UDC 661.632

S.T. Tleuova, A.N. Tileuberdi, M.M. Ulbekova, A.S. Taubaeva, G.S. Zhusupbek*
Cand.Tech.Sci., Professor, M.Auezov South Kazakhstan Research University, Shymkent, Kazakhstan
PhD, senior lecturer, M.Auezov South Kazakhstan Research University, Shymkent, Kazakhstan
lecturer, M.Auezov South Kazakhstan Research University, Shymkent, Kazakhstan
PhD, senior lecturer, M.Auezov South Kazakhstan Research University, Shymkent, Kazakhstan
doctoral student, M.Auezov South Kazakhstan Research University, Shymkent, Kazakhstan
***Corresponding author's email:** gul_dana_93@mail.ru

INVESTIGATION OF THE PHYSICO-CHEMICAL FEATURES OF A PHOSPHOROUS AGGLOMERATE USING PHOSPHATE-SILICEOUS SHALES AND OIL WASTE

Abstract

The article presents the results of the physico-chemical features of phosphorous agglomerates obtained by agglomeration firing of phosphorous fines with the addition of phosphate-siliceous shales and petroleum coke. IR spectrometric, X-ray fluorescence, microstructural, and element-by-element analyses of the initial and obtained materials were used to study the initial phosphate-siliceous shale and firing products. The IR spectrum of the Janatas phosphate-siliceous shale is characterized by a wide band in the range of 3400-3700 cm^{-1} corresponding to ν(O–H). The group of intense bands 1010-1058 cm^{-1} is caused by the asymmetric stretching of the ν(Si–O–Si) structural elements of silica. In the region 667-789cm^{-1}, ν(Si–O–Al) and ν(Si–O–Si) deformation vibrations of the aluminosilicate phase are detected. The IR spectra of the firing product at a temperature of 1100°C are represented as a phosphate-silicate composite in which a "matrix" (Ca–P) is combined with a glassy phase (Si–O–Al). Microstructure and element-wise composition of the batch firing product phosphate:phosphate-siliceous shales:coke:oil slage at a ratio of 65:26:6:3 is characterized by the main cementing component in the form of lamellar calcium phosphate, represented by aggregates of thin crystalline plates. The detected content of Si (9.18%) and Al (2.10%) indicates the formation of aluminosilicate minerals represented by elongated or spherical hydrosilicate aggregates.

Keywords: phosphorous agglomerate, phosphate-siliceous shale, petrocox, phosphate-silicate composite, glass phase, X-ray fluorescence spectrum, oil sludge.

Introduction

The traditional agglomeration firing of phosphorous fines provides dehydration, decarbonization and partial de-fluorination of the ore with hardening of the agglomerate due to high-temperature treatment [1-2]. The addition of silicon-containing rocks and hydrocarbon wastes can significantly affect the physico-chemical properties of the charge and the course of reactions during sintering. However, to date, the complex kinetics of phosphorite agglomeration in the simultaneous presence of phosphate-siliceous shale and hydrocarbon waste has not been sufficiently studied. This determines the relevance of the present study [3-5]

Methodology of the experiment

To determine the physico-chemical features of the obtained phosphorous agglomerates using phosphate-siliceous shale and petrocox, we performed an IR spectrometric analysis of the initial phosphate-siliceous shale.

Results and discussions

The IR spectrum of the Janatasa phosphate-siliceous shale shows the following characteristic absorption bands. A wide band in the range of 3400-3700 cm⁻1 corresponds to the ν(O–H) stretching vibrations of hydroxyl and water molecules adsorbed in the interlayer and interstitial positions of the silicate mineral. The bonds of the groups ν(Si–O⁻Al) and ν(Si–O–Si) and deformation vibrations of the aluminosilicate phase were determined in the region 667-789cm^{-1} (Figure 1).

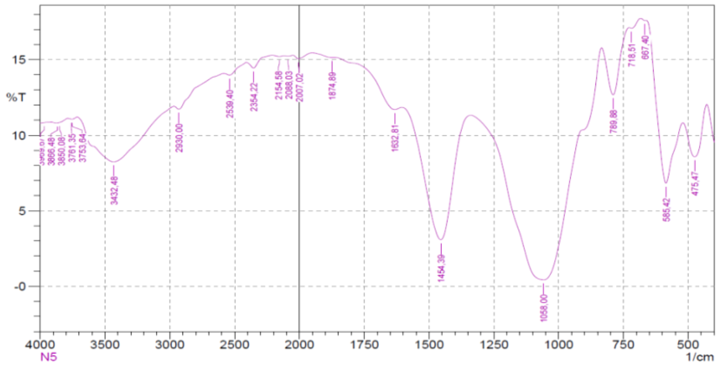

Fig 1. IR spectrogram of phosphate–siliceous shale of the Janatas deposit

The X-ray fluorescence spectrum of the phosphate-siliceous shale of the Janatas deposit reflects the complex mineral composition of the sample and confirms the presence of a wide range of chemical elements characteristic of silicate-phosphate rocks. The spectrogram shows intense peaks in the range up to 5 keV, corresponding to the lines Mg, Al, Si, K and Ca, indicating the dominance of silicate and aluminosilicate phases with an admixture of calcium. The pronounced Ca-Ka and Ca-Kß signals confirm the presence of calcium-containing minerals such as calcium phosphates and carbonates, which form the basic mineral matrix of the rock.

In the range of 10-15 keV, lines of heavy elements such as Pb and U, as well as As, are observed, which indicates the presence of impurity phases and trace elements in the shale that can affect the environmental and technological characteristics of the raw material. The characteristic peaks of Fe-Ka and Fe-Kß confirm the presence of iron oxides and silicates involved in the formation of the aluminosilicate structure. The presence of Ti and V indicates the presence of minor minerals characteristic of phosphate-silicate systems of sedimentary origin (Figure 2).

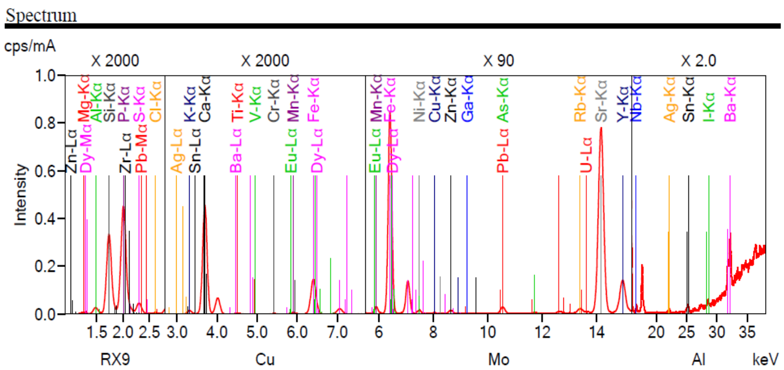

Fig. 2- X-ray spectrogram of phosphate-siliceous shale of the Janatas deposit

Spectrum analysis demonstrates that the investigated phosphate-siliceous shale is a multicomponent system, including calcium phosphates, aluminosilicates, iron oxides, as well as impurities of heavy metals. This confirms its complex geochemical nature and determines the need to use combined heat treatment and agglomeration technologies to effectively involve this type of raw material in processing. The results obtained indicate that Janatas shales can be used as an active component in charges for sintering low-grade phosphorites, providing both fluxing properties and additional introduction of a silicate phase that increases the mechanical strength of the agglomerate.

IR spectroscopic analysis of petrocox shows a characteristic spectrum of organocarbon material with the presence of functional groups of an oxygen-containing nature and traces of mineralized impurities. In the region of 3400-3600 cm^{-1}, a weakly pronounced band is recorded, corresponding to the valence vibrations of Oh groups, which indicates the presence of moisture or hydroxyl fragments retained on the surface of the coke residue. The absorbances in the 2850-2950 cm⁻1 zone reflects valence vibrations of C–H bonds in methyl and methylene groups, indicating partially preserved aliphatic fragments of organic matter (Figure 3).

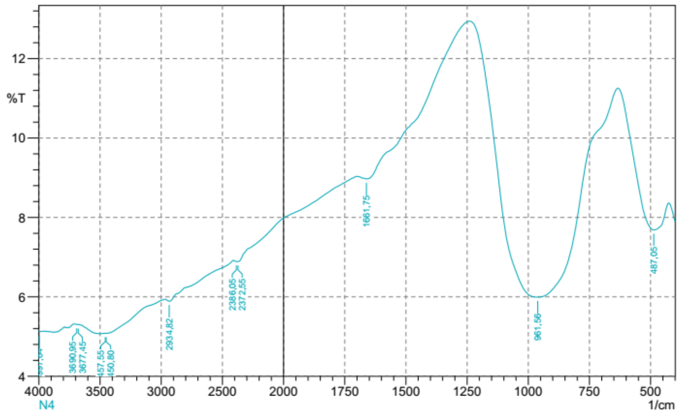

Fig 3. IR spectrogram of a sample of petroleum coke

In the region of 1600-1650 cm^{-1}, there is a band associated with fluctuations of the C=C aromatic type, which is a key indicator of the predominance of polycyclic aromatic structures in petroleum coke. The presence of signals in the region of 1100-1250 cm^{-1} indicates the presence of C–O bonds associated with esters or phenolic components, which confirms the incomplete removal of oxygen-containing organic residues during coking. Fluctuations of Si⁻O and Al–O are recorded in the low–frequency zone of 470-600 cm—1, which is associated with mineral impurities - silicates and alumina inclusions inherited from the source oil.

X-ray fluorescence analysis of the petrocox revealed its complex elemental composition, which reflects both the organic nature of the initial carbon-containing material and the presence of mineral impurities. The spectrogram clearly shows intense peaks in the low–energy range of 1.5-4.0 keV, corresponding to the Mg, Si, K, and Ca lines, which confirms the low-intensity peaks of silicate and calcium-containing phases characteristic of the initial petroleum raw materials. The presence of Fe-Ka and Fe-Kb peaks in the region of 6.4–7.1 keV indicates the content of iron-containing compounds, mainly oxides, which can play a significant role in the processes of catalytic interaction during the heat treatment of petroleum coke (Figure 4).

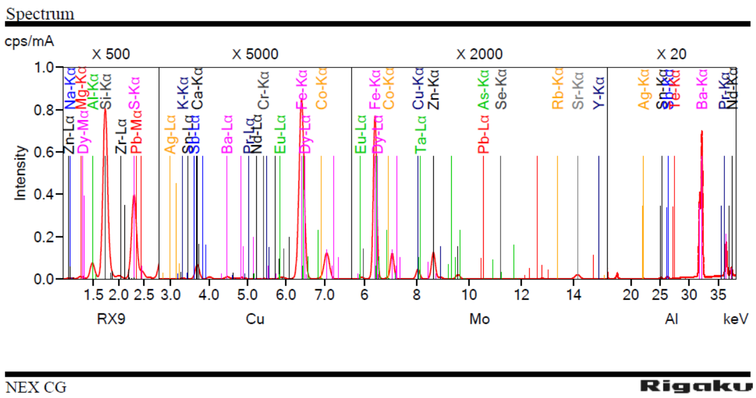

Fig 4. X-ray spectrogram of a sample of petrocox

The Ti and V signals characteristic of residual impurities in heavy oil fractions were also detected in the spectrum. The presence of Sr, Ba and Pb indicates the presence of trace elements, which is typical for petroleum cokes obtained from asphaltene fractions with a high content of organometallic compounds. Special attention should be paid to the detection of U and rare earth element (Dy, Eu, La) signals, which indicates the possibility of the presence in the oil coke of traces of geochemically stable impurities from the feedstock.

The results of the IR spectrogram of the charge firing product low-grade phosphorite – phosphate-siliceous shale – coke – oil sludge at a temperature of 1100^0C and a duration of 60 minutes are shown in Figure 5, which is characterized by a number of absorption bands associated with changes in the main functional groups formed during high-temperature firing.

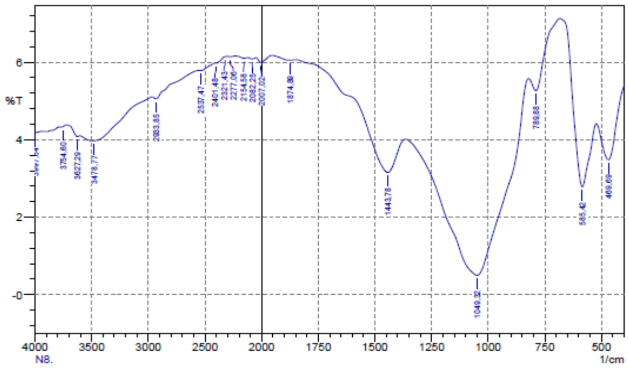

Fig. 5. IR spectrogram of the batch firing product low–grade phosphorite - phosphate-siliceous shale – coke – oil sludge

IR spectroscopic analysis of the firing product of the charge, including low-grade phosphorite, phosphate-siliceous shale, coke and oil sludge, revealed the formation of a complex multiphase structure due to thermochemical interactions between the organic and mineral components of the mixture. In the region of 3400-3600 cm^{-1}, residual wide bands of OH–H valence vibrations are observed, which indicates partially preserved hydroxyl groups of silicates and adsorbed moisture, despite the high-temperature firing regime.

The most characteristic changes are associated with the region of 1000-1100 cm^{-1}, where intense absorption is observed, corresponding to fluctuations in Si–O and P–O bonds. This confirms the formation of new phosphate-silicate phases resulting from the interaction of phosphorite and phosphate-siliceous shales. Bands corresponding to Al¯O and Mg–O fluctuations are distinguished in the 600-800 cm^{-1} zone, which indicates the participation of alumina and magnesia components in the formation of the mineral skeleton of the agglomerate.

Microstructure and element-wise composition of the batch firing product phosphate:phosphate-siliceous shales:coke:oil slage at a ratio of 65:26:6:3 (Figure 6).

Element	Weight %
C	6.85
O	46.30
F	0.49
Mg	1.76
Al	2.10
Si	9.18
P	9.13
S	0.50
K	0.28
Ca	21.97
Fe	1.43
Total	100.00

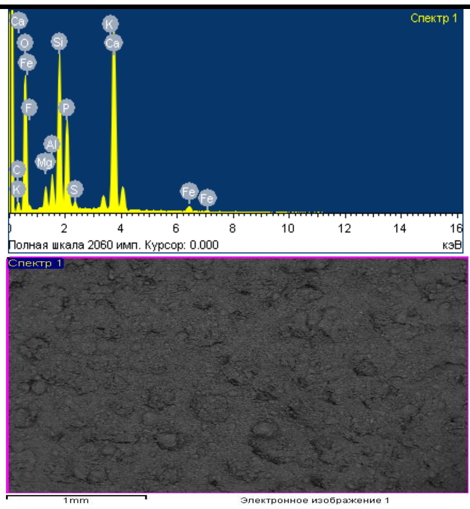

Fig.6. Microstructure and element-wise composition of the batch firing product phosphate:phosphate-siliceous shales:coke:oil slage at a ratio of 65:26:6:3

Analysis of the microstructure and EDS-element composition of the batch firing product phosphate:phosphate-siliceous shales:coke:oil slage (65 : 26 : 6 : 3) showed that the main cementing component is lamellar calcium phosphate, represented by aggregates of thin crystalline plates. The detected content of Si (9.18%) and Al (2.10%) indicates the formation of aluminosilicate minerals represented by elongated or spherical hydrosilicate aggregates. Mg (1.76%) and Fe (1.43%) are localized in fine–grained Ca-Fe–O inclusions, which perform a strengthening function similar to calcium ferrite.

Conclusion

Thus, the obtained results of X-ray fluorescence analysis allow us to conclude that neftekox is not an exclusively carbon product, but is a mineral-organic complex containing oxides of calcium, iron, aluminosilicates and a number of heavy and rare earth elements. This specificity has a significant impact on its physico-chemical properties and thermochemical behavior, determining the possibilities of using petroleum coke not only as a fuel, but also as a reducing agent and active component in sintering and metallurgical processes.

The microstructure and element-by-element composition of the batch firing product that the main cementing component is lamellar calcium phosphate, represented by aggregates of thin crystalline plates with inclusions of aluminosilicate and slightly ferritic minerals.

References

1. Elgharbi, S., Horchani-Naifer, K., and Férid, M. Study of Structural and Mineralogical Changes of Tunisian Phosphorite during Calcination. Journal of Thermal Analysis and Calorimetry, 2015, Vol. 119, No. 1, pp. 265–271. https://doi.org/10.1007/s10973-014-4132-5
2. Tleuova S.T., Anarbayev A.A., Pazylova D.T., Ulbekova M., Tileuberdi A.N. Mathematical modeling of sorptive extraction of lithium chloride from lithium-containing brine of the Aral Sea region. The Open Chemical Engineering Journal, Sharjah, U.A.E., 2024, Vol. 18, pp. 1–11. https://doi.org/10.2174/01187412313335492409090708331
3. Tleuov A.S., Shevko V.M., Tleuova A.Kh. Use of Hydrocarbon Raw Materials in the Processes of Decarbonization of Phosphate Ore. // Abstracts of the International Conference of the Institute of

General and Inorganic Chemistry of the Academy of Sciences of the Republic of Uzbekistan. – Tashkent, 2003. – p. 61.
4. Tleuov A.S., Tleuova S.T., Pazyllova D.T., Tileuberdi A.N., Ulbekova M.M., Turishbekov Zh.A. Utility Model Patent of the Republic of Kazakhstan. Method for Agglomeration of Phosphate Raw Material. No. 9772, dated 15.11.2024.
5. Tleuov A.S., Arystanova S.D., Tleuova S.T., Nazarbek U.B., Ulbekova M. Mathematical modeling of the process of obtaining sorbents for phosphorus extraction from sludges. Scientific Journal "Bulletin of KazNITU named after K.I. Satpayev", No. 1 (125), Almaty, 2018, pp. 387–393.
6. Da Silva EF, Mlayah A, Gomes C, Noronha F, Cristina Sequeira C, Estevesd V, Marquesd ARF. Heavy elements in the phosphorite from Kalaat Khasba mine (North-westernTunisia): potential implications on the environment and human health. J Hazard Mater. 2010;182:232–45.
7. Bojinova D. Thermal treatment of Tunisian phosphorite and additives of aluminium silicate. Thermochim Acta. 2003;404:155–62.

С.Т. Тлеуова, А.Н. Тілеуберді, М.М. Үлбекова, А.С. Таубаева, Г.С. Жүсіпбек*

т.ғ.к., профессор, М. Әуезов атындағы Оңтүстік Қазақстан зерттеу университеті, Шымкент, Қазақстан
PhD, аға оқытушы, М. Әуезов атындағы Оңтүстік Қазақстан зерттеу университеті, Шымкент, Қазақстан
оқытушы, М. Әуезов атындағы Оңтүстік Қазақстан зерттеу университеті, Шымкент, Қазақстан
PhD, аға оқытушы, М. Әуезов атындағы Оңтүстік Қазақстан зерттеу университеті, Шымкент, Қазақстан
*докторант, М. Әуезов атындағы Оңтүстік Қазақстан зерттеу университеті, Шымкент, Қазақстан
***Корреспондент авторы:** tul_dana_93@mail.ru

ФОСФАТ-КРЕМНИЙЛІ ТАҚТАТАСТАР МЕН МҰНАЙ ҚАЛДЫҚТАРЫН ҚОЛДАНА ОТЫРЫП, ФОСФОР АГЛОМЕРАТЫНЫҢ ФИЗИКА-ХИМИЯЛЫҚ ЕРЕКШЕЛІКТЕРІН ЗЕРТТЕУ

Түйін

Мақалада фосфат-кремнийлі тақтатастар мен мұнай коксын қосу арқылы фосфорлы айыппұлдарды агломерациялау арқылы алынған фосфор агломераттарының физика-химиялық ерекшеліктерінің нәтижелері келтірілген. Бастапқы фосфат-кремнийлі тақтатас және күйдіру өнімдерін зерттеу үшін бастапқы және алынған материалдардың ИҚ спектрометриялық, Рентгендік флуоресценциялық, микроқұрылымдық және элементтік-элементтік талдаулары пайдаланылды. Жанатас фосфатты-кремнийлі тақтатастың ИҚ спектрі ν(O-H) сәйкес келетін 3400-3700 см–1 диапазонындағы кең диапазонмен сипатталады. 1010-1058 см-1 қарқынды жолақтар тобы кремнеземнің ν(Si–O–Si) құрылымдық элементтерінің асимметриялық созылуынан туындайды. Аймақта 667–789см–1, алюмосиликат фазасының ν(Si–O–Al) және ν (Si-O-Si) деформациялық тербелістері анықталды. 1100°с температурада күйдіретін өнімнің ИҚ спектрлері фосфат-силикат композициясы түрінде ұсынылған, онда "матрица" (Ca–P) шыны фазамен (Si–O–Al) біріктіріледі.). Пакеттік күйдіру өнімінің микроқұрылымы мен элементтік құрамы фосфат:фосфат-кремнийлі тақтатастар:кокс:мұнай шламы 65:26:6:3 қатынасында жұқа кристалды агрегаттармен ұсынылған пластиналы кальций фосфаты түріндегі негізгі цементтеу компонентімен сипатталады.пластиналар. Анықталған si (9,18%) және Al (2,10%) құрамы ұзартылған немесе сфералық гидросиликат агрегаттарымен ұсынылған алюмосиликатты минералдардың түзілуін көрсетеді.

Кілттік сөздер: фосфор агломераты, фосфат-кремнийлі тақтатас, петрококс, фосфат-силикат композиті, шыны фазасы, Рентгендік флуоресценция спектрі, мұнай шламы.

С.Т. Тлеуова, А.Н. Тлеуберди*, М.М. Ульбекова, А.С. Таубаева, Г.С. Жусупбек*
к.т.н., профессор, Южно-Казахстанский исследовательский университет им. М.Ауэзова, Шымкент, Казахстан
PhD, старший преподаватель, Южно-Казахстанский исследовательский университет им. М.Ауэзова, Шымкент, Казахстан
преподаватель, Южно-Казахстанский исследовательский университет им. М.Ауэзова, Шымкент, Казахстан
PhD, старший преподаватель, Южно-Казахстанский исследовательский университет им. М.Ауэзова, Шымкент, Казахстан
*докторант, Южно-Казахстанский исследовательский университет им. М.Ауэзова, Шымкент, Казахстан
***Автора для корреспонденции:** tul_dana_93@mail.ru

ИССЛЕДОВАНИЕ ФИЗИКО-ХИМИЧЕСКИХ СВОЙСТВ ФОСФОРИСТОГО АГЛОМЕРАТА С ИСПОЛЬЗОВАНИЕМ ФОСФАТНОКРЕМНИСТЫХ СЛАНЦЕВ И НЕФТЯНЫХ ОТХОДОВ

Аннотация

В статье представлены результаты изучения физико-химических свойств фосфористых агломератов, полученных при агломерационном обжиге фосфористой мелочи с добавлением фосфатнокремнистых сланцев и нефтяного кокса. Для изучения исходного фосфатнокремнистого сланца и продуктов обжига были использованы ИК-спектрометрический, рентгенофлуоресцентный, микроструктурный и поэлементный анализы исходных и полученных материалов. ИК-спектр фосфатно-кремнистого сланца Джанатас характеризуется широкой полосой в диапазоне 3400-3700 см-1, соответствующей ν(O–H). Группа интенсивных полос 1010-1058 см⁻1 обусловлена асимметричным растяжением ν(Si–O–Si) структурных элементов кремнезема. В области 667-789 см-1 обнаружены деформационные колебания ν(Si–O–Al) и ν(Si–O–Si) алюмосиликатной фазы. ИК-спектры продукта обжига при температуре 1100°C представлены в виде фосфатно–силикатного композита, в котором "матрица" (Ca-P) сочетается со стеклообразной фазой (Si–O–Al). Микроструктура и элементный состав продукта периодического обжига фосфат:фосфатнокремнистые сланцы:кокс:нефтяной шлак в соотношении 65:26:6:3 характеризуется наличием основного вяжущего компонента в виде пластинчатого фосфата кальция, представленного агрегатами из тонких кристаллических пластинок. Обнаруженное содержание Si (9,18%) и Al (2,10%) указывает на образование алюмосиликатных минералов, представленных удлиненными или сферическими гидросиликатными агрегатами.

Ключевые слова: фосфористый агломерат, фосфатно-кремнистый сланец, петрококс, фосфатно-силикатный композит, стеклофаза, рентгенофлуоресцентный спектр, нефтешлам.