

Silicophosphate Sorbents, Based on Ore-Processing Plants' Waste in Kazakhstan

Sholpan N. Kubekova^a, Viktoria I. Kapralova^a and Shamil A. Telkov^a

^aKazakh National Research Technical University after K. I. Satpayev, Almaty, KAZAKHSTAN

ABSTRACT

The problem of ore-processing plants' waste and man-made mineral formations (MMF) disposal is very important for the Republic of Kazakhstan. The research of various ore types (gold, polymetallic, iron-bearing) MMF from a number of Kazakhstan's deposits using a complex physical and chemical methods showed, that the waste's main components are silicate and aluminosilicate compounds that can be used to produce adsorbents for fine purification of industrial and natural waters from heavy metals. According to the research, the only MMF of gold and polymetallic ores are environmentally safe for this purpose. Based on the samples, selected with thermal and acid methods, using phosphoric extraction acid, was synthesized a set of silicophosphate products. It was found, that under the optimum conditions, allowing to obtain insoluble porous products with high sorption activity, high the about 10-11 % of final product have the mechanical strength and a heat treatment temperature of 400 °C. It is shown, that the dynamic adsorption capacity of synthesized silicophosphate sorbents to copper cations is $1,85 \square 2,5 \text{ mg} = \text{Cu}^{2+}/\text{g}$. This allows conditioning of water for domestic and drinking purposes, cleaning waste water of heavy metal cations from enterprises, reduce the MMF deposits, or use the latter for the concentration of heavy metals to the level of economically viable industrial processing in the future.

KEYWORDS

Ore-processing waste, silicophosphates, sorption materials

ARTICLE HISTORY

Received 30 May 2016
Revised 11 July 2016
Accepted 19 July 2016

Introduction

The situation with technological waste in the Republic of Kazakhstan

The Republic of Kazakhstan holds the second place among the CIS countries in terms of mineral resources. Mining industry includes a considerable amount of bauxite, chromite, copper, iron, lead, manganese and zinc, such metals as beryllium, bismuth, cadmium, copper, ferroalloys, lead, magnesium, rhenium, steel, and titanium. The country produces a significant amount of other non-ferrous minerals and industrial products. Kazakhstan is rich in phosphorus raw material in the deposits of the Karatau and is one of five countries in the world, which owns 90 percent of the world's reserves of phosphorus (Yessirkepova, Missyul & Sabdenova, 2015). At the same time, mainly resource and raw material system of the Republic of Kazakhstan without any environmental restrictions led to the formation of zones and regions of high anthropogenic impacts ("National report on the state", 2011).

CORRESPONDENCE Sholpan N. Kubekova ✉ kubekova_10@mail.ru

© 2016 Kubekova, Kapralova and Telkov. Open Access terms of the Creative Commons Attribution 4.0 International License (<http://creativecommons.org/licenses/by/4.0/>) apply. The license permits unrestricted use, distribution, and reproduction in any medium, on the condition that users give exact credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if they made any changes.

At different stages of processing mineral raw materials, measurable amounts of man-made mineral formations (MMF) are produced, i.e. rock, tailings, sludge and slag - compounds and minerals not used in a commercial product. The main disposal method of the newly formed MMF is still to store them in the open air and pumping contaminated water in underground reservoirs, therefore the MMF accumulation is not reduced, so the environmental problems stay. The negative impact on the environment can be seen in the area, 10 or more times bigger than the area with waste (Nevskaya & Marinina, 2015).



Figure 1. The deposited copper ore waste of Zheksagan mining-and-metallurgical integrated works

As of the 1st half of 2015, the country has accumulated 28,015 billion tons of industrial waste. The main sources of industrial waste are the mining and metallurgical industry.

In the Republic of Kazakhstan MMF is summarized in (Government Report. (1988/1989). At the same time, due to an increase in the extracted raw ore with fine impregnation, minerals with similar physico-chemical properties, the efficiency of traditional processing technologies such as flotation, is significantly reduced ("Developments in Mineral Processing", 2000; Matis & Mavros, 1991).

Prospects of new sorption materials based on MMF

Usually, the main components of MMF are silicon compounds, allowing, in our opinion, to use them as an alternative source of raw materials in the process of producing porous silicon-containing sorbents. It is known, that the basis of most (both natural and synthetic) sorbents is a silicate matrix is built of SiO₄ tetrahedrons (Iler, 1979; Deng, 2015). However, wastes, containing clay minerals, swell in the sorption process, and as a result, filtering conditions

deteriorate and filtering liquid environments takes more time. Waste, containing quartz, has low sorption properties.

Thus, the investigation of MMF recycling possibility as waste of processing enterprises into new sorption materials is important. Solving this problem will not only improve the ecological situation in the enterprises of the regions with mining complexes, but also establish new productions and expand the range of chemical products in Kazakhstan.

Overview of producing methods for sorbents, based on silicon and aluminum oxides

Sorption processes are of great importance both for cleaning a variety of liquids and gases of impurities and the concentration technology of scattered elements. The compositions of sorption materials vary widely, but, usually, the basic compounds for the synthesis are aluminum oxides and silicon salts, phosphorus, and natural aluminosilicates (Uberoi & Shadman, 1991; "DAI Products", 2015; Gelfman et al., 2002; Gubaidulina et al., 2005; Su-Hsia & Ruey-Shin, 2002).

One of the common methods for the preparation of inorganic sorbents is mixing SiO_2 source with various additives and a subsequent hydrothermal crystallization or sintering of the resulting mixture. Thus, the authors (Pat. 6413492 USA; Pat. 6416732 USA; Sumer & Yuda, 2001) provide a method of producing synthetic aluminosilicate zeolite by mixing a source of SiO_2 and a source of Al_2O_3 (e.g., clay, kaolin, aluminum oxide or sulfate) in aqueous solution with addition of NaOH to a mixture of carbonate (or triphosphosphate) and crystallization of the sodium zeolites. The paper (Pat. 2024430 Russia) describes a method of producing silico-aluminophosphate through mixing alumina, phosphoric acid, silica, water and quaternary ammonium hydroxide, hydrothermal crystallization of the mixture, filtering, washing, drying and calcination. The aluminophosphate silicon-substituting molecular sieves were first described in 1984 and are constantly being improved (Pat. 20050090390 US). The members of this new class of silico-aluminophosphate material have a three-dimensional crystal framework structure of PO_4^{2-} , AlO_4^{2-} and SiO_4^{2-} tetrahedral fragments and have high sorption characteristics. (Shilina & Milinchuk, 2010; Marchenko et al., 2002) At the same time, the preparation of such sorbents requires expensive organic, organometallic reagents and complex equipment, including autoclaves and time (up to 15 days) to obtain the final product. All this eventually leads to a significant increase in the cost of synthetic adsorbents.

It should be emphasized that as a source of silica and alumina, most authors use either pure salts and oxides, or natural, clay minerals generally. To date, the scientific literature has no information on the use as a source of silicon and aluminum-containing materials to produce sorbents out of ore-processing waste, which will not only significantly reduce the production cost, but also improve the ecological situation in the industrial regions.

The purpose of this study is to investigate the possibility of using MMF of different types of ore Kazakhstan's deposits as a silicon-containing raw material in the preparation of silicophosphate materials.

The work tasks included:

- study the phase and substance MMF composition of various ore types of some Kazakh deposits;
- select promising MMF samples as silicon sources;
- synthesize silicophosphate materials in selected samples and show the possibility of their use as sorbents for wastewater treatment from heavy metal cations.

The research results presented in this paper are found as a part of a research project, funded by the Ministry of Education and Science of the Republic of Kazakhstan under the grant №757.MON.GF.15.RIPR.43 on the topic: “Technology development for recycling non-ferrous metal ore into silicophosphate sorption materials in Kazakhstan” issued by Kazakh national technical University named after K.I. Satpayev.

Materials and methods

Research objects

As the objects of the study were used MMF of various ore types of some Kazakh deposits, namely: gold ore (sample №1), polymetallic ore (sample №2) and iron-ore (sample №3).

Research methods

Phase composition of ore-processing waste was studied through X-ray diffraction with an automated DRON-3 diffractometer with $\text{Cu}_{K\alpha}$ -radiation, β -filter. X-ray analysis was performed based on semi-quantitative diffraction patterns of powder samples using the method of equal test portions and artificial mixtures. Interpretation of diffraction patterns was performed using the ICDD data files, database data PDF2 diffractometric powder diffraction patterns and minerals, clean of impurities.

The investigation of the chemical MMF composition of different ore types was conducted by electron microprobe analysis (EDX) using a JEOL-733 electron microscope firm X-ray analyzer.

To determine the solubility of the synthesized adsorbents, authors took 1g of sample, taken to the nearest 0.0001 g, dissolved it in 100 ml of distilled water and stirred in a shaker for 30 min. Then the solution was filtered, dried and the insoluble sorbent was weighed.

Studies of the material's porous structure were performed through mercury porometry. To determine the sorption capacity of the synthesized porous silicophosphate product, were prepared copper sulfate (CuSO_4) model solutions of “pure for analysis” reagent on distilled water. The research was conducted through the dynamic method, in a column with a diameter of 5 mm and a height of 150 mm, charged with about 0.5 g of the synthesized sorbent. Through a column was passed the CuSO_4 model solutions; researchers spectrophotometrically analyzed the flowing fluids on Cu^{2+} cations content through the formation of a colored complex with sodium diethyldithiocarbamate (Uddin et al., 2014).

Methods of obtaining

Authors used acid-thermal method to obtain silicophosphate porous materials based on ore-processing waste MMF.

First, according to the results of the analysis on the contents of oxygen-bearing components, number of extraction phosphoric acid (H_3PO_4) of domestic production was calculated. Mixing raw materials with 40-42% H_3PO_4 solution (density 1.2 g/cm³) was performed at a ratio of MMF : H_3PO_4 from 10: 1 to 10: 2, to receive pasty material. The wet paste was forced through an extruder, the resulting precursor grains were dried for one hour at 105°C, and then calcined at temperatures of 400, 600 and 800°C for 1 hour.

Results

X-ray diffraction results show that the mineral composition of gold ore MMF includes quartz SiO_2 (95,4 %), muscovite $KAl_2(AlSi_3O_{10})(OH)_2$ (3.6 %) and goethite $FeO(OH)$ (1 %). The polymetallic ore MMF mostly consists of various aluminosilicates: montmorillonite, $(Na, Ca)_{0,3}(Al, Mg, Fe)_2Si_2O_{10}(OH)_2 \cdot nH_2O$ (51,4 %), kaolinite $Al_2(Si_2O_5)(OH)_4$ (22.0 %), muscovite $KAl_2(AlSi_3O_{10})(OH)_2$ (6.7 %), quartz (11.8%), as well as carbonates in the form of dolomite, $CaMg(CO_3)_2$ (4.1 %) and calcite (3.9 %). The main phase in the iron ore MMF is goethite $FeO(OH)$ (41,5 %), as well as quartz (39 %), calcite $CaCO_3$ (19,0 %) and the CdI_2 trails.

To get more informative data on the chemical composition, the corresponding MMF samples were subjected to EDX-analysis, the results of which are presented in Table 1. EDX-analysis showed that iron ore waste includes not only cadmium iodide, but also barium compounds. The presence of cadmium and barium compounds in waste can be attributed to the use of heavy suspensions in processing this ore. Since the salts of these metals are toxic, the use of iron ore MMF as a precursor for the synthesis of silicophosphate sorbents is undesirable. Therefore, further experiments used only MMF of gold and polymetallic ores as a raw material for sorbents: the sample №1 and the sample №2 respectively.

Table 1. The original chemical composition of different ore types of MMF in Kazakhstan based on the EDX data - analysis

Sample No.	Component content in relation to oxides, wt.%										
	SiO_2	Al_2O_3	Fe_2O_3	K_2O	CaO	MgO	TiO_2	ZnO	CdO	I	BaO
1	81,52± 0,81	10,14± 0,21	3,85± 0,54	3,45± 0,19	0,00	0,70± 0,09	0,00	0,00	0,00	0,00	0,00
2	63,58± 1,17	17,76± 0,57	5,66± 0,28	3,05± 0,07	3,60± 0,09	4,91± 0,33	0,46± 0,07	0,98± 0,09	0,00	0,00	0,00
3	31,21± 3,03	9,58± 0,51	39,46± 1,65	1,29± 0,14	7,96± 0,35	0,79± 0,08	0,57± 0,16	0,00	1,59± 0,21	4,39± 0,19	2,21± 0,17

The chemical composition analysis results (Table 1) show that the main components of oxygen-bearing MMF is alumina, potassium, alkaline earth metals and iron oxides. According to the content of these components the amount of phosphoric acid for synthesis was calculated, based on the molar ratio $MeO_x / P_2O_5 = 1$ (in dihydrogenphosphate) and $MeO_x / P_2O_5 = 2$ (in hydrogenphosphates). It was found, that silicophosphate synthesis at the molar ratio of the starting components $MeO_x / P_2O_5 = 1$ requires a large energy consumption for the evaporation of the liquid phase, and the resulting products have high solubility, which limits their possible use as sorbents. Therefore,

further we studied the properties of the products obtained at a molar component ratio of $\text{MeO} / \text{P}_2\text{O}_5 = 2$.

X-ray analysis of two types of the synthesized silicophosphates showed no long-range order for phosphorus phases in the temperature range studied. The composition of silicophosphate crystalline phases, obtained from the sample №1, does not depend on synthesis temperature and is close to the raw material (96.2 % Silica and 3.8 % Muscovite). At the same time, the product's synthesis temperature change based on polymetallic ore waste (sample №2) from 400°C to 800°C substantially alters the composition of the crystalline phase (Table 2, Fig. 2). As it can be seen from Table 2, at 800 °C the complete decomposition of aluminosilicates of kaolinite, muscovite, albite occurs, that may be explained by the interaction of the ions Al^{3+} , K^+ , Na^+ with phosphate ions, as well as crystallization of the unbound SiO_2 in the form of stable cristobalite and tridymite.

Table 2. Phase contents of silicophosphate products, synthesized based on polymetallic ore MMF after thermal treatment at various temperatures

Phase	Phase content, wt.% after thermal treatment at	
	400 °C	800 °C
Quartz SiO_2	44,7	35,1
Cristobalite SiO_2	0,0	32,1
Tridymite SiO_2	0,0	25,7
Kaolinite $\text{Al}_2(\text{Si}_2\text{O}_5)(\text{OH})_4$	32,0	0,0
Muscovite $\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$	8,9	0,0
Albite $\text{Na}(\text{AlSi}_3\text{O}_8)$	7,4	0,0
Orthoclase KAlSi_3O_8	7,0	7,1

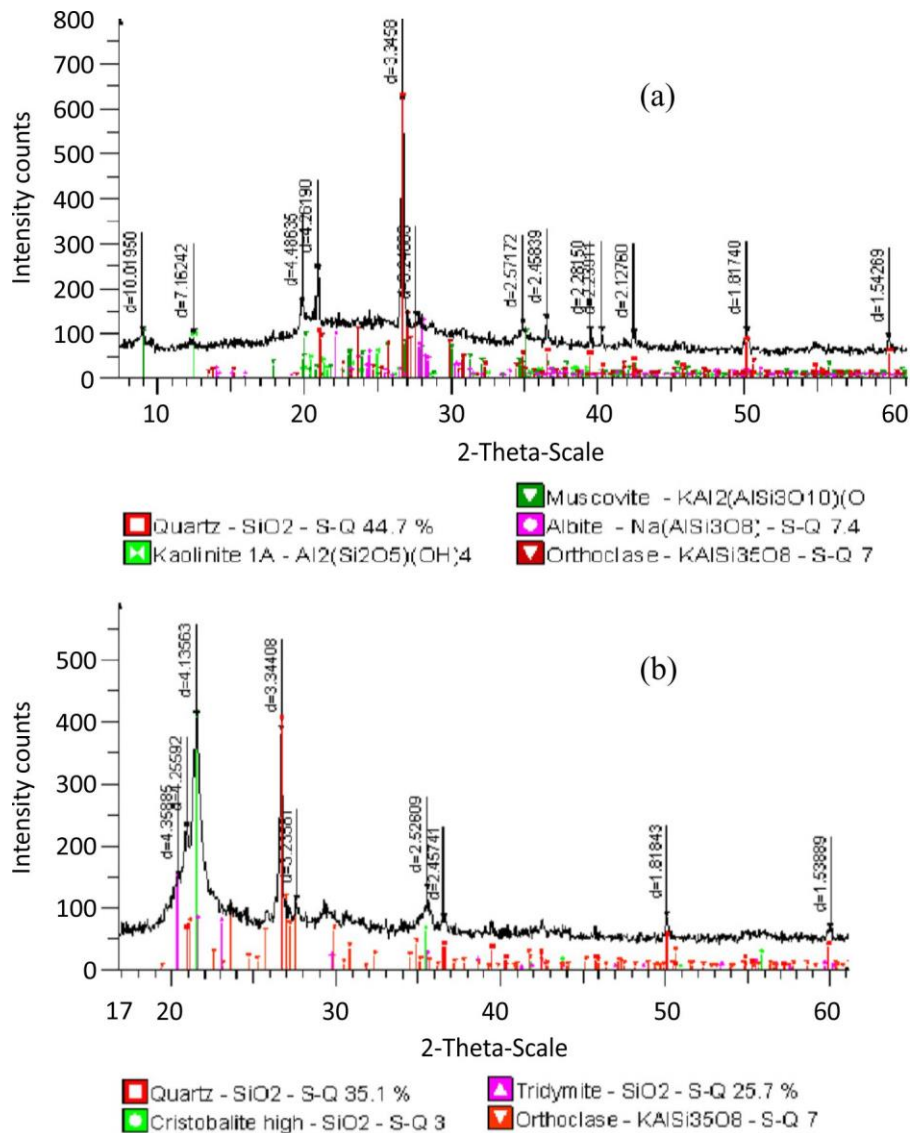


Figure 2. Diffractograms of silicophosphate products, synthesized based on polymetallic ore waste at 400 °C (a) and 800 °C (b)

Chemical composition of silicophosphate products from MMF samples №1 and №2 after heat treatment at 400 and 800°C, based on the EDX-analysis, is shown in Tables 3 and 4. Despite the different contents of aluminum, magnesium, silicon in both cases, the phosphorus content remains virtually the same (10,4 – 11,5 %).

For sorption materials used for water treatment, an important indicator is the stability during operation, i.e., the ability to maintain a constant composition in water. Synthesis temperature research on the solubility of the obtained products (Figure 3) showed that practically insoluble silicophosphate materials are synthesized at a temperature of 400°C. With increasing temperature an increase in the solubility of the products obtained; still, the silicophosphate solubility, obtained from polymetallic ore MMF throughout the

temperature range studied (except 400°C), is higher than the sample, prepared based on gold ore MMF. Solubilization of the first is probably due to the reaction of phosphoric acid with clay and micaceous minerals causes their degradation to form a soluble metal monophosphates, which are converted into poorly soluble condensed phosphates with the temperature rise to 400°C. The increased synthesis temperature to 600°C and especially up to 800°C probably leads to the translation of condensed phosphates of alkali metals (present in the starting waste samples) into vitreous, more soluble forms.

Table 3. The chemical composition of the synthesized silicophosphate products based on gold ore MMF (sample №1) after heat treatment at different temperatures

T, °C	Elements content, wt.%							
	O	Mg	Al	Si	P	K	Fe	total
400	53,72	0,30±	3,89±	27,27±	10,49±	2,04±	2,29±	100,00±
		0,28	0,03	0,20	0,59	0,32	0,15	0,10
800	53,76	0,33±	3,97±	27,25±	10,41±	1,99±	2,30±	100,00±
		0,22	0,05	0,20	0,49	0,30	0,07	0,21

Table 4. The chemical composition of the synthesized silicophosphate products based on polymetallic ore MMF (sample №2) after heat treatment at different temperatures

T, °C	Elements content, wt.%									
	O	Mg	Al	Si	P	K	Ca	Ti	Fe	Zn
400	54,25	2,12±	6,47±	19,32±	10,86±	1,79±	1,64±	0,24±	2,82±	0,50±
		0,19	0,28	0,33	0,43	0,08	0,09	0,14	0,10	0,21
800	53,15	2,03±	6,21±	19,78±	11,49±0	0,46±0	1,80±	0,24±	3,21±	0,36±
		0,22	0,12	0,35	,67	07	0,72	0,03	0,07	0,14

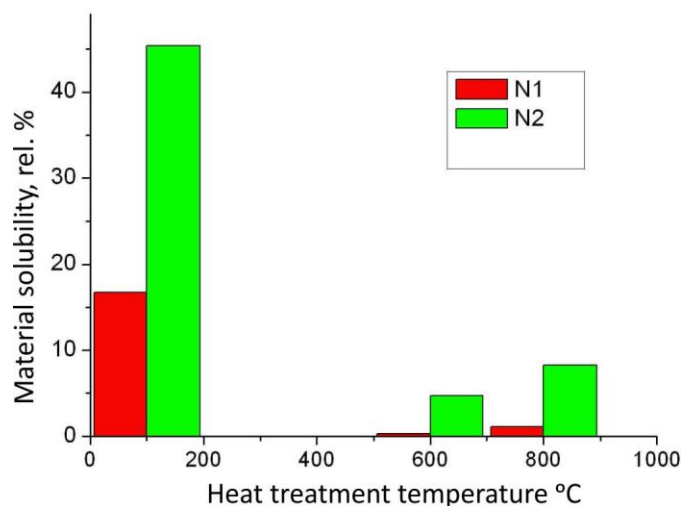


Figure 3. The influence of thermal treatment temperature of silicophosphates on solubility

This assumption was confirmed by electron micrographs of the synthesized sample surface (Figure 4). Samples, obtained at 400°C, based on both gold ore MMF (Figure 4a.) and polymetallic ores (Figure 4c.) are crystalline, with a free porous space in a form of labyrinth of widenings and narrowings of various shapes from 0.2 to 50 microns. Still, with temperature increase up to 800°C, sample №1 (based on gold ore MMF) becomes more dense, with observed glassy

needle formations (Figure 4b); even more glass phase is observed at the surface of sample №2 (polymetallic ore-based MMF (Fig. 4d).

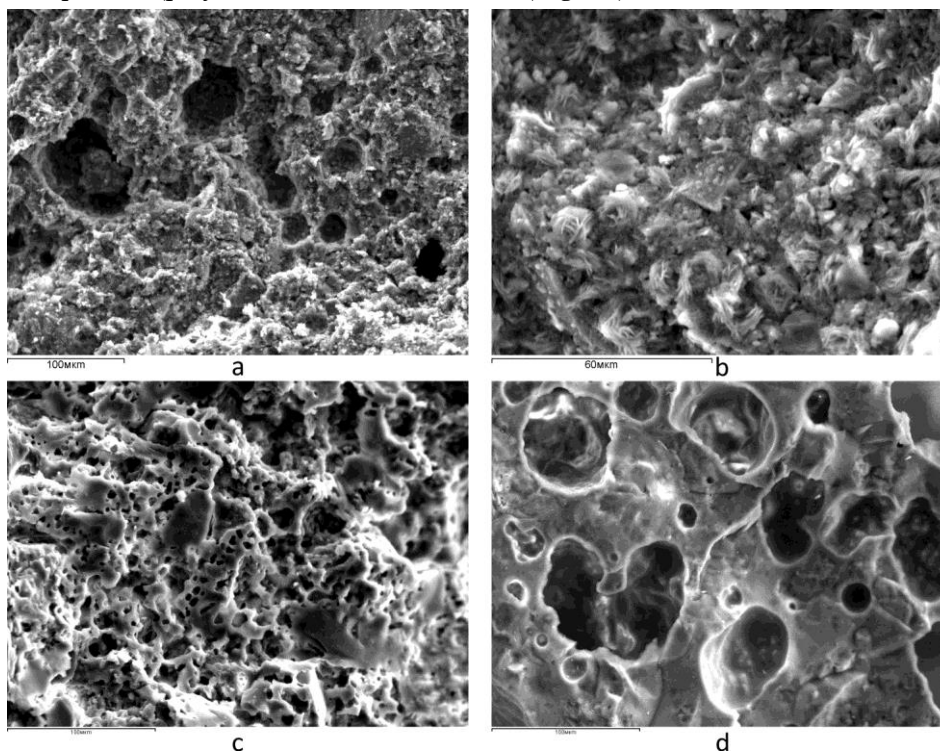


Figure 4. EM images of silicophosphates, synthesized from gold ore waste at 400°C (a) 800°C (b) and silicophosphates from polymetallic ores at 400°C (c) and 800°C (d).

Investigations of the porous structure of the two types of samples correlate well with the solubility data (Figure 3). Products, synthesized at 400°C, have a large total share of long pores and high surface activity, reaching in the case of gold ore waste utilization the quantities of 170 m²/g. At higher synthesis temperatures, sinters with more dense structure appear, resulting in the natural reduction of specific surface area and total pore volume, so the sorption properties decrease as well. Thus, insoluble silicophosphate porous materials may be obtained by acid-thermal treatment of gold and polymetallic ore waste at a molar ratio of the components, based on acid-absorbing oxides equal to phosphorus pentoxide MeOx / P₂O₅ close to 2: 1 and a temperature of 400°C. Nevertheless, Si / P ratio remains in the range 1.7 ÷ 2.6.

Aside from solubility was studied the dependence of total pore volume and specific surface of obtained samples by the synthesis temperature (Table 5), and the authors found, that the maximum porosity is observed for the silicophosphates, synthesized based on both gold and polymetallic ore waste at 400°C.

In testing the sorption properties of the abovestated silicophosphate products it was found, that the dynamic sorption capacity of silicophosphate, obtained from gold ore waste at the temperature of 400°C was 2.25 mEq Cu²⁺/g, and for polymetallic ore waste the dynamic sorption capacity was 1.85 mEq Cu²⁺/g.

Table 5. The dependence of total pore volume and specific surface of the obtained silicophosphate types from the synthesis temperature

<i>Initial feed contents</i>	<i>Synthesis temperature, °C</i>	<i>Total pore volume, cm³/g</i>	<i>specific surface, m²/g</i>
sample №1 + H ₃ PO ₄ (Si/P = 2,6)	400	0,209	170,5
	600	0,165	74,5
	800	0,103	11,4
sample №2 + H ₃ PO ₄ (Si/P = 1,7)	400	0,171	81,4
	600	0,133	15,7
	800	0,127	12,3

Conclusions

The authors studied the mineral, phase and chemical MMF composition of various ore types of some deposits of the Republic of Kazakhstan, and determined a set of environmentally-hazardous waste for the production of sorbents. Paper demonstrates the principal possibility of their use as a source of silicon oxide in the synthesis of silicophosphate sorbents. The initial silicon content of the waste in the form of silica or any silicate and aluminosilicate compounds may be 65-96% (based on SiO₂). The amount of added phosphoric acid, allowing to create porous products with high sorption activity, in the phosphorus content of the final product is about 10-11 %. A major role in obtaining sorbent plays the thermal treatment temperature, affecting both the solubility and the porosity, as well as the product's specific surface and its mechanical strength. The optimal synthesis temperature treatment is at 400°C. With the growth of the synthesis temperature, increases the solubility of silicophosphate materials through the formation of X-ray amorphous polyphosphate compounds.

The dynamic sorption capacity of silicophosphates was obtained based on gold ore waste in relation to the copper cations was 2.25 mEq Cu²⁺/g, and for polymetallic ore waste – 1,85 mEq Cu²⁺/g. This correlates with the study results of a specific surface of samples and allows synthetic materials to be used as sorbents in the process of cleaning the natural and waste waters from heavy metal cations. Waste processing will undoubtedly lead to improve environmental conditions both at ore-processing plants and regions.

Using ore-processing waste as a source of silicon oxides will reduce the cost of materials and silicophosphates production and exclude such technological operations as chemical vapor deposition, hydrothermal crystallization mixture, filtration, flushing from the obtaining process. The relatively low, up to 400°C, silicophosphate processing temperatures can reduce production costs at an industrial scale. It is also economically reasonable to use the available locally made products, along with MMF, i.e. wet-process phosphoric acid by “Kazphosphate” (Government Report, 2016). “Kazphosphate” plans to increase its production of phosphate fertilizer to 1 million tons by 2020, expanding the world product markets (24, 25). When the content of phosphorus in the synthesized sorbents is about 10.5 %, the equivalent proportion of phosphoric acid is about 30-31 %, which allows to estimate the unit cost.

It should be noted that the studies, which have shown the ability to produce silicophosphate sorbents based on the regional MMF ore that may be used in the purification of natural and waste waters from industrial heavy metal cations are the pioneer ones. In the future, the authors of the study plan a detailed study,

depending on the technological and sorption properties of developed materials from their composition, their producing conditions, the comparison of the sorption capacity of other toxic substances, as well as the study of sorption mechanisms.

Disclosure statement

No potential conflict of interest was reported by the authors.

Notes on contributors

Sholpan N. Kubekova is a PhD, Associate Professor at the Department of Applied Chemistry, Kazakh National Research Technical University after K. I. Satpayev, Almaty, Kazakhstan.

Viktoriya I. Kapralova is a Doctor of Engineering, Associate Professor at the Department of Applied Chemistry, Kazakh National Research Technical University after K. I. Satpayev, Almaty, Kazakhstan.

Shamil A. Telkov is a PhD, Associate Professor at the Department of Metallurgy of Precious Metals and Mineral Processing, Kazakh National Research Technical University after K. I. Satpayev, Almaty, Kazakhstan.

References

- Deng, S. (2015). Sorbent Technology. *Encyclopedia of Chemical Processing*, 2825-2845.
- Developments in Mineral Processing. (2000), *13 Proceedings of the XXI International Mineral Processing Congress*. July 23-27. Rome, Italy. Elsevier Science, Amsterdam, 364-369.
- Dinamic Adsorbents, Inc. (2015, March 15). *DAI Products. More about Adsorption, Desiccants and Sorbents*. Direct access: <http://dynamicadsorbents.com/products2.htm>
- Gelfman, M. I., Tarasov, Yu., Shevchenko, T. & Mandziy, M. R. (2002). The study of sorption characteristics of natural and modified sorbents based on silica-alumina raw material. *Chemical Industry*, 8, 50 – 56
- Government Report. (1988). *The inventory of resources and prospects of complex use of non-ferrous metal waste products*. Almaty, Kazakhstan, 64 p.
- Government Report. (1989). *The inventory of resources and prospects of complex use of ore and waste ferrous metals*, Almaty, Kazakhstan, 54 p.
- Government Report. (2016). *Plans for the development of the production of mineral fertilizers on the branches of LLP "Kazphosphate" 2016-2020*, Almaty, Kazakhstan, 36 p.
- Gubaidulina, G. M., Fishbein, O., Kapralova, V. I., Zhakitova, G. U. & Zhusupova, L. A. (2005). Optimization of technological parameters and conditions of silico-aluminophosphate sorbents. *Science News of Kazakhstan. Science & Technology Digest*, 2(85), 66-71.
- Iler, R. K. (1979). *The Chemistry of Silica: Solubility, Polymerization, Colloid and Surface Properties and Biochemistry of Silica*. Wiley-Interscience.
- Marchenko, L. A., Bokovikova, T. N., Poluliakhov, N. N., & Privalov, N. M. (2002). Sorption extraction of heavy metal ions in filtering wastewater through the activated aluminosilicate adsorbent. *Nature. and tehn. science*, 2. 36-38.
- Matis, K. A., & Mavros, P. (1991). Froth Lotation Part II. Removal of Particulate Matter. *Separation and Purification Methods*, 20(2), 163-198.
- National report on the state of the environment and use of natural resources for the 2011 - 2014 years (2011). Direct access: http://hdr.undp.org/sites/default/files/reports/271/hdr_2011_en_complete.pdf
- Nevskaya, M. A & Marinina, O. A. (2015). Regulatory Aspects of Mining Waste Management in the Russian Federation. *Biosci. Biotechnol. Res. Asia*, 12(3), 174-184.
- Pat. 20050090390 US, A1. Pub.No 27.10.2003, Pub.dat. Apr. 28. 2005 N. Venkatathri et al. Process for the preparation of porous crystalline silicoaluminophosphate molecular sieves.

- Pat. 2024430 Russia, A method of producing crystalline silico-aluminophosphates: 1994. IPC5 of 01 B 33/26 / S.P. Zhdanov, Feoktistov N.N., Smirnova E.I., Vasilyeva E.A.; Institute of Silicate Chemistry of the Academy of Sciences of the USSR. Ann. 26.06.91. Publ.15.12.94.№2
- Pat. 6413492 USA, Method of forming high aluminum aluminosilicate zeolites : IPC7 C 01 B 39/02% C 01 B 39/14; Engelhard Corp., Kuznicki Steven M., Langner Tadeusz W., Curran Jacqueline S., Bell Valerie A. - N 09/533606; Ann. 23.03.2000; Publ. 02.07.2002; CIS 423/700.
- Pat. 6416732 USA, Method of forming aluminosilicate zeolites : IPC7 C 01 B 39/02% C 01 B 39/18; Engelhard Corp., Curran Jacqueline S., Bell Valerie A., Kuznicki Steven M., Langner Tadeusz W. - N 09/533707; Announced 23.03.2000; Published 09.07.2002; CIS 423/700.
- Shilina, A. S. & Milinchuk, V. K. (2010). The sorption purification of natural and industrial waters from cations of heavy metals and radionuclides, a new type of high temperature aluminosilicate adsorbent. *Sorption and chromatographic processes*, 10(2), 237-245
- Su-Hsia, Lin, & Ruey-Shin, Juang. (2002). Heavy metal removal from water by sorption using surfactant-modified montmorillonite. *Hazardous Mater*, 92(3), 315-32
- Sumer, O. & Yuda, Ju. (2001). Synthesis of crystalline ZSM-5 type zeolites utilizing primary monoalkylamines. 1. Characterization. *Energy Sources*, 23(5), 475-485.
- Uberoi, M., & Shadman, F. (1991). Fundamentals of Heavy Metal Removal with Dry Sorbents. *New York. Symposium on Clean Energy*, 1742-1749.
- Uddin, M. N., Shah, N. M., Hossain, M. A., & Islam, Md. M. (2014). Copper and Mercury in Food, Biological and Pharmaceutical Samples. *American Journal of Analytical Chemistry*, 5, 838-850
- Yessirkepova, A. M., Missyul, E. E., & Sabdenova, Zh. O. (2015). The Level of Development of the Industrial Sector in Kazakhstan as a Major Source of Waste. *The virtual project of the IX Astana Economic Forum*, 114-120.