IRSTI 61.31.51 https://doi.org/10.58805/kazutb.v.2.23-352

INVESTIGATION OF THE CHEMICAL AND MINERALOGICAL COMPOSITION OF METALLURGICAL SLAGS OF JSC "QARMET" TEMIRTAU

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«Qarmet» JSC is one of the largest metallurgical enterprises in Kazakhstan, producing steel and other metals. Study of chemical and mineralogical composition of metallurgical slags from this enterprise can be crucial for its process optimization, environmental compliance improvement and efficient waste management.

Study of chemical and mineralogical composition of metallurgical slags from «Qarmet» JSC emphasizes importance of researching metal production waste for its efficient recycling. Further research in this area may facilitate development of new waste recycling technologies and improvement of metallurgical production sustainability.

During the study of the chemical composition of metallurgical slags of Qarmet JSC, it was found that they contain a significant amount of metal oxides such as iron, manganese, silicon and others. These elements can be potentially useful for reuse in other manufacturing processes or for the production of building materials.

In addition, mineralogical analysis has shown that metallurgical slags contain various mineral phases such as silicates, oxides and other compounds. This indicates the complex structure of the slags and the possibility of using them as additives to cement or other building materials.

Keywords: metallurgical blast furnace slag, properties, chemical composition, mineralogical composition, slag activity, building materials, wastes, oxides.

ТЕМІРТАУ ҚАЛАСЫНЫҢ «QARMET» АҚ МЕТАЛЛУРГИЯЛЫҚ ҚОЖДАРЫНЫҢ ХИМИЯЛЫҚ ЖӘНЕ МИНЕРАЛОГИЯЛЫҚ ҚҰРАМЫН ЗЕРТТЕУ

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Қазақстандағы ең ірі металлургиялық кәсіпорындардың бірі Болат және басқа металдар өндірумен айналысатын «Qarmet» АҚ болып табылады. Осы кәсіпорынның металлургиялық шлактарының химиялық және минералогиялық құрамын зерттеу өндірістік процестерді оңтайландыру, экологиялық қауіпсіздікті жақсарту және қалдықтарды тиімді пайдалану үшін маңызды болуы мүмкін.

«Qarmet» АҚ металлургиялық қождардың химиялық және минералогиялық құрамын зерттеу металдар өндірісінің қалдықтарын оларды тиімді басқару және қайта өңдеу мақсатында зерделеудің маңыздылығын атап көрсетеді. Осы саладағы қосымша зерттеулер қалдықтарды қайта өңдеудің жаңа технологияларын дамытуға және металлургия өндірісінің тұрақтылығын арттыруға ықпал етуі мүмкін.

"Qarmet" АҚ металлургиялық қождардың химиялық құрамын зерттеу барысында олардың құрамында темір, марганец, кремний және басқалары сияқты металл оксидтерінің едәуір мөлшері бар екендігі анықталды. Бұл элементтер басқа өндірістік процестерде немесе құрылыс материалдарын өндіруде қайта пайдалану үшін пайдалы болуы мүмкін.

Сонымен қатар, минералогиялық талдау металлургиялық шлактарда силикаттар, оксидтер және басқа қосылыстар сияқты әртүрлі минералды фазалар бар екенін көрсетті. Бұл токсиндердің күрделі құрылымын және оларды цемент немесе басқа құрылыс материалдарына қоспалар ретінде пайдалану мүмкіндігін көрсетеді.

Түйін сөздер: металлургиялық домна пешінің қожы, қасиеттері, химиялық құрамы, минералогиялық құрамы, қож белсенділігі, құрылыс материалдары, қалдықтар, оксидтер.

ИССЛЕДОВАНИЕ ХИМИЧЕСКОГО И МИНЕРАЛОГИЧЕСКОГО СОСТАВА МЕТАЛЛУРГИЧЕСКИХ ШЛАКОВ АО «QARMET» Г.ТЕМИРТАУ

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Одним из крупнейших металлургических предприятий в Казахстане является АО «Qarmet», которое занимается производством стали и других металлов. Исследование химического и минералогического состава металлургических шлаков этого предприятия может быть ключевым для оптимизации производственных процессов, улучшения экологической безопасности и эффективного использования отходов.

Исследование химического и минералогического состава металлургических шлаков АО «Qarmet» подчеркивает важность изучения отходов производства металлов с целью их эффективного управления и переработки. Дальнейшие исследования в этой области могут способствовать разработке новых технологий переработки отходов и повышению устойчивости металлургического производства.

В ходе исследования химического состава металлургических шлаков АО «Qarmet» было обнаружено, что они содержат значительное количество оксидов металлов, таких как железо, марганец, кремний и другие. Эти элементы могут быть потенциально полезными для повторного использования в других производственных процессах или для производства строительных материалов.

Кроме того, минералогический анализ показал, что металлургические шлаки содержат различные минеральные фазы, такие как силикаты, оксиды и другие соединения. Это свидетельствует о сложной структуре шлаков и возможности использования их в качестве добавок к цементу или другим строительным материалам.

Ключевые слова: металлургический доменный шлак, свойства, химический состав, минералогический состав, активность шлака, строительные материалы, отходы, оксидтер.

Introduction. Metallurgical slag is one of the main wastes of iron and steel production. They are formed as a result of the melting of agglomerates, fluxes and other additives during the processing process to obtain the main product - cast iron [1-2]. Chemical and mineralogical composition of metallurgical slags may vary significantly depending on initial materials' composition, production technology and other factors study [3-4].

It is widely known that one of specific features of metallurgical slags is their activity - ability to display hydraulic properties when interacting with water, similarly to cement. This study shows results of researching the process of obtaining non-clinker binder based on granulated blast furnace slag from Qarmet JSC.

Global concrete producers widely use metallurgical slag as cement replacement. The substitution of cement by slag provides two clear advantages; the first one is use of a waste that otherwise must be managed in a landfill, and the second one, even more relevant, is reduction in cement consumption, so the reduction of CO_2 emissions during its production. The authors of study [5] used metallurgical slags from a plant in Spain.

Besides, multiple studies have analyzed general tendencies of slag chemical composition which show that composition of different slags may vary depending on either place of production or year of steel production [6].

Considering the abovementioned, there is high importance of finding mineralogical and chemical composition of metallurgical slag produced by Karaganda metallurgical plant Qarmet JSC. Temirtau, Kazakhstan. This issue is addressed in this study.

Materials and methods. To conduct the study, granulated blast furnace slag of JSC Qarmet was used. Slag samples were taken from various points in the storage area, and the samples were averaged.

Slag activity is determined by its chemical composition including up to 30 elements, primarily CaO, MgO, SiO_2, Al_2O_3, FeO, MnO, and their mineralogical composition [7-10]. The most used in binder materials production are the slags with sufficient hydraulic activity characterized by basicity module M_b and activity module M_a, containing large amount of glass of helenite-melelite, wollastonite and aluminosilicate composition [11-14].

To determine the chemical composition of the slag, the content of oxides CaO, MgO, MnO, Al_2O_3 was analyzed according to SS 5382-2019. [15]

The most acceptable chemical composition for this article is the slag presented in table 1.

Table 1 - Chemical composition of active slags

CaO	S	MnO	Al2O3	MgO
More than 40%	No more than 4-5%	Less than 2%	No less than 9 %	No less than 4-10%

Table 2 - Chemical and mineralogical composition of metallurgical slags

Year of slag production	Content, % by mass							Basicity module, Mb	Activity module, Ma	Mineralogical composition
	SiO2	AL2O3	CaO	MgO	MnO	FeO	S			
Converter slag										
2020	9,103	1,612	42,542	8,173	3,424	19,103	0,122	4,733	0,177	
2021	9,61	1,6	42,94	7,71	2,96	19,36	0,13	4,518	0,166	
2022	9,65	1,34	41,34	7,18	2,54	26,38	0,12	4,415	0,139	
Average value	10,52	1,39	42,56	7,32	3,98	19,33	0,12	4,21	0,13	
Root mean square deviation	1,05	0,15	1,04	0,98	1,32	3,24	0,02	0,35	0,03	
Variation coefficient, %	10	10,55	2,45	13,32	33,27	16,79	19,14	8,21	19,4	
Blast furnace slag										
2020	36,99	13,05	39,52	9,46	0,56	0,44	1	0,979	0,353	Helenite-melilite glass, helenite, wollastonite
2021	36,63	13,81	39,72	9,42	0,39	0,42	0,98	0,974	0,377	
2022	35,31	14,86	38,67	10	0,5	0,51	0,99	0,97	0,421	
Average value	36,31	13,91	39,3	9,63	0,48	0,46	0,99	0,97	0,38	
Root mean square deviation	0,72	0,74	0,46	0,26	0,07	0,04	0,01	0,004	0,03	
Variation coefficient, %	1,99	5,34	1,16	2,75	14,56	8,45	0,82	0,37	7,34	

Basic slags (basicity module more than 1) display hydraulic activity at high alumina content and manganese oxide no more than 5%, when there is a shortage of raw materials. Acidic slags (basicity module less than 1) show sufficient activity at basicity module no less than 0,65 and activity module no less than 0,33 at manganese oxide no more than 4%.

In order to reveal and facilitate slags' hydraulic properties, they should be mixed with alkaline-containing solidification catalysts which saturate water solution during slag hydration with Ca^{2+}, OH^{-}, and SO_4^{2-} ions, thus creating conditions for alkaline and sulfate activation of slag glass. This process also yields low-basicity calcium hydrosilicates calcium which are the main product of granulated slag hydration and hydrolysis in presence of alkaline catalyst. Low-basicity calcium hydrosilicates after complete consolidation have hardness close to crystalhydrate newgrowths obtained through cement hydration and hydrolysis, and are better than the latter in deformation properties as hardness of bonds formed through consolidation is lower than hardness of chrystallization contacts through coalescence. The activity of the slag was determined according to the SS 25094-2015 [16] method.

Ore from the Lisakovsky deposit was used as raw material. The methods for testing the stability of blast furnace slag are based on standard methods according to SS for lime, silicate, sulfide decomposition (SS 3476-2019, SS 5382-2019) [15, 17]

Another important parameter of slags influencing their use for making construction materials is their disintegration property. There is limestone, silicate and sulphidic disintegration. Slag structure is considered to be resistant to limestone disintegration if its calcium oxide content equals or less than critical value calculated using the formula:

$$CaO \leq 0{,}92SiO_2 + Al_2O_3 + 0{,}2\ MgO_2 \qquad (1)$$

Silicate disintegration appears due to the fact that during crystallization slag oxides form dicalcium silicate $2CaOSiO_2$. This depends, firstly, on amount of lime, and secondly, on initial slag temperature when it is cooled down quickly. In case of absence of obvious connection between these two factors and disintegration, for practical purposes it is considered that slags with lime content over 45% are prone to disintegration. Slags are resistant at lime content under 45%. However, positive impact of alumina presence on resistance should be considered. At alumina content of approximately 18% slag is resistant to disintegration even if CaO content is over 50%. Magnesia presence also increases resistance. At MgO content increase from 5 to 15% resistance rises. Increase of structure resistance in presence of alumina and magnesia is explained by chemical reactions causing formation of helenite – $2CaOAl_2O_3SiO_2$ and okermanite – $2CaOMgO_2SiO_2$, which contain large amounts of calcium oxide. This, in its turn, creates conditions for decreasing amount of dicalcium silicate. It should be noted that these reactions facilitate slags resistance increase against limestone disintegration as well.

Results and discussion. Sulphidic disintegration can be seen in slags containing significant amount of iron or manganese sulphides. At sulphides' interaction with water the substance volume increase by up to 38% occurs, which causes slag cracking and destruction. At iron or manganese content over 2% (expressed as FeO or MnO) slag is considered unstable.

In order to estimate the opportunity of using metallurgical slags from Qarmet JSC for non-clinker binders' production, their chemical and mineralogical composition have been studied. Table 2 shows results of analyzing slags produced in different years. The goal of the research was to determine chemical-mineralogical stability of these materials' properties and estimate their hydraulic activity and structure's resistance against disintegration through computational methods.

Provided results of converter slag chemical-mineralogical definition characterize it as basic ferriferrous slag with Mb=4,21; FeO>5% with minor activity module Ma=0,13, high content of manganese oxide 3,98%, unstable from year to year – variation coefficient 33,27 %, and low content of Al_2O_3 1,39%, which classifies it as a slag without prominent hydraulic activity, which is also proven by mineralogical composition lacking active minerals. In terms of mineralogical composition, converter slag mostly consists of periclase and menganosite. It was researched that slags containing significant amount of helenite-melilite, wollastonite and aluminosilicate glass are the most suitable for binders' production.

Chemical composition of converter slag shows its tendency to various types of disintegration. Estimative ability of converter slag to lime disintegration is expressed in following:

CaO = 42,56

$$0{,}92SiO_2 + Al_2O_3 + 0{,}2\ MgO_2 = 12{,}53 \quad (2)$$

This way, content of calcium oxide significantly surpasses amount of other main components combined.

Contents of iron oxide (19,33%) and manganese (3,98%) in converter slag significantly surpass 2% limit providing slag resistance against sulphidic disintegration, and low content of alumina (1,39%) at relatively high share of CaO (42%) shows its tendency to silicate disintegration as well.

Table 3 shows chemical elements contained in blast furnace slag providing its resistance against various disintegrations.

Table 3 - Chemical elements in blast furnace slag providing its resistance against disintegrations for SS 3476-2019

Type of disintegration	Main conditions of disintegration	Chemical elements in providing its resistance against disintegrations
Lime	$CaO \le 0{,}92SiO_2 + Al_2O_3 + 0{,}2\ MgO_2$	39,3 % <49,24 %
Silicate	CaO>45 %; resistance rises at Al_2O_3 up to 18 % and MgO = 5 – 15 %	CaO = 39,3 % Al_2O_3 = 13,9 % MgO = 9,63 %
Sulphid	FeO>2 % MnO>2 %	FeO = 0,46 % MnO = 0,48 %

Considering the possibility of involving the composition of the charge in order to increase the volume of production of a commercial product, blast furnace production slag having a similar chemical composition, with the exception of the increased content of ferrous oxide, a study was carried out on the chemical and mineralogical components of steelmaking blast furnace slag, which is reflected in table 3.

Blast furnace slag in terms of its chemical composition can be classified as acidic magnesial slags with Mb=0,97%; with MgO=9,63%, activity module Ma=0,38 and Al_2O_3 and MgO within limits suitable for slags with latent potential hydraulic activity, which is proven by its mineralogical composition including minerals prone to hydrolysis and hydration forming hydraulically active compounds: helenite-melilite glass, helenite, wollastonite.

Chemical composition of blast furnace slag characterizes it as a material which is not prone to various disintegration.

Conclusion. During the study of the chemical composition of blast furnace and steelmaking, in particular converter slag of Qarmet JSC, it was discovered that they contain a significant amount of metal oxides, such as iron, manganese, silicon and others. These elements could be potentially useful for reuse in other industrial processes or for the production of building materials for fertilizer, neutralization of acidic soils and iron extraction.

In addition, mineralogical analysis has shown that metallurgical slags contain various phase structures, such as silicates, oxides and other compounds. This indicates the complex structure of slag with different proportions of chemical compounds and the possibility of using them as additives to cement or other building materials.

Financing. *The article was prepared based on the results of scientific research within the framework of the state order of the Ministry of Science and Higher Education for the implementation of the grant fundamental scientific and technical project IRN: AP19678263 on the topic «Rational use of man-made waste from metallurgical industries».*

Авторы выражают благодарность за выделенное грантовое финансирование.

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