

Enrichment Wastes' Processing of Manganiferous Ores with the Use of Mechanochemical Methods

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ABSTRACT

The aim of the research is the study of the chemical and phase composition of enrichment wastes of manganiferous ore in Ushkatyn-III deposit and the synthesis of new materials by mechanochemical activation and subsequent heat treatment of the mechanical activation products. The use of XFA, infrared spectroscopy and electron probe microanalysis showed that the main phase is spar CaCO₃ (65 % wt). A number of silicophosphate materials were obtained based on these wastes by mechanochemical method in the two-phase system "enrichment wastes - phosphoric acid" with subsequent heat treatment of the mechanical activation products. In addition, it is shown that their solubility has an extreme character depending on the annealing temperature with a minimum at 600 °C. These products can be used as fertilizer materials of prolonged action, as well as metal corrosion inhibitors for water environments.

KEYWORDS

Ore, manganiferous ore enrichment, silicophosphates, mechanochemical activation, IR-spectroscopic analysis of enrichment wastes

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Introduction

Mineral resources are non-renewable material sources (Kalimullin & Masalimova, 2016), long-term exploitation of which has led to the involvement of non-ferrous metals with low technological characteristics in the ores' extraction (Abishev & Eremin, 2000). Primarily, this is due to the production increase of refractory and oxidized ores, which are of dissemination (Studentsov & Klets, 1997). The useful components are presented by minerals with similar physical-chemical properties, which greatly reduces the effectiveness of traditional technologies for their enrichment and leads to the formation of large amounts of waste (Chanturiia, 2002).

Only a small proportion of the waste is used as secondary raw materials, the rest is stored in tailing dumps and storages of mining and processing

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complexes, which requires large safety exclusion areas, including tillable land (Zhakitova et al., 2000). In addition, the possible destruction of levees and dams of overflowed tailing dumps may result in environmental catastrophes, which makes the problem of these wastes' recycling very actual (Kapralova, 2004; Patkovskaya & Tsukerman, 2000).

Large-tonnage enrichment wastes of ore in the Republic of Kazakhstan include, in particular, enrichment wastes of manganiferous ore. Raw material base of Kazakhstan dominates in the world for its reserves of manganese and iron ores, with the main deposits located in Central Kazakhstan and represented by Atasuy, Zhezkazgan and Ushkatyn groups (Telkov, Studentsov & Klets, 1995).

One of the promising directions of technological processing of enrichment waste of nonferrous metal ores is their use as raw materials in the new inorganic materials manufacturing of multifunctional purpose, in particular, phosphate fertilizers with microelements, silicophosphate inhibitors of metals' corrosion (Saginzhan, Kapralova & Kubekova, 2012), silicophosphate sorption-filtering materials (Gelfman et al., 2002; Clarke et al., 1995; Gladun et al., 2000; Kapralova et al., 2008), etc.

In addition, the practice of ferrous metal ores processing shows that manganiferous and iron ores are enriched by technologies that use the processes of jigging, washing, screening of ore and magnetic separation (Buketov, Gabdullin & Takenov, 1979; Mineral fertilizers. Methods for phosphates determination, 1990).

Literature Review

In most cases, chemical processing of solid materials without preliminary grinding is almost impossible, therefore machining with the objective of dispersing and activation is one of the most important technological operations (Sidenko, 1977).

V.I. Molchanov & M.S Yusupov (1981) and E.G. Avvakumov (1986) believe that the change of physico-chemical properties of solids during mechanical processing is the result of the formation of a new surface (i.e., dispersion) and the result of accumulation of various kinds of defects (activating) in the crystal. That is, mechanochemical activation can be considered as one of the methods of obtaining solid substances in the unstable, active form.

Mechanochemical activation, in particular, is used in the process of producing phosphate fertilizers by acid-free method, thus, the dispersion of natural phosphate proceeds both in a single-phase system or in a dry mode, and in a two-phase system or wet regime (Kochetkov & Lembrikov, 1979). Moreover, it allows not only increasing the surface of the solid phase, but also substantially changing material parameters that influence the kinetics of solid-phase reactions with their participation (1978).

Scientists note that the most common process is the jigging process (Buketov, Gabdullin & Takenov, 1979; Kochetkov, Zorikhina & Klevtsov, 1979). Thus, the enrichment of manganiferous ore in Ushkatyn–III deposits is carried out on gravitational technology with the use of concentrating tables at a total extraction of 70,6% of manganese content in the ore. Process of mill tailing jigging of manganiferous ore with particle size 60 – 14 mm and 14 – 1.0 mm

moves with insufficient effectiveness, therefore this waste currently is not recycled, not utilized and is deposited (Telkov, Raivich & Bezginova, 1975).

The simplest way of mechanochemical treatment in a two-phase system is the activation in the aquatic environment. Water as a dispersion medium, in many cases plays a positive role (Kochetkov & Khriashev, 1978). When dispersing, the liquid phase (water) exerts a wedging action and thus accelerates the process. Further, the liquid phase prevents the leakage of unwanted opposite processes: aggregation, agglomeration, and flocculation.

The liquid phase can also play an active role in the phases' interaction during mechanical activation. G.V. Permitina (1984) in her study cites the example of positive role of water and water solutions in the exchange of fluoride for hydroxyl directly upon activation of phosphates in the aquatic environment.

Based on the above, we proposed to use mechanochemical activation of enrichment wastes of manganiferous ore during its processing to new inorganic materials.

Aim of the Study

The aim of this study is the examination of the chemical and phase composition of enrichment wastes of manganiferous ore, the synthesis of new materials by mechanochemical activation and subsequent heat treatment of the mechanical activation products; the study of the obtained products' properties.

Research questions

What are the features of phase and material compositions of enrichment wastes of manganiferous ore in Ushkatyn-III deposit? What are the possible application fields of new materials, synthesized by annealing the products of mechanochemical activation in a two-phase system "wastes - phosphoric acid"?

Method

The phase composition of enrichment wastes of manganiferous ore in Ushkatyn-III deposit was studied with the help of X-ray diffraction analysis on an automated diffractometer DRON-3 with $Cu_{K\alpha}$ - radiation, β -filter. Conditions for recording of diffraction patterns: $U=35$ kV; $I=20$ mA; scale: 2000 imp.; time constant 2 s; survey of θ -2 θ ; detector 2 deg/min. X-ray diffraction analysis on semiquantitative basis was performed on powder samples' diffraction patterns using the method of equal sub-samples and artificial mixtures. Quantitative ratios of the crystal phases were determined. Interpretation of diffraction patterns was performed using the data of ICDD filing: powder diffractometric database PDF₂ (Powder Diffraction File) and diffraction patterns of pure minerals.

Recording the infrared absorption spectra was performed on the IR Fourier spectrometer "Nicolet 5700" in the range of 400-3600 cm^{-1} . To obtain the IR spectra, the studied substance (0.7-1.0 mg) was introduced in the sub-sample of potassium bromide (0.25 mg) and after thorough mixing, was compressed into a tablet.

Material composition of technological samples of enrichment wastes of manganiferous ore was studied by electron microprobe analysis using electron microscope JEOL-733 with X-ray analyzer.

The synthesis of new materials was carried out by "wet" activation of the selected samples of enrichment wastes with particle size $-14+1$ mm in vibration mill for 30 minutes in the identical conditions, using phosphoric acid as the liquid phase. The products of mechanochemical activation with grain size $-20+0$ μm were dried at 105°C for one hour and then were annealed at a temperature of 400; 600 and 800°C .

The quality of the synthesized products as phosphate-based fertilizer materials were evaluated according to their content of water and accessible forms of phosphorus pentoxide P_2O_5 . Phosphorus oxide (V) P_2O_5 was determined colorimetrically by the absorption of the yellow phosphorus-vanadium-molybdc complex (Mineral fertilizers. Methods for phosphates determination, 1990).

Data, Analysis, and Results

Infrared spectrum analysis of enrichment wastes of manganiferous ore in Ushkatyn-III deposit (Figure 1) showed the presence of intense absorption bands in the range 1425; 875; 713 cm^{-1} , characteristic of valence vibrations CO_3^{2-} -ion and the absorption bands in the range 1033 and 795 cm^{-1} , characteristic of valence vibrations of SiO_4 -tetrahedron and Si-O-Si-bonds. This indicates the presence of carbonate and silicate compounds in the sample.

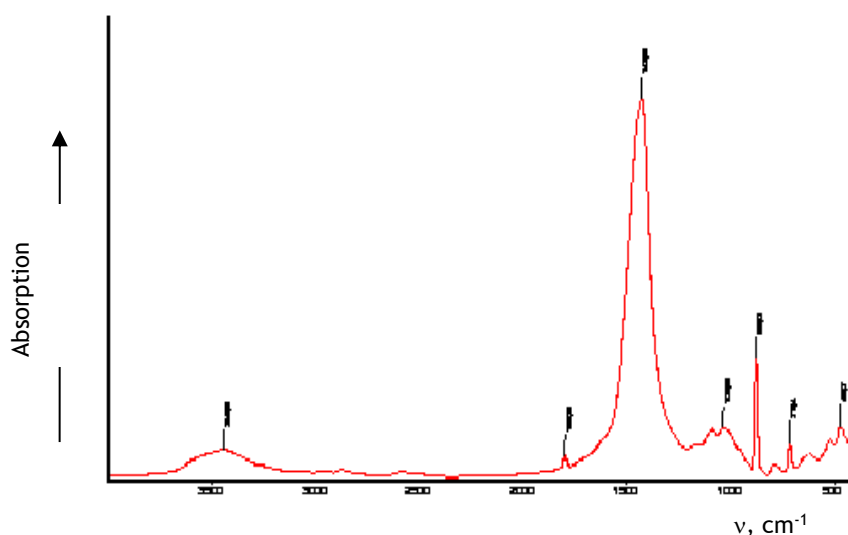


Figure 1. Infrared spectrum of process sample of gravitational enrichment of manganiferous wastes of ore in Ushkatyn-III deposit

The results of the infrared spectroscopy are confirmed by XFA (Figure 2, Table 1), which showed that the main phase of enrichment wastes are spar (65.7 % wt) and silicon dioxide (28.5 % wt). There is also a small number of silicate compounds in the form of albite $\text{Na}(\text{AlSi}_3\text{O}_8)$ and braunite $(\text{Mn}_2\text{O}_3)_3\text{MnSiO}_3$.

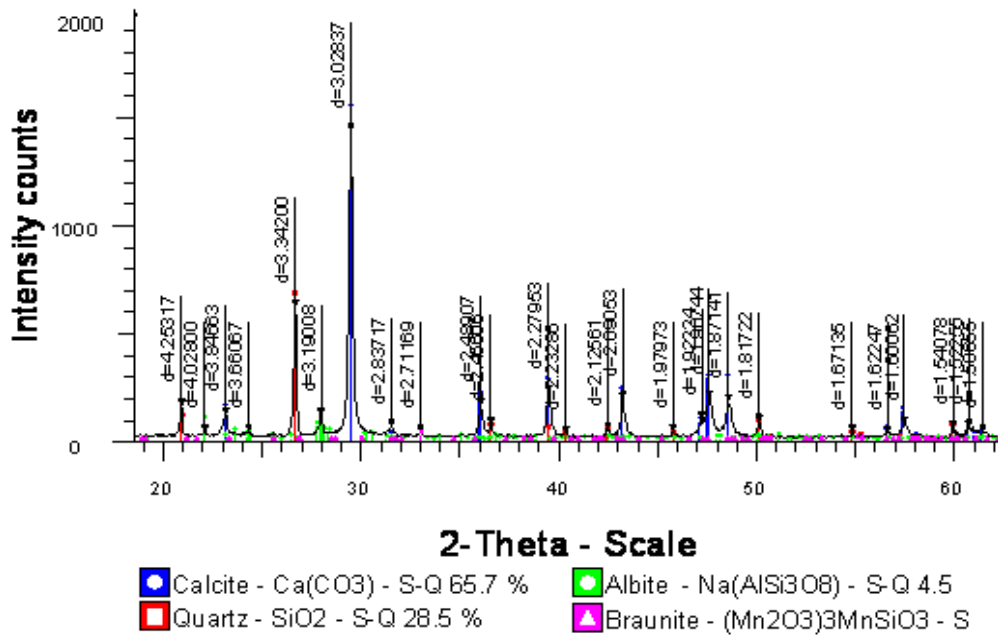


Figure 2. X-ray diffraction pattern of process sample of enrichment wastes of manganese ore in Ushkatyn-III deposit

Table 1. Semiquantitative XFA results of enrichment wastes of manganese ore in Ushkatyn-III deposit

The phase name	Chemical formula	The content, % wt
Calcite	CaCO ₃	65,7
Quartz	SiO ₂	28,5
Albite	Na(AlSi ₃ O ₈)	4,5
Braunite	(Mn ₂ O ₃) ₃ MnSiO ₃	1,3

The material composition study of technological samples of enrichment wastes of manganese ores also showed that the bulk of the waste is represented by the compounds of calcium (the content of CaO is 65.51 % wt); the content of aluminum and manganese oxides is almost the same and equals 2.28 and 2.29 % wt respectively; the content of silicate compounds in terms of silicon dioxide is 28% (Figure 3, Table 2).

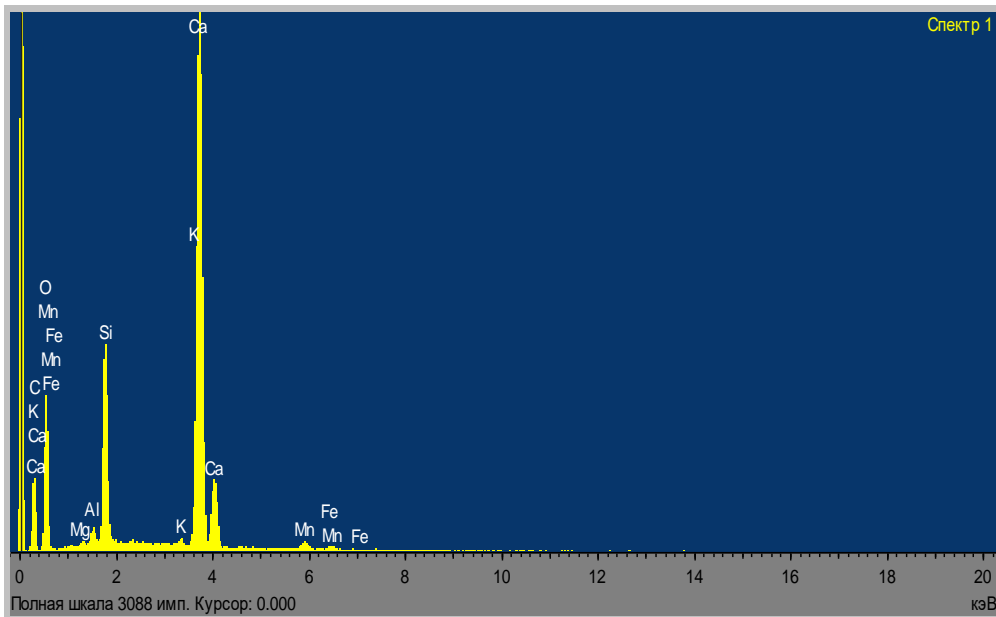


Figure 3. The sample spectrogram of the process samples of enrichment wastes of manganese ore in Ushkatyn-III deposit

Table 2. Material composition of the original sample of enrichment wastes of manganese ore

Sample	The content of components, % wt						
	MgO	Al ₂ O ₃	SiO ₂	K ₂ O	CaO	MnO	FeO
The original	0,71	2,28	28,00	0,51	65,51	2,29	0,69
enrichment wastes	±0,10	±0,42	±2,42	±0,09	±3,00	±0,26	±0,08

In the synthesis process we noted losses associated both with water allocation, and carbonates' destruction and CO₂ emission in the gas phase (Figure 4).

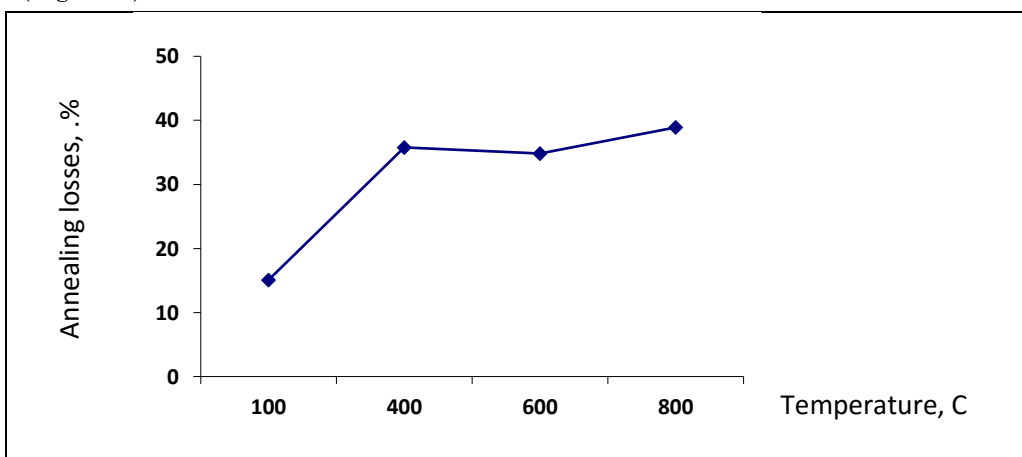


Figure 4. Samples' mass loss during the silicophosphate materials synthesis based on enrichment wastes of manganese ore in Ushkatyn-III deposit

It has been shown that the products of mechanochemical activation, as after drying at 105°C and after heat treatment at 400°C, had a high hygroscopicity and blurred on the air, which did not allow analyzing their phase composition with instrumental methods. Products, heat-treated at 600° and 800°C, was a hard, nonporous sinters of gray color.

The XFA results of silicophosphate products are shown in Figures 5-6 and Table 3, it was found that in contrast to the source samples, the MOSS product, heat-treated at 800°C, contains a certain amount of amorphous phase, as evidenced by the presence of halo in the range of 20-30 Θ (Figure 6). Moreover, the composition of crystalline phases is significantly changing with increasing annealing temperature of activation products. The main crystalline phase of the product, heat-treated at 600°C, is calcium polyphosphate $\text{Ca}(\text{PO}_3)_2$, and calcium, iron and aluminum monophosphates.

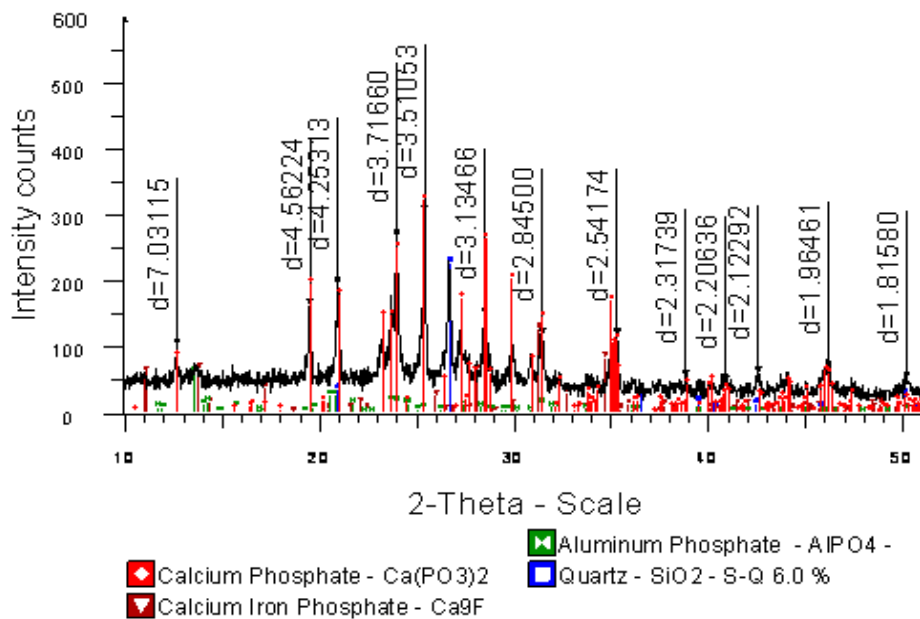


Figure 5. X-ray diffraction pattern of MOSS product of manganese ore's enrichment wastes with phosphoric acid, heat-treated at 600°C

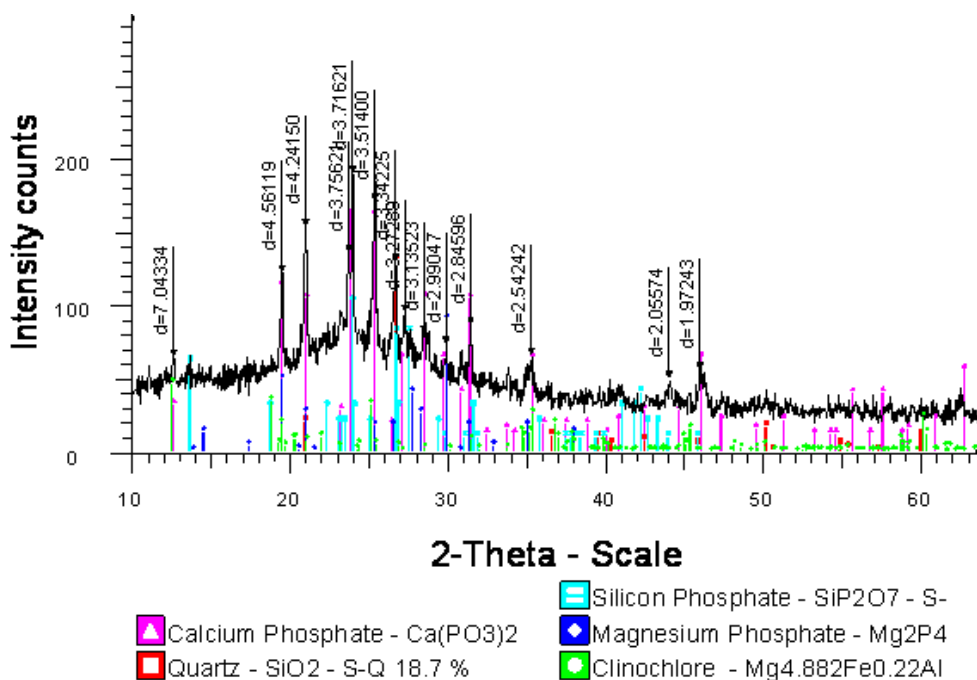
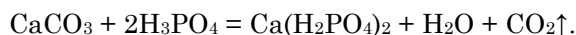


Figure 6. X-ray diffraction pattern of MOSS product of manganiferous ore's enrichment wastes with phosphoric acid, heat-treated at 800 °C

Table 3. The results of semi-quantitative X-ray phase composition of the products obtained on the base of MOSS product of manganiferous ore's enrichment wastes, heat-treated at 600° and 800 °C

Phase	The content, %	
	Annealing temperature, °C	
	600	800
Calcium polyphosphate, Ca(PO ₃) ₂	73,6	51,5
Calcium-ferrum phosphate, Ca ₉ Fe(PO ₄) ₇	12,0	-
Aluminium phosphate, AlPO ₄	8,4	-
Silicon diphosphate, SiP ₂ O ₇	-	18,3
Magnesium cyclotetraphosphate Mg ₂ P ₄ O ₁₂	-	16,2
Silica, SiO ₂	6,0	12,7
Clinocllore, Mg _{4.882} Fe _{0.22} Al _{1.881} Si _{2.96} O ₁₀ (OH) ₈	-	1,3

In the products of heat treatment at 800°C the presence of silicon phosphate SiP₂O₇ and cyclotetraphosphate magnesium Mg₂P₄O₁₂ is marked. Probably, during mechanical activation of the source of enrichment waste of manganiferous ore with phosphoric acid, proceeds the reaction:

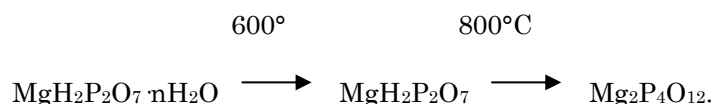


In addition, the formation of dihydrogen phosphates and other cations included in the waste composition is possible. The resulting calcium dihydrogen phosphate with increasing temperature undergoes dehydration with the formation of calcium polyphosphate (Permitina, 1984):



Magnesium dihydrogen phosphates dehydrate with the formation of cyclotetraphosphate, and aluminium and ferrum dihydrogen phosphates - with the formation of secondary phosphates.

The 1-hour heat treatment at 400°C is insufficient to remove structurally bound water, and the product is highly hygroscopic. At 600°C the process of dehydration is completed with the formation of crystalline phases, whereas further increase in temperature to 800°C may, at first, lead to a transition of the condensed phosphates, especially alkali metal) in a glassy amorphous state, and second, by further condensation of phosphates (Permitina, 1984), for example:



The study of solubility of heat-treated samples, obtained by mechanochemical activation with phosphoric acid, showed that the solubility dependence on annealing temperature has an extreme character with a minimum at 600°C (Table 4). Whereas the solubility of enrichment wastes dispersed in the dry mode (without using phosphoric acid) and annealed at the same temperatures, decreases with increasing annealing temperature (Table 4).

Table 4. Solubility of heat-treated MOSS products of enrichment wastes of manganiferous ore

Dispersion mode	The annealing temperature of the dispersion products, °C		
	400	600	800
Enrichment wastes + phosphoric acid	59,5	6,8	48,3
Enrichment wastes	7,8	4,2	2,3

The samples, dispersed in the wet mode and heat-treated at 600°C are crystal and quite porous (Figure 7), while the increase of annealing temperature up to 800°C leads to the formation of a fully glassy products, and this is confirmed by the results of electron-microscopic analyses (Figure 8).

Products of the enrichment wastes dispersion in dry mode and annealing at 800°C are crystal (Figure 9).

High solubility of MOSS products, heat-treated at 800°C, is due to not only the formation of a glass phase, but also the appearance in their structure of silicon diphosphate, since the interaction of silica with phosphoric acid proceeds already at normal temperature, especially in a wet dispersion.

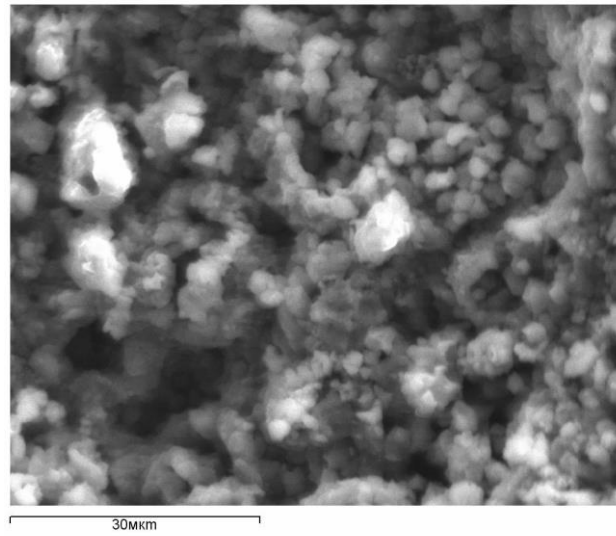


Figure 7. Electron micrograph of MOSS product of enrichment wastes in wet mode, heat-treated at 600°C

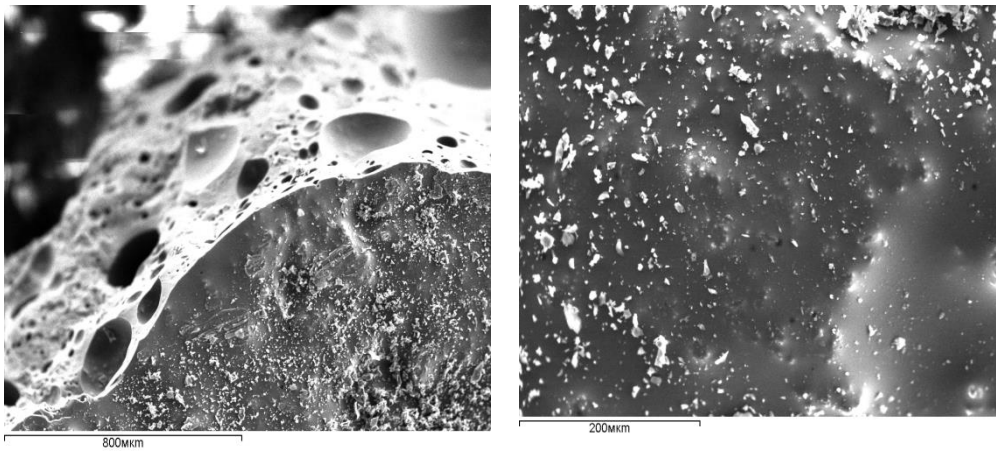


Figure 8. Electron micrograph of MOSS product of enrichment wastes in wet mode, heat-treated at 800°C

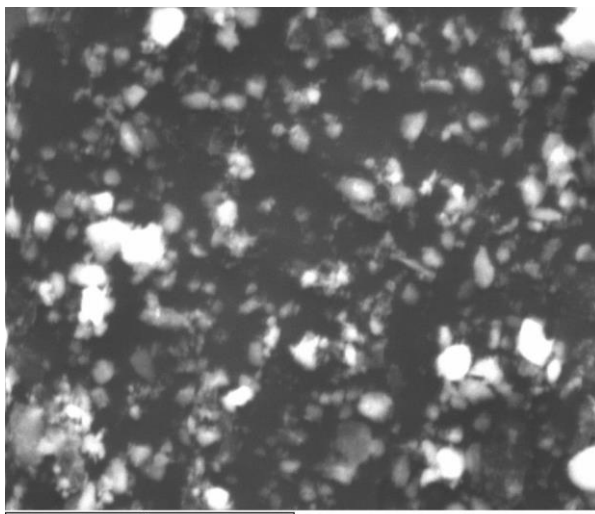


Figure 9. Electron micrograph of MOSS product of enrichment wastes in dry mode, heat-treated at 800°C

The resulting compound of silicon diphosphate SiP_2O_7 exists in two versions: water-soluble low-temperature (250-350°C) and high temperature (697°C), insoluble in water and in mineral acids. The transition of the low-temperature modification to insoluble high-temperature is carried out at 1027°C and as the temperature of annealing in our case did not exceed 800°C, the product contains soluble SiP_2O_7 , and that causes the increase of solubility.

Material composition of silicophosphate products, studied by electron microprobe analysis, is presented in Table 5.

Table 5. Material composition of thermal acid treatment products at 600° and 800°C of enrichment wastes of manganiferous ore

Temperature, °C	The content of components, % wt							
	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	K ₂ O	CaO	MnO	FeO
600	0,41	1,28	8,00	67,42±1	0,51	20,51	1,09	0,59
	±0,02	±0,42	±0,42	,16	±0,09	±3,00	±0,16	±0,08
800	0,40	1,15	8,96	66,76	0,50	20,55	1,03	0,65
	±0,01	±0,14	±0,50	±1,26	±0,06	±0,49	±0,14	±0,09

High solubility products of the enrichment wastes dispersion of manganiferous ore in the wet mode using phosphoric acid and subsequent heat treatment at 800°C allows recommending them to be used as a phosphate fertilizer materials of prolonged action, containing, in addition to the main nutrients of phosphorus and potassium, a valuable trace element such as manganese. For this purpose, we studied the kinetics of the transition into a solution of accesible forms of P₂O₅, products derived from enrichment wastes of manganiferous ore by wet-mechanochemical activation and annealed at 800°C (Table 6). For comparison, we used ground phosphate rock from Karatau deposit.

Table 6. The kinetics of the transition of accessible forms of P₂O₅ into a solution, products derived from enrichment wastes of manganiferous ore

The studied product	The content of accessible phosphates, ratio %					
	water-soluble			lemon-soluble		
	Dissolution time, hour					
	0,5	24	72	0,5	24	72
Ground phosphate rock, comparison sample	0,16	0,21	0,35	1,14	3,57	7,68
Heat-treated at 800°C MOSS product with wastes rate: H ₃ PO ₄ = 1,00:0,25	0,56	1,10	3,84	2,75	6,61	12,40
Heat-treated at 800°C MOSS product with wastes rate: H ₃ PO ₄ = 1,00:0,50	2,93	5,91	4,25	62,95	88,96	92,77

The results imply that the content of water-soluble and lemon-soluble forms in new materials obtained by dispersing a two-phase system "enrichment wastes – H₃PO₄" followed by annealing of the products at 800°C, is almost an order of magnitude higher than in the known fertilizer – ground phosphate rock. Besides, these products, as mentioned above, additionally contain elements such as potassium and manganese.

Less soluble porous crystalline silicophosphates, synthesized at 600°C after optimization of their production conditions and solubility decrease, can be used as a sorption or filtration materials for purification of water environments (Esembekova, Kubekova & Kapralova, 2016).

Discussion and Conclusion

As M.V. Chaikina (2002) in her study notes a positive effect of spar and quartz during mechanical activation of Ca₁₀(PO₄)₆(F, OH)₂ + CaCO₃ + SiO₂ system, leading to the apatite amorphization acceleration and increase in soluble forms of phosphate, we used this fact in the enrichment wastes processing of manganiferous ore by the method of mechanochemical activation in a two-phase system, "enrichment wastes - phosphoric acid" followed by heat treatment of the mechanical activation products.

It is also worth noting that unlike previously studied enrichment wastes of polymetallic (Eszhanov & Kapralova, 2013) and gold (Kubekova, Kapralova & Neverova, 2015) ores, the main components of which (80-90%) were silica and alumina-silicate compounds, the analysis of physical composition of enrichment wastes of manganiferous ores showed that they contain significant amount of calcium carbonate with a low content of silicates. E.V. Kazakova (2015) also describes similar results on the example of the Ulu-Teliak deposit study.

In the end, using the complex of physicochemical research methods, we studied the phase and mineral composition of enrichment wastes of manganiferous ore in Ushkatyn-III deposit. The results indicate that the main phase is calcium carbonate when its content exceeds 60 % wt. Silicon-containing part is represented by silicon dioxide and a small amount of silicate compounds.

Based on the studied wastes by mechanochemical activation methods in a wet mode using phosphoric acid and subsequent calcination products of dispersion at different temperatures, a number of new silicophosphate materials is obtained. The study demonstrated that their solubility is determined by the phase composition of the products and the annealing temperature. The results show that highly soluble products containing a glass phase are formed at 800°C,

and their solubility is due to not only the presence of the glass phase, but also the presence of low-temperature modification of silicon diphosphate.

Implications and Recommendations

The obtained research products may be used as phosphorus fertilizer materials of prolonged action, containing, in addition to the main nutrients of phosphorus and potassium, a valuable trace element such as manganese. In addition, these same products can be used as metal corrosion inhibitors for water environments. Poorly soluble crystalline porous silicophosphate product after acid activation can be used as a sorption or filtration material for cleaning water from various contaminants.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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