solubility of chloride salts of alkali metals and magnesium in the KCl – NaCl – $MgCl_2$ – H_2O system under varying temperatures has revealed key findings. The solubility of potassium and sodium chlorides increased by only 4% between 25°C and 65°C, while magnesium chloride's solubility rose by 15%, highlighting differing behaviours. A novel method for partial separation of magnesium from potassium and sodium chlorides at lower temperatures was developed, which could optimize industrial processes in the chemical and metallurgical sectors. The phase analysis identified crucial minerals like carnallite, halite, and erythrosiderite, contributing to the understanding of these compounds during processing. The research offers practical solutions for improving resource extraction from industrial waste, aligning with sustainable practices, and lays a foundation for further technological advancements.

***CRediT author statement*: R.Abdulvaliyev:** Conceptualization, Methodology, Software. **A. Ultarakova:** Data curation, Writing draft preparation. **A. Mukangaliyeva:** Visualization, Investigation. **A. Yessengaziyev:** Supervision. **N. Lokhova:** Software, Validation. **K. Kassymzhanov**: Reviewing and Editing

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