

Physicochemical Interactions in Melting of Basalt in a Furnace with Horizontally Located Graphite Electrodes

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Abstract. This paper analyzes the energy characteristics of various fuels, which are used in smelting furnaces for melting basalt. The technical and economic analysis showed that among them the most effective application is the electric arc furnace. An experimental-industrial electric melting furnace with horizontal graphite electrodes was built. Further, the processes of basalt melting in electric and flame furnaces, physicochemical interactions of mineral compounds and constituent chemical elements at high temperatures were analyzed.

Keywords: Petrurgy, Non-equilibrium mineral formation, Industrial furnaces of flame and electric heating, Graphite and molybdenum electrodes, Basalt melt, Polymetallic alloy

1. INTRODUCTION

The choice of a method for melting raw materials in petroleum production is decisive. The raw material melts congruently, that is, the melt has a chemical composition similar to the original raw material, taking into account the loss of volatile substances. Atoms have their ionic character. At the same time, thanks to the electron shells of the same name, atoms are subject to repulsive forces. The interaction of opposite forces in a solid creates balance and determines the mutual arrangement of atoms in the crystal lattice. In a solid, atoms vibrate around the nodes of the crystal lattices while maintaining long-range order. Atoms periodically exchange places in the nodes of crystal lattices, but when heated, the exchange rate increases, and then turns into chaotic motion. From the point of view of the ionic theory, a silicate melt is considered as a liquid consisting of simple cations, anions, and complex anions of varying complexity. In petrugic melts, the most common cations are Al^{3+} , Si^{4+} , Ca^{2+} , Mg^{2+} , Fe^{2+} . The electrical conductivity of melts confirms the ionic theory of melts. The phenomenon of electrical conductivity related to the properties of cations, while physical properties such as viscosity depend on anions [1].

The task of the integrated use of mineral raw materials, in particular basalt, and the creation of inorganic materials on its basis requires the use of modern methods of analysis to determine the chemical composition, including the content of valuable elements present in small quantities.

Physicochemical analysis makes it possible to solve many technological problems in the field of petrugy and technology for the manufacture of basalt fibers, namely: to assess the mineralogical and chemical homogeneity of the original rocks, stone casting, basalt fiber, to study the processes of non-equilibrium mineral formation and heteromorphism during crystallization of castings, and also to determine monominerality of stone casting [1-8].

This work aims to study the physicochemical interactions of the multicomponent chemical system of basalt at high temperatures in a melting furnace with horizontally located electrodes.

2. RESEARCH METHODS AND MATERIALS

To compare the efficiency of the furnaces, we will use Table 1, comparative characteristics of various types of fuels.

TABLE I
ENERGY CHARACTERISTICS OF VARIOUS FUEL

Fuel	Measure unit	Specific heat combustion kCal; kW; MJ	Equivalent Natural gas(m ³); Diesel fuel (l); Fuel oil (l)
Electrical energy	1 kW/h	864; 1.0; 3.62	0.108; 0.084; 0.089
Diesel fuel	1 liter	10300; 11,9; 43,12	1.288; -, 1.062
Fuel oil	1 liter	9700; 11,2; 40,61	1,213; 0,942; -
Kerosene	1 liter	10400; 12.0; 43.50	1,300; 1,010; 1,072
Oil	1 liter	10500; 12.2; 44.00	1,313; 1,019; 1,082
Petrol	1 liter	8000; 9.3; 33.50	1,313; 1,019; 1,082
Natural gas	1 m ³	10885; 12.6; 45.57	1,313; 1,019; 1,082
Liquefied gas	1 m ³	11950; 13.8; 50.03	-, 0,777; 0,825
Methane	1 kg	10885; 12.6; 45.57	1,350; 1,049; 1,113
Propane	1 m ³	11470; 13.3; 48.02	1,494; 1,160; 1,232
Ethylene	1 m ³	28700; 33.2; 120.00	1,361; 1,057; 1,122
Hydrogen	1 m ³	6450; 7.5; 27.00	1,434; 1,114; 1,182
Hard coal (W = 10%)	1 m ³		3,588; 2,786; 2,959
	1 kg		0,806; 0,626; 0,665

Comparing the technical characteristics of gas-flame and electric furnaces in terms of fuel consumption to obtain 1 kg melt, you can compare the heating efficiency depending on the type of fuel. Let us compare large industrial furnaces with flame and electric heating. For 1 kg melt electric furnace requires 1 kW [9]. For 1 kg melt in a gas furnace requires 0.4 m³ [10] of natural gas corresponds to 3.72 kW. The efficiency of an electric oven is almost four times that of a gas fired combustion oven. The cost of gas for 1 m³ is 6.36 rubles, and 0.4 m³ is 2.54 rubles. The cost of electrical energy is 1 kW/hour (night + day) 4.5 rubles (Russian data), for Kyrgyzstan, the cost of gas is 14.78 rubles, the cost of electricity is 2.31 rubles. Thus, for Kyrgyzstan, the efficiency of using an electric furnace in comparison with a gas one will be

$$\eta = 3,72 \cdot \frac{14,78}{2,31} = 23,8 \quad (1)$$

In a combustion furnace, only a certain volume of gas can be effectively burned, which is determined by the space above the flame above the melt. The maximum flame temperature is 2050 °C. The practical heating of the melt will be 1500-1600 °C, the heating depth will be 250-300 mm. The mirror of the melt has a high reflectivity of heat, and the melt itself does not conduct heat well, having low thermal conductivity, therefore, the productivity of a gas furnace depends mainly on the area of the melted mirror.

The temperature of the melt can be increased by using an oxygen blast. With oxygen blast, the temperature of natural gas combustion can reach 2700 °C, while burning acetylene with oxygen blast 3150 °C. The use of oxygen (acetylene) to melt basalt is expensive, therefore it is used in exceptional cases. Gas tariff in terms of one kg melt is 42% cheaper (for Russian conditions). Even so, an electric oven is more economical (Fig. 1)

Electric oven with horizontal electrodes

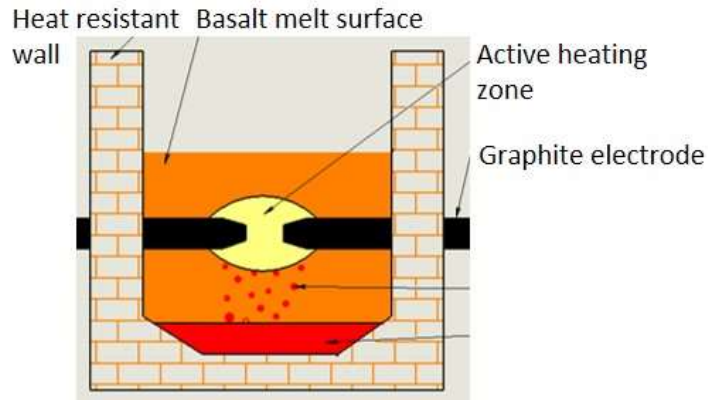


FIGURE 1

OPERATION PRINCIPLE DIAGRAM OF ELECTRIC MELTING FURNACE WITH HORIZONTAL ELECTRODES

Let us consider some of the results of the operation of an electric furnace (Fig. 2) with horizontal electrodes, technologically tuned to obtain a melt for the production of basalt fiber.



FIGURE 2

PILOT INDUSTRIAL ELECTRIC ARC FURNACE WITH HORIZONTAL GRAPHITE ELECTRODES

Charge melting in electric furnaces differs significantly from melting in flame furnaces. If we use the term “thermal power per unit of melt in the active heating zone” and compare electric and combustion furnaces, then the electric furnace will not compete. As shown in [1], the melt has electrical conductivity; therefore, we will use Ohm's law for this:

$$R = \frac{U}{I} \quad (2)$$

here, R is the resistance of the basalt melt layer between the graphite electrodes; U is the voltage between the electrodes; I is the current flowing between the electrodes.

The power of the electrical circuit is

$$P = UI = \frac{U^2}{R} \quad (3)$$

Analysis of this formula shows that if R tends to 0, then the power P tends to infinity, which means that an "infinitely" large power, limited only by technical capabilities, can be brought into the active heating zone.

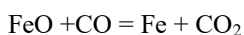
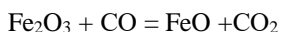
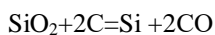
3. RESULTS AND DISCUSSIONS

The melting point of the charge depends on the chemical and mineralogical composition of the constituent components. Oxides of the elements included in the charge have a rather high melting point: silicon oxide SiO₂ 1713 °C; aluminum oxide Al₂O₃ 2050 °C; calcium oxide CaO 2627 °C; magnesium oxide MgO 2825 °C; nickel oxide NiO 1230 °C; manganese oxide MnO 1569 °C; chromium oxide CrO 2000 °C; titanium oxide TiO₂ 2020 °C. Considering that the raw materials consist mainly of minerals, the melting point of which is much lower, the working temperature of the melt is in the range from 1300 °C to 1500 °C.

The process of melting rocks [11] is complex, the melt has a high viscosity and low thermal conductivity, and an increased temperature used to intensify it. For the preparation of the melt, flame and electric arc furnaces were used: we analyze the process of melting basalt. In fired furnaces, the heat from the burner flame transferred to the heated raw material through the surface of direct contact, the contact of the flame and the surface of the heated raw material.

At the stage of heating the raw material to a temperature of 500 °C, inter crystalline water is removed, inorganic compounds are burned out, and minerals crack. There is no change in the chemical and mineralogical composition at this temperature. Upon reaching the temperature of 1100 °C, a change in the mineralogical and chemical composition of the feedstock begins to occur, the removal of chemically bound water occurs, and the glassy phase melts.

When the temperature reaches 1300 °C, the melt was formed and refractory minerals dissolve in it, the melt degassing occurs. The melting process is complex; various physical and chemical processes take place in it, depending on the composition of the charge, temperature, melting atmosphere, and furnace design. In the molten state, the surface of the melt acquires a significant reflectivity, which leads to increased consumption of gas, fuel oil; the practical temperature of the melt in flame furnaces does not exceed 1500 °C. Under reducing environment conditions, the transition reaction is happening from Fe₂O₃ to FeO and after that to Fe:



This process is carried out in both directions, but almost complete oxidation of iron does not occur, and, depending on the environmental conditions, equilibrium is established.

The precipitated iron at the bottom of the furnace forms a dark gray mass of ferrosilicon with an increased melting point, this reduces the useful volume of the melt and leads to a decrease in the furnace productivity. During cold repairs, this sediment must be removed.

The chemical composition of basalt from the Suluu-Terek deposit in the Kyrgyz Republic is given in table 2.

Basalts belong to effusive, basic rocks, the mineralogical composition of basalt mainly consists of plagiopase, augite, magnetite and olivine.

TABLE 2
CHEMICAL COMPOSITION OF BASALT FROM SULUU-TEREK DEPOSIT

Indicators	Composition, %
SiO ₂	49,36
FeO	3,89
Fe ₂ O ₃	4,45
TiO ₂	2,06
MnO	0,15
Al ₂ O ₃	16,04
CaO	9,72
MgO	4,60
K ₂ O	2,03
Na ₂ O	3,49

SO ₃	0,1
P ₂ O ₅	0,56
LOI	3,55

Mineralogical composition of basalt:

Plagioclase NaAlSi₃O₈, anorthite CaAl₂Si₂O₈; Olivine (Mg, Fe)₂[SiO₄]Mg₂Si₂O₆ (enstatite (Mg, Fe)₂Si₂O₆ (bronzite and hypersthene); Magnetite FeO · Fe₂O₃; Augit (Ca, Mg, Fe²⁺) (Mg, Fe²⁺, Al, Fe³⁺) [(Si, Al)₂O₆].

The external manifestation of the operation of an electric furnace with graphite and molybdenum electrodes is markedly different.

During the operation of molybdenum electrodes on the surface of the melt, ascending heat fluxes are visually observed; intensive release of CO and CO₂ is not observed. Intensive mixing of the melt also does not occur. The adjusted voltage and current parameters retain their parameters for a long time.

The operation of the experimental electric furnace on graphite electrodes of the EG-1 brand differs significantly from the operation with molybdenum electrodes, there is intense gas evolution, mixing of the melt, chemical interaction of the melt and electrodes.

During the operation of the furnace, from 1.0 % to 1.5% of a metallic substance of a silvery color constantly dropped out to the bottom, depending on the number of products obtained. The polymetallic alloy had to be removed daily through a special taphole made of MLS-72 refractory. Failure to remove the melt from the melting part of the furnace on time led to an emergency. The polymetallic alloy had a high fluidity and escaped through the smallest cracks, eroding the refractory and depressurizing the melting space.

The results of spectral analysis summarized in table 3 and a photo of the fracture of the polymetallic alloy are shown in Fig. 3 and Fig. 4. The analysis was carried out on a MBS-2 binocular microscope (manufactured by LOMO Russia, Leningrad), a NEOPHOT 30 microscope (manufactured in Germany).



FIGURE 3
POLYMETALLIC MELT MICROSTRUCTURE
(RESOLUTION 500X)



FIGURE 4
POLYMETALLIC MELT MICROSTRUCTURE
(RESOLUTION 1000X)

From Fig. 4 it is seen that the inclusion of metal particles in the slag material and the alloy has a high hardness HRC 60 to 62 units.

The results of the spectral analysis of the polymetallic alloy are shown in Table 3.

TABLE 3
SPECTRAL ANALYSIS RESULTS FOR POLYMETALLIC MELT

Chemical element	Melt 1	Melt 2	Melt 3	Average value
Fe	38,5	39,0	38,75	38,75
Al	0,06	0,065	0,0625	0,0625
Ni	8,2	8,0	8,1	8,1
Cu	3,2	3,4	3,3	3,3
Mn	25,0	25,2	25,1	25,41
Cr	24,81	24,25	24,54	24,54
Ca	0,06	0,05	0,055	0,055
Mg	0,04	0,035	0,075	0,075
In	0,1	0,12	0,11	0,11

The results of photometric analysis of the polymetallic alloy listed in Table 4.

TABLE 4
PHOTOMETRIC ANALYSIS RESULTS OF POLYMETALLIC ALLOY

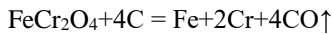
Chemical element	Composition, %
Fe	39,8
Al	0,04
Ni	7,4
Cu	2,6
Mn	19,6

Cr	25
Ag	0,3
Other	5,26

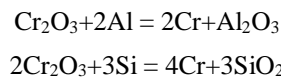
From table 4 that the highest content is represented by Fe 38.75%, Mn 25.41%, Cr 24.54%. These metals were precipitated in their pure form. Fe gets into the sediment as a result of the reaction of the transition of Fe₂O₃ to FeO and then to Fe. All chemical reactions of metals that take place in the melt are redox reactions and can be of only two types: compounds and substitutions.

The typical operating temperature in the active heating zone of an electric furnace is from 2200 °C to 2300 °C.

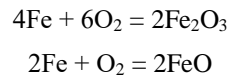
Chromium is most often found in basalt rock in the form of chromium iron ore FeCr₂O₄ and at high temperatures in the presence of graphite electrodes decomposes into ferrochrome according to the formula; it is used in the industry without further separation:



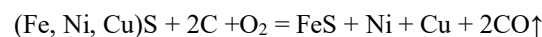
To obtain pure chromium, a reduction reaction is used, reducing chromium oxide with aluminum or silicon:



After conducting a quantitative analysis (Table 2 and Table 3) (from FeO 3.89% + Fe₂O₃ 4.45%, 38.75% Fe is obtained, and from losses on ignition were 3.55% where Cr, Ni, Cu, Ag and other elements, 24.54% Cr is obtained. As shown above, the reduction reaction Fe₂O₃ ⇒ FeO ⇒ Fe is not final and Fe adds oxygen from the melt:



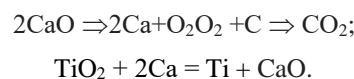
or other negatively charged ions and, depending on the conditions, a certain oxidation/reduction equilibrium is established. Nickel is most commonly found in basalt rock as garnierite (Mg, Ni)₆(Si₄O₁₁)(OH)₆·H₂O, magnetic pyrite (Fe, Ni, Cu)S, pentlandite (Fe, Ni)₉S₈.



According to table 2 losses on ignition were 3.55% includes the presence of copper pyrite 1.5% from which Ni, Cu is obtained, the reduction reaction proceeds much more efficiently than the Fe reduction in one direction. From 8.34% FeO + Fe₂O₃ tab. 2, 38.75% Fe is reduced, from 1.5% Fe, Ni, Cu) S, Ni 8.1% + Cu 3.3% is reduced (table 3.)

In the raw material, Al₂O₃ is 16.04% (Table 2) is much more than MnO 0.15%, MgO 4.6%, CaO 9.72%. The low Al content in the polymetallic alloy can be explained by the low specific gravity of Al 2.7 g/cm³. The density of the basalt melt is from 2.7 from 3.0 g/cm³, it simply cannot sink and remains on the surface of the melt, which is confirmed by gravitational stratification of the melt, high temperature and carbon are catalysts of the process.

In the absence of titanium in table 3, it is necessary to look for the chemical properties of titanium. To isolate it in its pure form, you need to create the FFC Cambridge process, named after its developers Derek Frey, Tom Farthing and George Chen from the University of Cambridge, where it was created. This electrochemical process allows direct continuous reduction of titanium from oxide in a molten mixture of calcium chloride and quicklime in a bath under the influence of direct current:



As it can be seen, in an alternating current electric furnace, there are no conditions for obtaining titanium in its pure form, and it remains in the melt. The main methods for producing copper Cu are pyrometallurgy, electrolysis, hydrometallurgy. To obtain copper, several stages are carried out: enrichment by flotation, roasting, smelting into matte, in which copper is concentrated, converting the resulting matte, refining using cathode copper. Copper is an accompanying element of nickel in magnetic pyrite

(Fe, Ni, Cu) S and their separation causes certain technological difficulties, therefore they are released together. A more detailed study of the chemical processes during the melting of basalt may provide a new way of obtaining Cu, Cr, Ni from basalts with a very low content of these elements.

Interesting is the appearance of small amounts of Ca and Mg 0.055 and 0.075%, the melting point for CaO is 2627 °C, for Mg is 2825 °C.

As shown in Fig. 2, the electric furnace does not have automatic control of the set current parameters. The operator sets this value manually, by tamping the electrodes to the minimum distance between the ends (a closer distance leads to the occurrence of a short circuit mode), thereby setting the maximum allowable current. This leads to the release of maximum power in the active heating zone which leads to an increase in temperature up to 3000 °C. But this mode cannot last for a long time due to the active destruction of the electrode itself, thereby the distance between the ends spontaneously increases, the current falls and with it the power and temperature in the active heating zone. In a short period, a small amount of Ca and Mg precipitates, whether this assumption is still to be answered, because in the industry Mg, Ca are obtained by the reduction of oxides with more active metals: silicon, aluminum, calcium, carbon and other metals, while the reduction takes place at a temperature where magnesium/calcium is in a vapor state, the magnesium/calcium vapors are removed (the remaining products remain liquid or solid) and condense in the cooler zone of the oven.

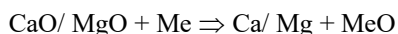


Fig. 5, and fig. 6 show the results of research carried out in the laboratory of the Joint Institute for Nuclear Research in Dubna (Russia) of the scanning electronic microscope S-3400N from Hitachi.

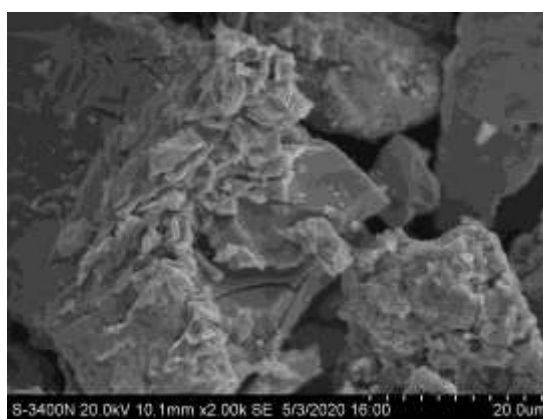


FIGURE 5
MICROSTRUCTURE OF CRUSHED POLYMETALLIC POWDER

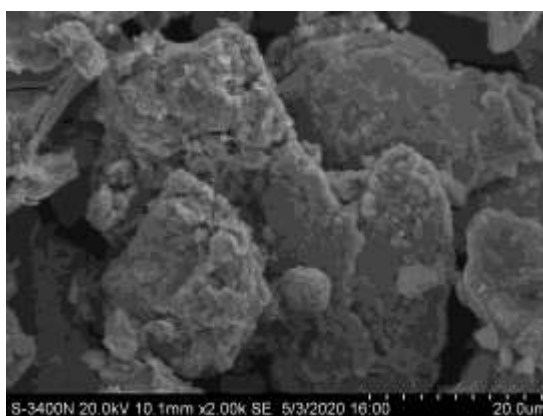


FIGURE 6
MICROSTRUCTURE OF CRUSHED POLYMETALLIC POWDER

Figures 5 and 6 confirm the complex composition of the polymetallic alloy in which the various elements are located separately, and there are empty spaces separated by different metal structures. Further, chemical structural analysis was carried out using an X-ray energy-dispersive spectrometer of the NORAN type. Polymetallic alloy sprayed with gold metal powder. The research results are shown in Fig. 7 and table. 5.

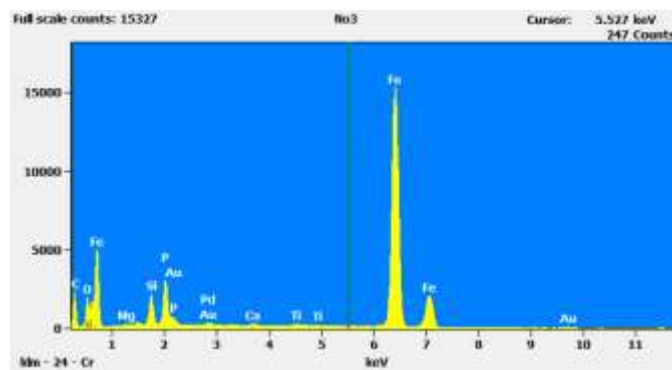


FIGURE 7

X-RAY DIFFRACTION PATTERN OF ELEMENTS IN A POLYMETALLIC ALLOY

The results of X-ray energy dispersive analysis of the polymetallic alloy show that iron, nickel and chromium reduced. In basalt raw materials, this element contains an insignificant amount, but due to the gravitational process of the melt and interaction with graphite, reduced chromium particles are collected at the bottom of the furnace.

When choosing an electric furnace for the production of stone casting or basalt fiber, it is necessary to use all the available positive and negative factors. Knowledge about the processes in the active melting zone lets us establish operating modes that minimize the identified drawbacks and allow obtaining petrugic melts with desired properties. Electric furnaces with molybdenum electrodes and motor drive control operate successfully in the glass industry, the melt is not clogged with the decomposition products of graphite electrodes, there are no conditions for the chemical interaction of the electrode material and the melt itself. With proper operation in an oxygen-free environment, they can serve for several years, justifying their high cost by long-term work. Motor drive control allows you to set automatic control of the set parameters in terms of temperature and limiting current density, eliminating the human factor.

CONCLUSIONS

In summary, the following conclusions were made:

1. For basalt melting, it is more economical to use an electric heating furnace with graphite or molybdenum electrodes.
2. The physicochemical interactions at high temperatures of the basalt melt have been substantiated. The processes of gravitational sedimentation of a polymetallic alloy due to burnout of graphite electrodes and its interaction with the melt have been established.
3. Investigated the chemical composition and structure of the polymetallic alloy. The analysis showed that the polymetallic alloy deposited on the bottom of the furnace mainly consists of iron, titanium, chromium, etc. Not all heavy and valuable metal elements were deposited on the furnace bottom.

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