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- 19. Graphite. Minerals Database. Minerals Education Coalition. 2018. Retrieved 9 December 2018. https://mineralseducationcoalition.org/minerals-database/graphite/
- 20. Характеристика схем збагачення графітових руд завалівського, балахівського та буртинського родовищ українського щита / Н.М. Лижаченко, В.П. Ніколаєвський, І.В. Ніколаєвський та ін. // Геологічний журнал. -2013. -№ 2. -C. 51-58.

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METHODS OF GRANULATION OF MOLTEN SLAG AND USE OF GRANULATED SLAG WATER

Relevance of the topic. One of the most important processes in a blast furnace, determined its operation, is slag formation.

Metallurgical slag is the most valuable coproduct material.

More than 50% of the volume of molten slag obtained in a blast furnace is processed into granulated slag. Crushed stone, pumice-stone, slag wool (high-alumina clinker) and cast products (in small quantities) are also produced from the blast furnace slag.

Nowadays in Ukraine about 80-85% of blast furnace slag is being processed. Part of the slag is shipped to dumps, which causes environmental problems such as pollution of land, air, water. Therefore, the use and processing of slag, as a valuable byproduct, are urgent problems of our time.

Granulated Slag Production. Granulation is the process of transformation of molten slag into glassy granules by quenching with water, steam, air or another gas.

There are three systems of granulation process: water, semi-dry and dry. Water granulation methods are most commonly used in the production of granulated slag.

During the water granulation the slag granules are formed due to the property of molten slag to crack under the influence of thermal stresses and spray by microexplosions when the melt contacts with water.

The water granulation production of slag is the oldest and simplest one and is divided into basin and grooved methods.

The analysis of methods of granulation of molten slag. There are plenty of dif-

ferent methods of slag granulation which are presented in the references [1,2]. The disadvantage of these methods, especially in the case of the blast furnace granulation, is a high temperature, about 1450-1500 °C, of the molten slag flowing to granulation. Exposure of high-temperature water to granulated molten slag causes hydrogen sulfide gas and a porous structure of slag, holding the extra moisture, which requires additional energy to the remove.

Rapid cooling and crystallization of molten slag (about 3 min), occurring at a melt temperature of $t = 1150\,^{\circ}\text{C}$ [2], excludes the formation and emission of hydrogen sulfide gas into the environment.

Besides, the existing slag granulation technology does not provide the removal of molten metal from the slag, the content of which reaches up to 5% for the blast-furnace slag [2] and even more for the steelmaking slag. Such a big content of the metal in the granulated slag complicates the technology of its further processing. It is rational while developing the new technologies for granulation to provide the preliminary removal of metal from the melt. Water, remaining from the process of granulation of the molten slag, is not being recycled and pollutes the natural water resources, seeps into the ground, evaporates hydrogen sulfide gas, which adversely affects the ecology of the environment. Therefore the recycling of water is a relevant problem.

The objective of the article is to improve the process of granulation of molten slag, which will allow to eliminate hydrogen sulfide emissions and remove metal from the molten slag.

Presentation of the main work. The purpose is implemented in three developments, two of them are concerning the blast furnace granulation (water and for semi-dry granulation), and the third one is the analysis of the possibility of using water from granulated slag in balneology.

1. The method of producing water granulated slag. Fig. 1 shows the schematic of an improved plant for the water granulation of metallurgical slag [3].

The plant (Fig. 1) comprises a storage tank for molten slag 1, with an inclined bottom for emptying deposited liquid metal through a notch 2 into a ladle 3, a notch 4 for discharging the liquid slag through a spout 5. In the upper part, the storage tank is equipped with a receiving hopper 6 for discharging the molten slag into the storage tank 1. Under the spout 5 are installed: a granulator 7, which equipped with nozzles for feeding cooling water by a pump 8, a receiving hopper 9, a clarified water tank 10.

In the upper part, the receiving hopper 9 has gratings 11 and in the lower part – an overflow window 12, which is connected to a chamber 13 by an airlift 14, which is connected through the separator 15 to the carousel-type dehydrator 16, under which a water collector 17 and a granulated slag hopper-receiver 18, a conveyor 19 with a cover 20 are installed.

In the lower part, the hopper 18 has an air supply through the collector 21, which is installed with the possibility of air supply both to the hopper 18 and under the case 20, which closes the conveyor 19. The conveyor 19 transmits the granulated slag to the warehouse and rigidly joins to the bottom of the hopper 19. A pump 22

serves the airlift camera 13.

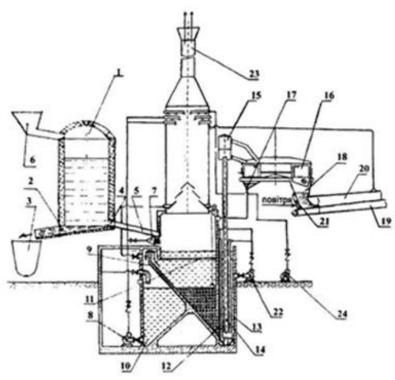


Fig. 1. The plant for water granulation of metallurgical slag

The upper part of the hopper 9 goes into a vent pipe 23 for discharging vapour, formed during granulation process and air-stream mixture, that comes from the dehydrator 16. A pump 24 recharges the system with circulation water in case of water loss during vaporization. The pump 24 is turned on automatically when the water level falls in the receiving hopper 9 below a predetermined value.

The advantages of this slag granulation plant are as follows. It has been established, that hydrogen sulfide emissions to a greater extent (up to 50%) depend on the intensity of slag discharge, its temperature and the temperature of supplied to the granulation water [2]. The reduction of these parameters can be used in production as a way to reduce sulfur emissions during granulation.

The introduction of the storage tank-settler 1 to the proposed technological scheme (Fig. 1) of processing of the molten slag allows adjusting the rate of slag discharge via the notch 4. The temperature of the slag, feeding to granulation according to the scheme in Fig. 1 (1200 °C), less than the temperature of the slag (1500-1450 °C), discharged from the blast furnace. These factors (reducing the intensity of the slag output and lowering the temperature of the slag) contribute to the reduction of hydrogen sulfide emissions during the slag granulation.

The removal of metal from the molten slag before granulation by sedimentation in the storage tank increases the safety of the installation due to the exclusion of explosions and eliminates the need for magnetic separation of granulated slag.

In addition, the setting of the storage tank into the granulation technological scheme allows to combine and process slags from several blast furnaces in one granu-

lation plant, which makes the granulation process continuous with predefined and constant parameters of the granulation technological process.

2. The method of producing semi-dry granulated slag. A feature of the semi-dry method of granulation of the molten slag is the cooling of the dispersed molten slag in the air stream in order to solidify it and so to avoid sticking of slag particles in a dewatering conveyor, which excludes the formation of porosity in granulated slag. But the flight time in the air stream is not enough to solidify the dispersed slag, since, as mentioned above, the minimum crystallization time of the molten slag at t = 1150 °C is 3 minutes, which is significantly longer than the cooling time during the flight of dispersed slag particles.

In order to improve the method of producing semi-dry granulated slag the same tasks, as in the case producing water granulated slag (Fig. 1), are being solved: reducing hydrogen sulfide emissions and removing liquid metal from the molten slag before granulation.

This method of producing semi-dry granulated slag is implemented in the developed plant [4], presented in Fig. 2.

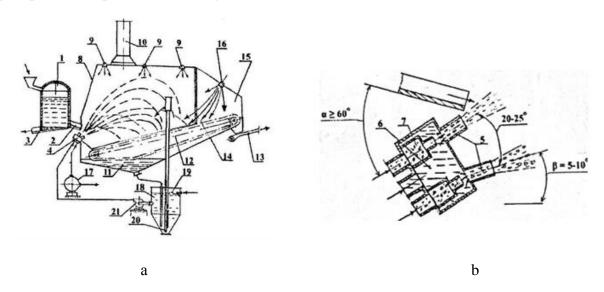


Fig. 2. The plant for producing semi-dry granulated slag: a – longitudinal section of general view; b – cross section of dispersant

The plant for producing semi-dry granulated slag (Fig. 2) contains a liquid slag storage tank 1, a slag a spout 2 for supplying the melt to granulation, an additional notch 3 for releasing precipitated liquid metal, a dispersant 4 with air nozzles 5, made in the form of an air-water ejector, water collector 6 and air collector 7. The receiving hopper is made in the form of a steam collection funnel 8 and is equipped with water-air nozzles 9 for cooling the walls of the hopper and lowering the temperature in it. The receiving hopper is equipped with a pipe 10 for discharging the vapour-gas mixture in the upper part and is connected to a water collector 11 in the lower part. For additional cooling, a part of the branch of a dewatering box conveyor 12 is immersed into the water collector 11. A belt conveyor 13 is connected with the receiving hopper 8 through a window 14. An air chamber 15 is equipped with air nozzles 16. All air

nozzles and manifolds are connected to an air blower 17. A circulating water chamber 18 is equipped with a level regulator 19, a slag air-lift 20 and a pump 21.

The dispenser 4 is equipped with two rows of water-air nozzles (Fig. 2b) with an angle of $20\text{-}25^{\circ}$ between their axes. The upper row of the dispenser nozzles is arranged at an angle $\alpha \ge 60^{\circ}$ relatively to the base of the spout 2, and the lower row of the nozzles – at an angle $\beta \ge 5\text{-}10^{\circ}$ relatively to the dewatering conveyor 12.

The water-air nozzles 5 of the disperser allow to transfer the part of the kinetic energy of the air to drops of water, reduce the airspeed and get a dispersed water-air mixture. Water drops in the air stream contribute to the more intense crushing of the melt and cooling of the slag particles in the flight process. The location of the water-air nozzles at different angles increases the exposure time of the cooling water-air stream to the slag particles, since the particles of the slag before falling onto the dewatering box conveyor 12 are exposed to the air stream created by the lower row of nozzles, which change the direction of the water-air stream guided by the upper row of nozzles at an angle of $\beta = 5\text{-}10^0$ to the axis of the box conveyor. Thus, the cooling air-water mixture in the chamber affects the slag particles throughout the flight starting from the dropping out from the spout 2 to the falling down on the conveyor.

The water-air nozzles 9 are installed additionally in the receiving hopper to exclude possible sticking of the melt particles to the inner surface of the hopper and lowering the temperature in the middle of it.

In addition, as in the case of the water granulation (Fig. 1), the presence of the storage tank allows the granulation process to be carried out continuously, to maintain the optimal temperature of the slag (1150 °C) and to obtain high-quality granulated slag by removing metal from the molten slag before granulation.

Both granulation methods, shown in Fig. 1 and 2, positively affect the environment by reducing emissions of hydrogen sulfide gas.

3. The method of using granulation slag water. This section analyzes the possibilities of using granulation slag water for medicinal purposes is being carried out. The general schematic of obtaining and using of granulation slag water is shown in Fig. 3.

The reactions during granulation of the molten slag by water in the pool

$$CaS + 2H_2O = Ca(OH)_2 + H_2S,$$

$$MnS + 2H_2O = Mn(OH)_2 + H_2S,$$

$$2CaS + 2H_2O = Ca(OH)_2 + Ca(SH)_2,$$

$$Ca(SH)_2 + H_2O + Q = Ca(OH)_2 + 2H_2S.$$

The water used for granulation of molten slag dissolves some of the compounds of slag, mainly sulphurous, and thus sulphurous (sulphide-sulphurous) mineralized water is being formed. The similarity of the properties of this water with natural sulfide (hydrogen sulfide) mineral water has been established, which makes it possible to use granulation slag water for appropriate therapeutic purposes. The experience of such use of the granulation water in the 30th of the last century in the USSR and Germany had quite favourable results. But due to notorious historical events, the results of the experiments were lost.

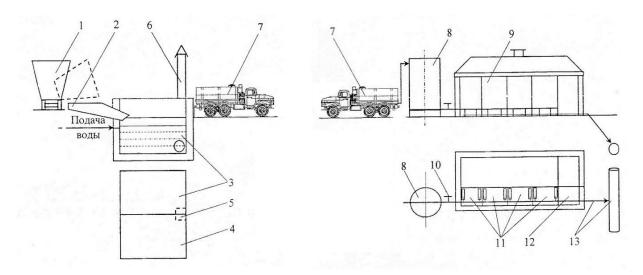


Fig. 3. The schematic of obtaining and using of granulation slag water: 1 – slag truck; 2 – outlet channel; 3 – granulation pool with water; 4 – sump for granulation water; 5 – overflow branch pipe; 6– steam outlet pipe; 7 – tanker truck for granulation slag water; 8 – storage tank of slag water with heating up to +40 °C; 9 – balneological hospital;

10 – shutoff valve; 11 – bathrooms; 12 – laboratory; 13 – drain into the sewer

Hydrogen sulfide water of various salinity and ionic composition from natural sources contains more than 10 mg per litre of hydrogen sulfide.

Chemical analyses of the slag water showed the presence of such sulfur compounds: 372-475 mg/l of thiosulfate, 218-385 mg/l of sulfate, 10-16 mg/l of sulfite and 134 mg/l of HS′ semi-bound hydrogen sulfide (20-30 mg/l of free H₂S). According to the prevailing anions, the slag water is thiosulfate-sulfate, and to cations – calcium. The presence of free hydrogen sulfide H₂S and semi-bound HS′ in the indicated amounts refers the slag water to specific hydrogen sulfide water.

For a more complete study of the physicochemical properties of the slag water and its effects on the human body, a number of additional studies are required.

The slag hydrogen sulfide water certainly has huge healing potential, but before broad usage of it in the medicine scientific substantiation of the water influence on the effect of the treatment is required.

From the available information, the therapeutic effect of treatment with the slag water is known for the following types of diseases: polyarthritis, psoriasis, eczema, joint diseases, chronic inflammatory diseases of the female genital area, and many

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other. For a more complete study of the impact of the slag sulfide water on the human body, a number of medical research is necessary to supplement the available results.

Currently, the research is being conducted to adjust the granulation hydrogen sulfide slag water to the chemical composition and properties of the hydrogen sulfide water from natural mineral sources (Matsesta, Pyatigorsk, etc.). This will allow using the granulation hydrogen sulfide slag water at metallurgical enterprises for medicinal purposes (balneology) to improve the health of workers. The proposed method of using the granulation slag water will give, in addition to an economic, also an environmental effect, as the water is not discharged into natural water sources (rivers, seas) and the pollution of them is excluded.

The final solution of the problem and practical application of the granulation hydrogen sulfide slag water in balneology is possible provided the interest of metal-lurgical enterprises and sponsoring firms.

The research results were reported at the conference "University Science", PSTU, 2017, Mariupol, Ukraine.

Conclusions

- 1. The proposed methods for water and semi-dry production of the granulated slag, implemented in the developed plants, are characterized by the following factors: the reduction of sulfur emissions into the environment due to the ability to control the intensity of the output of the molten slag with a certain temperature (1150°C); the removal of metal from the molten slag before granulation process, which improves the quality of the slag and makes unnecessary magnetic separation.
- 2. The use of the storage tank in the technological scheme of producing the granulated slag allows to combine and process the molten slag from several furnaces in one granulation plant, which makes the granulation process continuous.
- 3. The method of application of the granulation slag water for medicinal purposes (balneology) is promising and can be developed and implemented provided that the funding of the relevant studies and the involvement of medicine institutions.
- 4. All three methods, discussed in this paper, ensure environmental and economic advantages.

References

- 1. Cherepanov K.A., Chernysh G.I, Dilnet V.M. and Sukharev YU.I (1994), Utilizatsiia vtorichnykh resursov v mrtalurgii [Utilization of secondary material resources in metallurgy], Metalyrgiya, Moscow, Russia.
- 2. Panfiov M.I., Shkolnik Ya.SH., Orinskiy N.V, Kolomiets V.A and Grabeklis A.A. (1987), Pererabotka shkakov i bezotkhdnaia tekhnologiia v metalurgii [Slag processing and waste-free technology in metallurgy], Metalyrgiya, Moscow, Russia.
- 3. Kravchenko V.P. Ruskykh V.P., State higher educational institution "Azov state technical university" (2016) Pat. Ukraine 104664, Ustanovka dlia granuliatsii metalurgiinykh shlakiv [Installation for granulating slag steel slag hopper], State Register of Patents of Ukraine, Kiev, UA, Pat. № 104664.

4. Kravchenko V.P. and Ruskykh V.P., State higher educational institution "Azov state technical university" (2016), Ustanovka dlia granuliatsii rasplavu shlaku [Slag granulation plant], State Register of Patents of Ukraine, Kiev, UA, Pat. № 106822.

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МЕТОДЫ И ПОДХОДЫ К ОПРОБОВАНИЮ МИНЕРАЛЬНОГО СЫРЬЯ

Постановка проблемы. Особую роль в обогащении полезных ископаемых отводится опробованию, как методу получения информации о свойствах перерабатываемого сырья. В процессе поисков и разведки опробование месторождений полезных ископаемых производится с целью установления их состава и качества для дальнейшего обогащения и использования в промышленности. Данные результатов опробования представляют собой одну из основных составляющих геолого-экономической оценки месторождения. Для подсчета промышленных запасов, выбора способа извлечения и схемы переработки полезных ископаемых используют результаты опробования. Значительные капитальные и эксплуатационные затраты идут на получение такой массы информации. И обогатительные фабрики идут на такие затраты, что подчеркивает прямое влияние опробования на экономические результаты расчета, говорит о важности опробования.

Опробование является весьма специфичным процессом получения информации об исследуемых полезных ископаемых. Для ее получения необходимо выполнять определенные правила отбора, подготовки и анализа проб [1]. На основании такого опробования оценка содержания ценного минерала должна быть достоверной и соответствовать содержанию его в месторождении. Таким образом, вопрос метода выбора оптимального размера пробы всегда является актуальным.

Цель работы заключается в анализе методов опробования минерального сырья для оценки его показателей.

Получение необходимой информации о свойствах некоторой массы продукта является основной целью опробования. В практике обогащения и переработки полезных ископаемых процесс опробования понимается как выбор из общего массива некоторого количества материала, который обладает всеми ос-