



Effect of Production Conditions on Composition and Properties of Phosphating Solutions Based on Kazakhstan Ore Dressing Wastes

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Abstract

The material and phase composition of manganese ore-processing waste from the Altyn-Shoko deposit were comprehensively analyzed, and the optimal conditions for producing phosphating solutions from this technogenic material were established. Phosphate coatings formed on St3 carbon steel using these synthesized solutions were evaluated using gravimetric corrosion tests, electrochemical measurements, and Scanning Electron Microscopy (SEM) – Energy-Dispersive X-ray Spectroscopy (EDS) analyses. Mechanical activation of the waste, intended to break down mineral aggregates, increased the phosphoric acid leaching efficiency at 25 °C from 66.9% to 72.9% but simultaneously reduced the free H₃PO₄ content in the solution. Although this treatment improved dissolution, it also accelerated sludge formation during phosphating and decreased the corrosion resistance of the resulting coatings. In contrast, phosphating solutions prepared from non-activated waste produced uniform, dense, and compact phosphate layers composed of iron, calcium, manganese, and phosphorus compounds, yielding superior protective performance. Coatings derived from mechanically activated waste were more porous and consisted mainly of iron–calcium–phosphate phases, which correlated with their reduced barrier properties. Overall, the results demonstrate the potential of Altyn-Shoko beneficiation waste as a sustainable feedstock for low-cost phosphating solutions while highlighting the limitations introduced by mechanical activation.

Keywords: Beneficiation waste; Phosphating solutions; Phosphating process; Phosphate coatings; Corrosion protection.

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1. Introduction

The annual extraction of minerals in the Republic of Kazakhstan amounts to millions of tons and is inevitably accompanied by the generation of large volumes of waste, including overburden rocks and ore-processing residues, which form significant technogenic mineral accumulations. Although certain mining enterprises have initiated efforts to utilize part of this waste for producing construction materials, a substantial proportion is still disposed of on the surface, in tailings ponds, and in landfills (Fig. 1), occupying vast land areas and contributing to environmental pollution.^[1] At the same time, these waste materials contain valuable mineral components and can therefore be considered as secondary raw materials. A promising approach to the valorization of mining

waste is the development of technological processes for converting it, directly during deposit exploitation, into inorganic products such as long-acting phosphorus fertilizers enriched with micronutrients or materials suitable for forming protective anti-corrosion coatings on metals.

Currently, numerous methods exist for the corrosion protection of metals, particularly low-carbon steel, which remains the most widely used structural material across various industries.^[2,3] Among these methods, surface coatings are the most commonly applied and include paint coatings,^[4–6] polymer coatings,^[7–11] and inorganic coatings.^[12–16] However, paint and polymer-based organic coatings often require toxic solvents that negatively impact the environment. Under modern environmental and industrial requirements, inorganic anti-corrosion coatings, especially conversion phosphate coatings, are considered the most rational and promising solution. Protective phosphate coatings on carbon steel can be produced in two main ways: (i) phosphating using concentrated solutions of phosphate salts,^[17] or (ii) using low-concentration phosphate solutions that act as corrosion inhibitors in aqueous environments where metal structures

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operate.^[18]

Depending on the structure of the resulting layer, phosphating processes yield either amorphous or crystalline phosphate coatings.^[19,20] Treatment with acidic salts of orthophosphoric acid and monovalent metals typically forms an amorphous phosphate conversion layer consisting mainly of metal phosphates derived from the steel substrate, such as iron phosphates. In contrast, phosphating with salts of zinc, manganese, or nickel produces crystalline coatings predominantly composed of the corresponding metal phosphates.^[21–24] Although crystalline coatings generally demonstrate superior protective properties, their production is more expensive due to the need for high-purity technical salts of zinc, manganese, and other metals. In this context, research aimed at obtaining manganese-containing phosphating solutions from technogenic raw materials, particularly waste generated during manganese ore processing, is of practical importance.

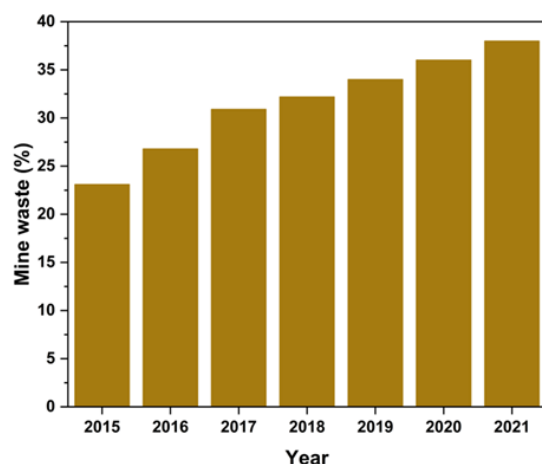


Fig. 1: Current situation in industrial waste management.

Kazakhstan has a well-developed industrial sector for the extraction and processing of manganese ores. These ores typically contain low levels of phosphorus and sulfur and virtually no arsenic or antimony, which ensures stable demand for Kazakhstani manganese products in global markets and supports continued growth in ore production.^[25–27] As ore extraction increases, the volume of processing waste correspondingly rises. Gravity separation is the primary beneficiation method used in local processing plants, resulting in substantial manganese losses into fine fractions that accumulate in tailings ponds and landfills without further utilization.^[28–30]

This work aims to evaluate the possibility of converting manganese ore enrichment waste from selected deposits in Kazakhstan into phosphating solutions and to assess their suitability for producing anti-corrosion phosphate coatings on low-carbon steel. The study focuses on determining optimal phosphating solution compositions, establishing appropriate preparation conditions, and evaluating the protective performance of the resulting phosphate coatings. Through this investigation, we aim to provide useful insights into the

practical application of phosphating solutions derived from manganese ore processing waste. Overall, this research contributes to the sustainable valorization of mining waste by developing technological approaches for transforming manganese-containing tailings into effective, low-cost phosphating solutions for producing anti-corrosion coatings on steel products.

2. Materials and methods

2.1 Preparation of steel samples

Phosphating experiments were carried out on carbon steel (grade St3) samples with the following chemical composition (wt.%): 0.12 C, 0.20 Cr, 0.17 Mn, 0.025 P, 0.17 Si, 0.018 S, 0.25 Ni, 0.25 Cu, and the remainder Fe. The samples were cut into plates measuring $20 \times 50 \times 1$ mm. Prior to phosphating, all specimens were mechanically polished with fine-grit sandpaper, degreased with ethyl alcohol, rinsed with distilled water, and dried in a desiccator containing calcined calcium chloride to constant weight.^[31] The initial mass of each sample was determined using a high-precision analytical balance (accuracy ± 0.1 mg), and the surface area was measured geometrically. All experiments were performed in triplicate to ensure reproducibility.

2.2 Phosphating process and coating evaluation

Phosphating was performed using solutions prepared from leached manganese ore beneficiation waste under optimized conditions. The corrosion resistance of the resulting phosphate coatings was assessed gravimetrically, by monitoring mass loss in accordance with standard corrosion-testing protocols.^[32] The test measured the deterioration of the coating under exposure to a corrosive medium over time. Electrochemical measurements were conducted in a custom-designed corrosion cell to ensure experimental reproducibility and minimize external interference. The working electrode consisted of either an uncoated or phosphate-coated St3 steel sample, mounted at the cell base such that the exposed area was confined by a circular gasket (diameter (14 mm) and area (1.54 cm^2)). Only this exposed portion was in contact with the electrolyte, while the remaining surface was isolated. The electrolyte was untreated tap water, used without additional mineralization or neutralization. All measurements were carried out under natural aeration at room temperature ($20\text{--}25^\circ\text{C}$). The electrochemical setup included a working electrode (St3), a silver/silver chloride reference electrode (Ag/AgCl, 3 M KCl), and a vertically positioned graphite counter electrode. Before polarization testing, the coated specimens were immersed in the electrolyte for 5 h to stabilize the open-circuit corrosion potential (E_{corr}) and minimize transient surface effects. Linear potentiodynamic scans were then conducted within ± 150 mV of E_{corr} at a potential sweep rate of 0.5 mV s^{-1} , starting from the cathodic direction.

2.3 Characterization of materials

The elemental and phase compositions of manganese ore

beneficiation waste from the Altyn-Shoko deposit, along with its derived products, were characterized using a multifunctional, high-performance energy-dispersive X-ray fluorescence spectrometer (EDXRF, NEX CG, Rigaku, Japan). The textural and structural features of the waste were investigated on polished artificial briquettes (anschliffs) and glifs prepared for optical analysis under a microscope (OLYMPUS BX-51, Japan). To fabricate these briquettes, the crushed manganese waste was washed, dried, and uniformly blended with epoxy resin. The mixture was cast into 1 cm³ molds, hardened, and subsequently polished to obtain a smooth, reflective surface suitable for detailed microscopic examination. The morphology and microstructure of the resulting phosphate coatings were further explored using a scanning electron microscope (SEM, HITACHI TM3030, Japan) equipped with a Bruker XFlash MIN-SVE energy-dispersive spectroscopy (EDS) detector. The accelerating voltage was varied up to 15 kV, and micrographs were acquired at magnifications reaching 1500×. Elemental composition and spatial distribution were determined through EDS mapping, complemented by X-ray fluorescence mapping to reveal the uniformity and dispersion of Fe, Ca, P, and Mn across the coating surface. The crystalline phase composition of the samples was identified by X-ray diffraction (XRD) using an automated diffractometer (DRON-3, Russia) operating with CuK α radiation ($\lambda = 1.5406 \text{ \AA}$) and a nickel β -filter. Diffraction data were collected under the following conditions: 35 kV accelerating voltage, 20 mA current, 2000-impulse scale, 2 s time constant, θ – 2θ scanning mode, and a detector speed of 2° min^{-1} . Semi-quantitative phase analysis was carried out using the equal-sample and artificial-mixture methods, and the quantitative proportions of crystalline phases were established by correlating experimental diffraction peaks with reference data from the ICDD PDF-2 (Powder Diffraction File) database and standards of impurity-free minerals.

3. Results and discussion

The beneficiation waste used in this study originates from the enrichment of manganese ores from the Altyn-Shoko deposit. Its bulk chemical composition, determined by X-ray fluorescence analysis (Rigaku NEX CG II), is presented in

[Table S1](#). According to these results, the waste contains 6.77 wt.% manganese expressed as MnO, indicating that the material is a relatively low-grade manganese source. The semi-quantitative X-ray phase analysis of the initial sample and of the residues obtained after leaching with 10% H₃PO₄ at 20 °C and 75 °C is presented in [Table 1](#).

The mineralogical composition of the initial waste is dominated by calcite (CaCO₃, 75.0 wt.%), quartz (SiO₂, 15.0 wt.%), and albit (Na(AlSi₃O₈), 5.0 wt.%). Brownite, (Mn₂O₃)₃MnSiO₃, is the primary manganese-bearing phase and occurs at approximately 5.0 wt.% of the total sample. Additional iron-bearing minerals, trace sulfides, and minor elements such as potassium, barium, and titanium were also detected by EDXRF ([Fig. S1](#)). The prevalence of carbonate and silicate phases is characteristic of sedimentary-type manganese ores, where manganese oxides are finely dispersed and partly incorporated within a carbonate–silicate matrix. This composition explains both the relatively low Mn concentration and the limited potential for direct metallurgical recovery without beneficiation. The leaching of this waste with 10% phosphoric acid resulted in significant mineralogical transformations. Calcite, which constituted the majority of the bulk material, was completely dissolved under both leaching conditions, confirming its high reactivity toward phosphoric acid and explaining the strong reduction in total mass of the solid residue. The disappearance of calcite led to an apparent increase in the relative abundance of acid-resistant minerals such as quartz and albit. At 75 °C, the albit content increased to 20 wt.% in the residue, which can be attributed to the relative enrichment effect resulting from the removal of easily soluble carbonate and manganese phases. Quartz similarly increased to 68–86 wt.% depending on the leaching temperature, reflecting its chemical inertness under acidic conditions. The leaching process also promoted the formation of new crystalline phosphate phases. Phosphate-bearing minerals such as serra-brancaite (MnPO₄·H₂O) and lipscombit (Fe_{1.375}(PO₄)(OH)) were absent in the initial waste but appeared in the leached residues, particularly at the higher temperature of 75 °C. Their presence indicates that phosphoric acid not only dissolves carbonate and partially dissolves manganese and iron oxides but also facilitates the subsequent precipitation of stable manganese and iron

Table 1: Semi-quantitative X-ray phase analysis of crystalline phases of manganese ore processing waste (Altyn-Shoko deposit) and solid residues after leaching with 10% H₃PO₄.

The mineral	Chemical formula	Content, mass (%)		
		Initial sample	Residue after leaching at 20°C	Residue after leaching at 75°C
Calcite	CaCO ₃	75.0	0.0	0.0
Quartz	SiO ₂	15.0	86.0	68.0
Brownite	(Mn ₂ O ₃) ₃ MnSiO ₃	5.0	4.0	3.0
Albit	Na(AlSi ₃ O ₈)	5.0	8.0	20.0
Serra-brancaite	MnPO ₄ ·H ₂ O	0.0	0.0	8.0
Lipscombit	Fe _{1.375} (PO ₄)(OH)	0.0	2.0	1.0

phosphates. This behavior aligns with previously reported dissolution–precipitation pathways for Mn- and Fe-oxide systems in phosphoric acid media and reflects the thermodynamic favorability of phosphate formation under such conditions. In general, the phase transformations observed during leaching demonstrate the complete removal of the carbonate component, partial dissolution and conversion of manganese- and iron-bearing phases into their corresponding phosphates, and the persistence of silicate minerals. These results confirm that treatment of manganese ore processing waste with phosphoric acid produces manganese- and iron-containing phosphate phases in the solid residue while simultaneously generating phosphate-rich leachates. Such transformations provide a mineralogical foundation for further utilization of the leachates as phosphating solutions for steel surface treatment, supporting the broader concept of converting mining waste into value-added functional materials.

The textural characteristics of the ore-processing waste were investigated using an OLYMPUS BX-51 optical microscope on polished briquettes (anschliffs) prepared from crushed material. The reflected-light micrographs reveal that brownite is the dominant manganese-bearing mineral and occurs as coarse grains and irregular aggregates dispersed within a quartz–carbonate matrix. In the polished sections,

brownite appears as bright, high-reflectance patches contrasting with the darker silicate–carbonate groundmass (Fig. 2A–D). In several areas, brownite forms compact aggregates in direct contact with the quartz–carbonate framework, indicating a close mineralogical association and limited liberation from the gangue material (Fig. 2A). Granular clusters of brownite inclusions are also observed in non-ore matrix zones, suggesting that part of the manganese oxide occurs as fine disseminations (Fig. 2B). Coarse fragments of brownite, ranging from subrounded to irregular anhedral shapes, are embedded within the heterogeneous silicate–carbonate assemblage (Fig. 2C). Some elongated grains with straight or gently curved boundaries are present, reflecting mechanical breakage during ore processing or recrystallization features inherited from the original ore fabric (Fig. 2D). The overall textures indicate that brownite is partly intergrown with quartz and carbonate minerals and partly present as discrete grains. This mixture of intergrown and free brownite implies incomplete liberation during comminution and explains the relatively low manganese upgrading efficiency during physical beneficiation. The petrographic evidence therefore supports the need for chemical processing approaches, such as phosphoric acid leaching, to effectively release manganese from the tightly bound silicate–carbonate matrix.

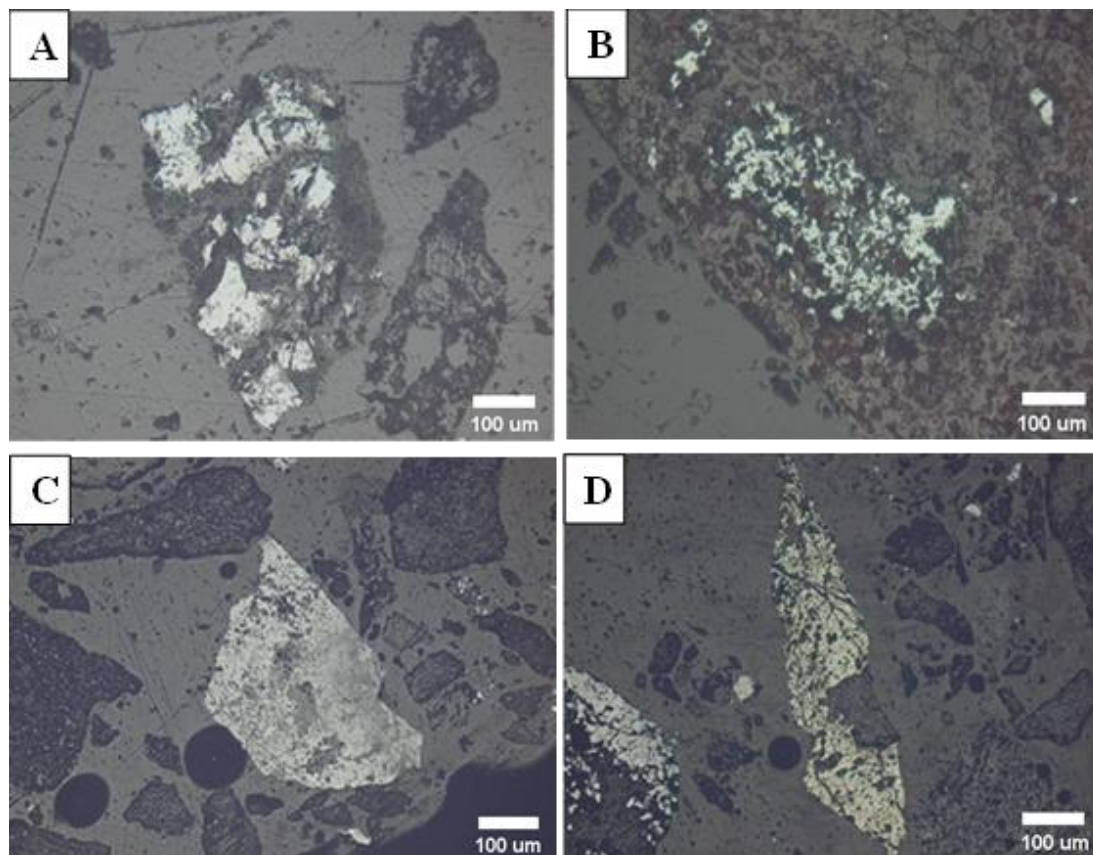
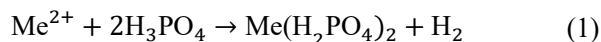


Fig. 2: Reflected-light micrographs of Anschliff sample 1 showing the textural relationships of brownite within the ore-processing waste (A) Brownite aggregates in direct contact with a quartz–carbonate groundmass (B) Granular clusters of brownite disseminated within a non-ore silicate–carbonate matrix (C) Coarse brownite fragments embedded in a heterogeneous silicate–carbonate assemblage (D) Elongated brownite grain enclosed within a fine-grained matrix.

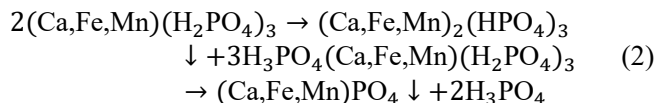
The phosphoric acid leaching process was conducted to evaluate the potential of the aforementioned waste materials for conversion into functional phosphating solutions. A 40% orthophosphoric acid (H_3PO_4) solution was employed as the leaching reagent. The experiments were carried out under various solid-to-liquid (S:L) ratios at a controlled temperature of 25 °C, with continuous mechanical stirring of the slurry for a duration of 30 minutes. Upon completion of leaching, the resulting pulp was filtered through a dense filter medium, and the solid residue was subsequently dried at 105 °C for 1 hour to achieve constant mass. This temperature was selected to prevent dehydration of newly formed phosphate phases while ensuring complete removal of physically adsorbed moisture. The filtrate was analyzed for elemental composition using titrimetric methods to quantify calcium compounds and photocolometric techniques to determine the concentrations of aluminum, manganese, iron, and soluble silicates. These combined analytical methods provide a reliable assessment of metal dissolution efficiency and solution purity, as demonstrated in previous studies on acidic leaching of manganese-bearing residues. The overall degree of leaching was determined gravimetrically, based on the difference in mass between the samples before and after the leaching process. The corresponding results are summarized in [Table S2](#). This gravimetric approach enables a direct estimation of total solid dissolution and has been widely adopted in evaluating leachability of low-grade mineral residue. It was established that under the studied conditions, an increase in the solid-to-liquid (S:L) ratio from 1:10 to 1:25 enhanced the overall leaching efficiency from 66.8% to 70.9%. However, a further increase in the liquid phase to an S:L ratio of 1:50 had only a marginal effect on the leaching rate ([Table S2](#)). The filtrate obtained after leaching at S:L (1:50) contained the following concentrations (g/L): $\text{Ca}(\text{H}_2\text{PO}_4)_2$ (93.5); $\text{Mn}(\text{H}_2\text{PO}_4)_2$ (6.5); $\text{Al}(\text{H}_2\text{PO}_4)_3$ (4.7); $\text{Fe}(\text{H}_2\text{PO}_4)_3$ (4.3); H_2SiO_3 (0.9); and free H_3PO_4 (411.0). The high concentration of monocalcium and manganese dihydrogen phosphates indicates efficient conversion of the primary carbonates and oxides into soluble phosphate salts, suitable for use as phosphating agents. This leachate was subsequently used to produce anti-corrosion coatings on low-carbon steel by the immersion phosphating method. Phosphating was carried out by immersing three steel plates in the solution at 85 °C. The reaction was accompanied by vigorous hydrogen evolution, necessitating a controlled process time of 60 minutes. After phosphating, the samples were rinsed with distilled water, and their corrosion resistance was evaluated by immersion in tap water in accordance with standard protocols.^[31] After 24 hours, the tests were discontinued due to partial peeling of the coatings and pronounced corrosion on the steel surface, evidenced by an orange coloration of the water, indicative of active oxidation. Surface morphology analysis ([Fig. S2](#)) revealed coatings composed of grains of irregular shape and variable size, interspersed with large voids. This microstructure indicates the formation of a non-uniform,

porous coating with poor adhesion and low protective performance. Elemental mapping ([Fig. S3](#)) showed the coating composition to be (mass %): Fe (58.99 ± 0.41); O (28.31 ± 0.46); P (9.99 ± 0.27); and Ca (2.72 ± 0.24). The dominance of Fe and O confirms the presence of mixed iron–phosphate phases, while the low Ca content suggests incomplete incorporation of calcium phosphates into the coating matrix. The inferior corrosion resistance of the coating is primarily attributed to the high concentration of free H_3PO_4 in the leachate. Elevated acidity accelerates the phosphating reaction, leading to uncontrolled crystal growth and the formation of a loosely packed, porous layer. Moreover, excess H_3PO_4 suppresses the hydrolytic conversion of soluble iron dihydrogen phosphates into stable hydro- and orthophosphates, further weakening the coating integrity. To enhance coating quality, the leaching conditions were optimized. A 10% H_3PO_4 solution was employed as the leaching reagent, with the process conducted at an S:L ratio of 1:25 and temperatures of 25 °C and 75 °C. Given that more than half of the manganese minerals were found to occur as intergrowths with non-metallic phases, the initial sample was subjected to mechanical activation using a high-energy planetary ball mill (KT-SRVM type) operating at 1000 rpm for 30 minutes. This treatment aimed to increase the specific surface area and disrupt mineral associations, thereby enhancing metal extraction efficiency. Such mechanical activation has been shown to increase reactivity by inducing lattice strain and amorphization of aluminosilicate minerals. Phosphating solutions were prepared from both the untreated waste and the mechanically activated samples, each leached with 10% orthophosphoric acid under the specified conditions. Since the total acidity-to-free acidity ratio is a critical performance parameter for phosphating baths,^[32] these indicators were determined for the resulting filtrates. The total acidity, representing the combined content of free H_3PO_4 and dissolved phosphate ions, was measured by titration with 1 M NaOH using phenolphthalein as the indicator. Free acidity, corresponding to the concentration of unreacted H_3PO_4 , was determined by titration with 1 M NaOH in the presence of methyl orange.^[33] The results are presented in [Table S3](#). The findings indicate that mechanical activation significantly enhances leaching efficiency at room temperature, increasing the total leaching degree from 66.9% (unactivated) to 72.9% (activated) ([Table S3](#)). The concentrations of dissolved metal phosphates also increased, manganese by 19%, iron by 34%, aluminum by 59%, and silicon by threefold, reflecting the improved breakdown of mineral lattices. This enhancement is attributed to increased dispersion and partial amorphization of aluminosilicate phases, particularly albite, which facilitates the release of aluminum and silicon into the solution. The calcium content in both filtrates remained nearly constant, confirming nearly complete conversion of CaCO_3 to $\text{Ca}(\text{H}_2\text{PO}_4)_2$ during acid leaching. Raising the leaching temperature to 75 °C accelerated the reaction between phosphoric acid and the acid-absorbing components of the

waste, resulting in the formation of soluble dihydrogen phosphates according to the reaction Eq. (1):



However, elevated temperature also promoted the hydrolysis of these primary phosphates, leading to the precipitation of poorly soluble hydro- and orthophosphates Eq. (2):



Consequently, the accumulation of insoluble phosphate precipitates increased the solid residue mass, reducing the overall leaching efficiency from 66.9% to 34.0% for the unactivated waste and from 72.9% to 33.7% for the mechanically activated sample (Table S3). This inverse relationship between temperature and dissolution efficiency is consistent with thermodynamic predictions, where higher temperatures favor the precipitation of secondary phosphate phases. This interpretation is supported by EDXRF analysis (Figs. S3, S4, S5, Table 2), which revealed that the solid residues after leaching at 75 °C contained substantial quantities of calcium, manganese, and iron phosphates. These findings are corroborated by the XRD results, confirming the predominance of crystalline phosphate phases in the leached solids.

For subsequent investigations, productive leachates obtained at 25 °C were selected as potential phosphating solutions. Their chemical compositions are summarized below:

- **Solution 1** – derived from the initial ore-dressing waste of the Altyn-Shoko deposit, with the following composition (g L⁻¹): Ca(H₂PO₄)₂ (93.4); Mn(H₂PO₄)₂ (5.7); Al(H₂PO₄)₃ (4.9); Fe(H₂PO₄)₃ (3.5); H₂SiO₃ (0.8); free H₃PO₄ (15.1); **Total acidity/Free acidity (7.0)**.

- **Solution 2** – prepared from mechanically activated waste, with the following composition (g L⁻¹): Ca(H₂PO₄)₂ (93.5); Mn(H₂PO₄)₂ (6.8); Al(H₂PO₄)₃ (7.8); Fe(H₂PO₄)₃ (4.7); H₂SiO₃ (2.5); free H₃PO₄ (10.3); **Total acidity/Free acidity (10.2)**.

The compositional differences between the two solutions primarily reflect the enhanced dissolution of aluminosilicate and transition-metal phases during mechanical activation,

resulting in increased Al and Fe phosphate concentrations and a higher total-to-free acidity ratio, favorable for uniform film formation. Phosphating was performed by immersing pre-cleaned St3 steel plates into each solution at 85 °C for 1 hour, and the procedure was repeated three times to ensure reproducibility. The protective performance of the resulting phosphate coatings was assessed by gravimetric analysis, measuring the mass loss after immersion in tap water for 1, 4, and 8 days in accordance with standardized corrosion testing protocols.^[34] This method allowed for the evaluation of the coatings' ability to withstand prolonged exposure to aqueous environments. For comparative purposes, a commercial “Mazhef” phosphating solution was used as a reference system. The experimental results are illustrated in Fig. 3. Visual inspection after 8 days of immersion revealed distinct morphological differences between the coatings. The coating produced from **Solution 1** was uniform, dense, and dark gray in color, indicating the formation of a well-developed crystalline phosphate layer (Fig. 3A). In contrast, coatings obtained from **Solution 2** exhibited a greenish tint with light-gray surface efflorescence (Fig. 3B), suggesting partial surface dehydration and the presence of micro-porosity. These coatings also appeared less compact and more heterogeneous, likely due to variations in metal-to-phosphate ratios in the activated leachate. Gravimetric corrosion testing confirmed these visual observations. During the initial 4 days of immersion, the coating mass loss for St3 samples phosphated in **Solution 1** was **0.0228 g**, whereas that for coatings formed using the **commercial Mazhef solution** was **0.0335 g**. This indicates that the phosphate film derived from the waste-based leachate provided superior resistance to aqueous corrosion compared to the industrial benchmark. During the subsequent testing period (up to 8 days), the mass of both coatings remained nearly unchanged, demonstrating the stability and water-resistance of the phosphate layers (Fig. S7, curves 1 and 3). The improved performance of Solution 1 may be attributed to its balanced acidity and moderate Mn²⁺ and Fe³⁺ contents, which promote fine-grained, adherent phosphate film growth. In contrast, excessive Al and Si compounds in Solution 2 may interfere with crystal nucleation, yielding porous and less protective coatings. These findings suggest that waste-derived phosphating baths can effectively replace commercial



Fig. 3: Appearance of samples with phosphate coatings formed in solution 1 (A) and solution 2 (B) after 8 days of testing in water.

Table 2: Composition of solid residues after leaching of ore processing waste from the Altyn-Shoko deposit with 10% H₃PO₄, depending on the temperature.

Sample	T, °C	Component content, mass (%)							
		Al ₂ O ₃	SiO ₂	P ₂ O ₅	K ₂ O	CaO	TiO ₂	MnO	Fe ₂ O ₃
initial	25	9.310	71.300	1.020	1.070	0.376	0.381	8.110	8.400
		±0.056	±0.053	±0.005	±0.005	±0.002	±0.002	±0.007	±0.006
	75	3.640	25.800	36.000	0.482	22.900	0.154	6.010	4.700
mechanical activation	25	±0.042	±0.046	±0.026	±0.003	±0.018	±0.001	±0.007	±0.005
		8.770	73.300	0.892	0.990	0.326	0.491	7.150	7.800
	75	±0.052	±0.051	±0.004	±0.005	±0.002	±0.001	±0.006	±0.005
		3.910	27.600	36.100	0.476	22.100	0.171	4.940	4.370
		±0.040	±0.042	±0.025	±0.003	±0.016	±0.001	±0.006	±0.005

formulations when optimized for acidity, temperature, and composition.

The phosphate coating produced from solution 2 exhibited an initial mass loss of 0.0125 g after the first day of immersion testing; however, a subsequent increase in coating mass by 0.0035 g was observed during the later stages of exposure (Fig. S7, curve 2). This anomalous mass gain, combined with visible changes in surface coloration and texture, suggests a partial dissolution followed by reprecipitation and structural reorganization of the phosphate film under prolonged contact with water. Such post-formation rearrangements are commonly associated with hydration–dehydration cycles and the transformation of metastable phosphates into more stable phases. In addition to gravimetric testing, the corrosion resistance of phosphate coatings formed on steel samples using phosphating solutions derived from manganese ore processing waste (Altyn-Shoko deposit) was further examined through electrochemical techniques, including potentiodynamic polarization and electrochemical impedance spectroscopy (EIS).

Polarization curves were recorded within a potential range of ± 250 mV relative to the open-circuit corrosion potential (E_{corr}) at a scan rate of 1 mV s^{-1} , starting from the cathodic direction. The corrosion potential (E_{corr}) and corrosion current density (I_{corr}) were determined by fitting the experimental polarization data to the Butler–Volmer equation, from which the corrosion rate and protection efficiency of the coatings were calculated. This methodology provides a quantitative evaluation of coating performance, capturing both anodic dissolution kinetics and cathodic reaction suppression effects.

Analysis of the polarization behavior (Fig. 4) revealed that uncoated St3 steel exhibited the most negative corrosion potential ($E_{\text{corr}} = -0.643 \text{ V}$) and the highest corrosion current ($I_{\text{corr}} = 19.65 \text{ } \mu\text{A}$), corresponding to a corrosion rate of $0.015 \text{ mm year}^{-1}$ (Table 3). In contrast, the phosphate-coated steel prepared using Solution 1 (derived from the leaching of initial ore-dressing waste) demonstrated a substantial improvement in corrosion resistance. The corrosion potential shifted positively to -0.454 V , while the

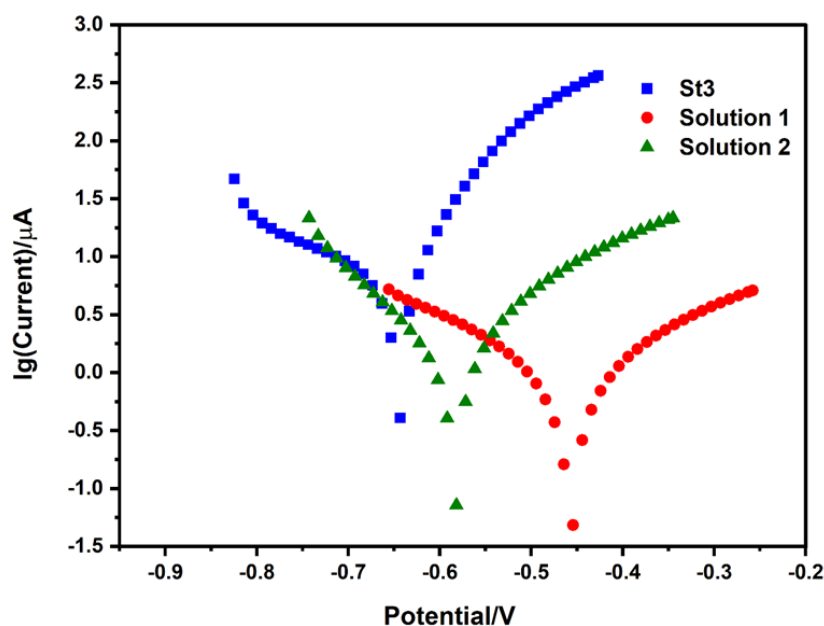


Fig. 4: Potentiodynamic polarization curves recorded in water for low-carbon steel (St3): (1) with a phosphate coating formed in a solution based on the initial ore processing waste, (2) with a phosphate coating formed in a solution based on the mechanically activated ore processing waste, and (3) for the uncoated St3 reference sample.

Table 3: Electrochemical parameters derived from potentiodynamic polarization measurements for uncoated St3 steel and phosphate-coated St3 samples formed in solutions prepared from ore processing waste of the Altyn-Shoko deposit.

Sample	E_{corr} (V)	I_{corr} (μA)	R_p (Ω)	β_a (V/dec)	β_c (V/dec)	Corrosion rate, mm/year	Protection effectiveness, %
St3 uncoated	-0.643	19.650	3084	0.143	6.531	0.015	-
Phosphating Film formed in solution 1	-0.454	1.687	47550	0.332	0.417	0.005	91.4
Phosphating Film formed in solution 2	-0.590	2.933	20590	0.240	0.331	0.009	85.1

corrosion current decreased to 1.687 μA , resulting in a corrosion rate of 0.005 mm year^{-1} and a protection efficiency of 91.4%. This significant enhancement in corrosion resistance can be attributed to the formation of a dense, adherent phosphate layer that effectively suppresses anodic dissolution and restricts ionic transport at the metal–solution interface. The observed positive shift in E_{corr} confirms the passivating nature of the coating, consistent with the behavior of manganese–calcium phosphate films reported in earlier studies.

The curves illustrate the effect of coating composition on corrosion potential and current density in aqueous conditions. The phosphate coating formed on St3 steel in **Solution 2**, prepared from the leaching of mechanically activated ore-processing waste, exhibited a **corrosion potential (E_{corr})** of **−0.590 V**, with a corresponding **corrosion current density (I_{corr})** of **2.933 μA** and a **corrosion rate** of **0.009 $\text{mm}\cdot\text{year}^{-1}$** . This performance corresponds to a **protection efficiency of 85.1%** (Table 3).

Although the coating still provides notable corrosion resistance, the higher current density compared to Solution 1 suggests the formation of a less compact or partially porous phosphate layer, consistent with the morphological observations discussed earlier.

The **electrochemical impedance spectra (EIS)** of the coated and uncoated samples are displayed as **Nyquist and**

Bode plots (Fig. 5a–b). These spectra provide complementary insight into the charge-transfer processes and dielectric behavior of the coating systems. The experimental data were fitted to equivalent electrical circuit models, enabling the determination of **resistance (R)** and **capacitance (C)** values for the distinct layers within the coating (Fig. 5c–d). Such modeling allows separation of the contributions from the solution resistance, charge-transfer resistance, and coating capacitance, thereby quantifying the protective performance of each layer.

The Nyquist plots (Fig. 5) revealed that for the uncoated St3 steel sample, the semicircle radius was the smallest, corresponding to resistance values of $R_1 = 263 \Omega$ and $R_2 = 616 \Omega$ (Table 4). These low resistance values indicate a limited charge-transfer resistance (R_{ct}) and thus high corrosion activity, consistent with an unprotected metal surface exposed to an aqueous electrolyte. In contrast, the phosphate coating formed on St3 in Solution 1 (derived from the leaching of initial ore-processing waste) significantly increased the semicircle diameter and total resistance ($R_1 + R_2$). This behavior reflects an enhanced barrier effect of the coating, reducing ionic conductivity and slowing corrosion reactions at the metal–electrolyte interface. For the coating formed in Solution 2 (prepared from mechanically activated waste), the impedance parameters further changed to $R_1 = 3386 \Omega$ and $R_2 = 1244 \Omega$, while an additional element $R_3 = 1.0 \times 10^{12} \Omega$

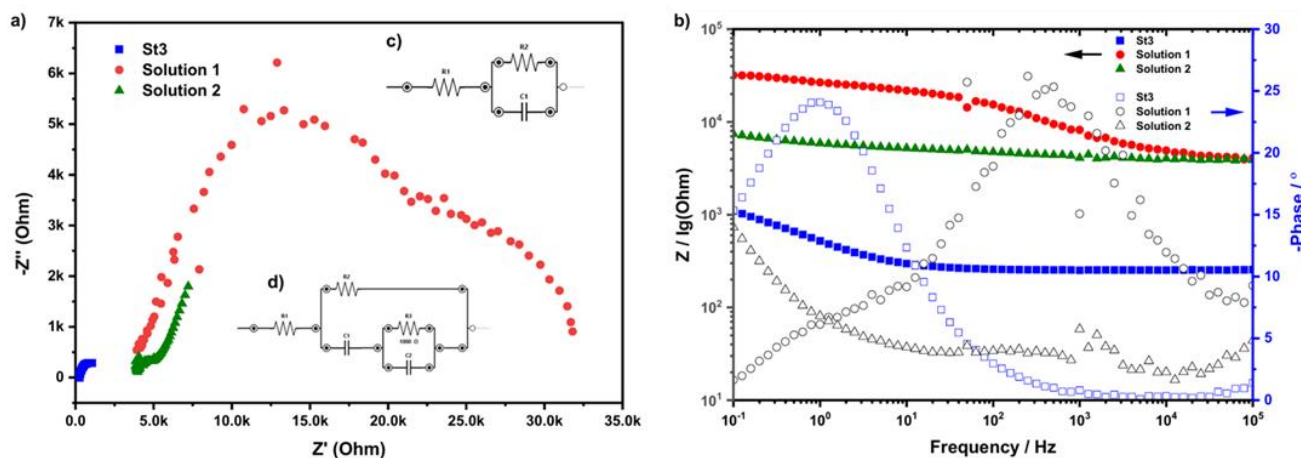


Fig. 5: Nyquist and Bode diagrams for St3 steel and phosphate coatings formed on St3 in solutions 1 and 2.

appeared, accompanied by capacitances $C_1 = 1.25 \times 10^{-10} \text{ F}$ and $C_2 = 0.001 \text{ F}$ (Table 5). The emergence of this high-resistance element and dual capacitance response suggests a more complex multilayer structure containing localized defects and micro-porous regions within the coating. These imperfections may act as ionic pathways, reducing the long-term protective efficiency of the film. The Bode plots showed an increase in the impedance modulus ($|Z|$) and a phase angle shift toward higher values for the coated samples compared with bare steel. These observations indicate that the coatings exhibit pronounced capacitive behavior and retardation of electrochemical charge transfer, confirming their role as effective dielectric barriers. Overall, the electrochemical impedance analysis demonstrated that the phosphate coating produced in Solution 1, based on the initial ore-processing waste, provides superior corrosion protection, achieving a protection degree of 91.4%. In comparison, the coating formed in Solution 2 exhibited higher porosity and lower impedance, leading to a higher corrosion rate ($0.009 \text{ mm} \cdot \text{year}^{-1}$) and a reduced protection efficiency of 85.1%. These findings are consistent with the morphological data, confirming that mechanical activation, while enhancing dissolution, may also promote the incorporation of less stable phosphate phases that compromise coating compactness.

The surface morphology of phosphate coatings formed in the two phosphating solutions was examined using SEM (HITACHI TM3030). The coating produced in Solution No. 1 exhibited a compact and crystalline microstructure composed of densely packed, uniformly distributed grains, indicative of a well-formed phosphate layer with strong adhesion to the steel substrate (Fig. 5A). This homogeneous granular surface explains the superior corrosion protection observed in both electrochemical and gravimetric evaluations. In several local regions, dendritic protrusions were also observed, most likely corresponding to secondary calcium-phosphate crystallites that nucleated during the later stages of film formation under conditions of local supersaturation (Fig. 5A). After 8 days of immersion in water, the coating from Solution No. 1 showed the presence of microcracks (Fig. 5B). These are interpreted as artifacts produced during sample drying rather than actual signs of coating degradation. EDS analysis revealed a decrease in calcium and phosphorus after immersion, suggesting partial dissolution or desorption of the more soluble calcium-

phosphate phases. Conversely, the iron content increased to $30.89 \pm 0.37 \text{ wt.}\%$, consistent with the exposure of the substrate and the relative enrichment of insoluble iron-phosphate species. The overall elemental ratio O:Fe:Ca:Mn:P = 1.2:1.0:0.5:0.02:0.5 confirms the coexistence of iron and calcium phosphates with minor manganese incorporation. In contrast, coatings produced from Solution 2, repared using mechanically activated ore-processing waste from the Altyn-Shoko deposit, displayed a distinctly different morphology. Prior to immersion, the surface exhibited loosely arranged petal-like and dendritic structures consisting of irregular, variably sized grains (Fig. 5C). Numerous microvoids and cavities were present throughout the coating, indicating weaker cohesion and higher intrinsic porosity compared to films formed from Solution 1. Upon immersion testing, these defects enlarged substantially (Fig. 5D), demonstrating the poor structural stability of this coating in aqueous environments.

Compositional differences further support the weaker protective performance of coatings from Solution 2. The film lacked detectable manganese and contained approximately 3.3-fold less calcium than coatings from Solution 1 (Table 5), indicating the predominance of iron-phosphate phases rather than mixed metal phosphates known to improve barrier properties. After immersion, calcium decreased sharply from $7.54 \pm 0.16 \text{ wt.}\%$ to $2.23 \pm 0.28 \text{ wt.}\%$, while the iron content rose to 57.65 wt.%, reflecting dissolution of calcium-phosphate crystallites and greater exposure of the steel substrate. The resulting elemental ratio O:Fe:Ca:P = 0.55:1.00:0.04:0.15 highlights substantial iron enrichment and depletion of Ca-P species, consistent with the reduced corrosion resistance observed in performance tests. Although both phosphating solutions were obtained by leaching ore-processing waste from the same deposit, the differences in coating quality can be traced primarily to variations in free phosphoric acid and the concentration of primary phosphate species. Solution No. 1 exhibited a total-to-free acidity ratio of 7.0 (Table 4), which lies within the optimal range (7–8) reported for producing compact, protective phosphate layers on St3 steel.^[35,36] In contrast, Solution 2 showed a markedly higher ratio of 10.2, indicating a larger fraction of unbound acid capable of accelerating crystal growth and promoting the formation of coarse, porous coatings.

Table 4: Parameters obtained from the analysis of electrochemical impedance spectra (EIS) for uncoated St3 steel and St3 coated in phosphate solutions prepared from initial (Solution 1) and mechanically activated (Solution 2) ore-processing waste from the Altyn-Shoko deposit.

Sample	R1 (Ω)	R2 (Ω)	R3 (Ω)	C1 (F)	C2 (F)	χ^2
Ct3 (uncoated)	263	616	—	3.85×10^{-4}	—	0.0094
Phosphating Film formed in solution 1	263	616	—	3.85×10^{-4}	—	0.0094
Phosphating Film formed in solution 2	3386	1244	1.0×10^{12}	1.25×10^{-10}	0.001	0.0406

Table 5: Changes in the elemental composition of phosphate coatings on the surface of steel samples after testing in water.

Sample	Test time, day	Elemental composition, mass (%)					
		O	Fe	Ca	P	Si	Mn
Phosphating Film formed in solution 1	0	41.90±0.74	10.12±0.72	25.21±0.31	20.45±0.21	0.69±0.25	1.62±0.37
	8	37.45±0.74	30.89±0.37	15.49±0.20	15.35±0.20	0.00	0.82±21
Phosphating Film formed in solution 2	0	43.54±0.45	27.40±0.28	7.54±0.16	21.52±0.14	0.00	0.00
	8	31.49±0.50	57.65±0.48	2.23±0.28	8.62±0.31	0.00	0.00

Mechanical activation of the waste through intensive grinding led to a disturbance of the crystalline structure of solid-phase particles, thereby increasing both the overall leaching efficiency at room temperature and the chemical reactivity of the main waste components toward phosphoric acid.^[37] As a result, Solution 2 exhibited a lower free H_3PO_4 content, an elevated concentration of primary phosphates, and an increased Total Acidity/Free Acidity ratio of 10.2. In addition, a higher amount of soluble silicon compounds, most likely in the form of metasilicic acid (H_2SiO_3), was detected. These compositional differences significantly influence the stability and structure of the resultant phosphate films. During phosphating, a decrease in H_3PO_4 concentration occurs due to the electrochemical dissolution of the metal according to the reaction Eq. (1):

The reduction of free phosphoric acid content, combined with the elevated process temperature (85 °C), accelerates the hydrolysis of primary dihydrogen phosphates (H_2PO_4^-) to hydrophosphates (HPO_4^{2-}). In the absence of excess free H_3PO_4 , the equilibrium of this hydrolysis reaction cannot shift toward the left, which compromises the stability of the phosphating bath. Consequently, phosphating in Solution 2 was accompanied by intense sludge formation.

According to EDXRF analysis (Fig. S6), the sludge consisted mainly of iron and calcium phosphates with the following composition (wt.%): $\text{Fe}_2\text{O}_3 - 50.400 \pm 0.020$; $\text{P}_2\text{O}_5 - 43.800 \pm 0.033$; $\text{CaO} - 3.810 \pm 0.015$; $\text{MnO} - 0.154 \pm 0.001$; $\text{Al}_2\text{O}_3 - 0.744 \pm 0.041$; and $\text{SiO}_2 - 0.523 \pm 0.012$. The high content of Fe_2O_3 and P_2O_5 confirms the preferential precipitation of insoluble ferric and calcium phosphates under conditions of acid depletion and elevated temperature. During the phosphating process, these slurry particles were adsorbed onto the metal surface, competing with iron phosphate crystals produced via electrochemical reactions. This competitive deposition hindered the formation of a compact and uniform phosphate layer, thereby reducing the protective performance of the coating obtained from Solution 2 (mechanically activated waste). Based on the experimental results, the optimal phosphating solution derived from the enrichment waste of the Altyn-Shoko manganese ore deposit for producing dense, corrosion-resistant phosphate coatings on low-carbon steel has the following composition (g L^{-1}): $\text{Ca}(\text{H}_2\text{PO}_4)_2 - 93.4$; $\text{Mn}(\text{H}_2\text{PO}_4)_2 - 5.7$; $\text{Al}(\text{H}_2\text{PO}_4)_3 - 4.9$; $\text{Fe}(\text{H}_2\text{PO}_4)_3 - 3.5$; $\text{H}_2\text{SiO}_3 - 0.8$; free $\text{H}_3\text{PO}_4 - 15.1$; Total Acidity/Free Acidity (7.0). The optimal leaching and phosphating conditions were determined as follows: Solid-to-

Liquid ratio (1:25), 10% H_3PO_4 , room temperature, and leaching time of 60 min. While pre-mechanical activation of the waste increases the leaching degree at room temperature, it simultaneously promotes excessive sludge formation during phosphating, leading to less compact coatings and diminished corrosion protection. Overall, this study demonstrates that the valorization of manganese ore processing waste in Kazakhstan provides a technically viable and environmentally sustainable pathway for producing low-cost domestic phosphating solutions. Such utilization not only supports waste minimization and circular economy objectives but also contributes to reducing environmental risks associated with the accumulation of ore-processing residues.

4. Conclusion

This study demonstrates that ore-processing waste from the Altyn-Shoko deposit, composed primarily of calcite, quartz, feldspar, and brownite, represents a viable secondary raw material for the preparation of phosphating solutions. Under optimized leaching conditions (S:L = 1:25, 10 wt.% H_3PO_4 , 60 min, ambient temperature), the resulting solution exhibited a Total/Free Acidity ratio of 7.0, consistent with the established optimum for producing compact and adherent phosphate coatings on low-carbon steel. Phosphate films formed from non-activated waste showed a dense, homogeneous crystalline structure enriched in calcium–manganese phosphate phases, which imparted excellent corrosion protection. These coatings achieved a corrosion rate of $0.005 \text{ mm} \cdot \text{year}^{-1}$ and a protection efficiency of 91.4%, maintained structural integrity during immersion, and exhibited superior stability compared to commercial analogues.

In contrast, coatings obtained from mechanically activated waste possessed a porous, petal-dendritic morphology with significantly reduced calcium content and no detectable manganese. These microstructural deficiencies resulted in lower barrier performance, evidenced by an increased corrosion rate of $0.009 \text{ mm} \cdot \text{year}^{-1}$ and reduced stability upon aqueous exposure. Overall, the findings confirm that non-activated Altyn-Shoko ore-processing waste is an effective and environmentally sustainable feedstock for producing low-cost phosphating solutions capable of generating high-performance anti-corrosion coatings. The work highlights the broader potential of technogenic mineral waste valorization in advancing circular-economy practices and promoting resource-efficient corrosion protection technologies.

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Conflict of Interest

Authors declare that there is no conflict of interest

Supporting Information

Applicable.

CRedit Statement

Sh. N. Kubekova: Conceptualization, Project administration and Supervision. **A. S. Raimbekova:** Project administration, Methodology and Supervision. **V. I. Kapralova:** Supervision, Methodology, and Formal analysis. **A. Dalbanbay:** Carried out Electrochemical experiments, Investigation, Methodology, Data curation and Validation. **Zn. Kuli:** Investigation and Data curation. **V. E. Kuznetsov:** Investigation. **E. A. Varol:** Writing – Review and editing, Supervision.

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