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Study of Physico-chemical Properties of High-ash Coal from the Saryadyr Deposit

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Abstract. *The article presents the results of physical and chemical studies of high-ash coal of the «Saryadyr» deposit. The method of X-ray phase analysis on X-ray diffractometer DRON-2 established that the main phases of oxides in the high-ash coal field «Saryadyr» presented in the form of quartz and kaolinite. In the course of the research the differential thermal analysis (DTA) of coal was carried out. DTA was carried out on derivatograph system F. Paulik, I. Paulik, L. Erdey, which allows to fix the change in mass and the rate of change in mass of the sample. As part of the research work, experimental studies were carried out to determine the resistivity of coal when heated. The measurements were carried out in a Tammann high-temperature electric furnace. The studies to measure the electrical conductivity of coal were carried out in the temperature range of 25-1500°C, heating rate 25 deg/min. The research is funded by the Science Committee of the Ministry of Education and Science of the Republic of Kazakhstan (Grant No. AP13068023).*

Keywords: *high-ash coal, carbothermy, ligature, ferroalloys, X-ray diffractometric analysis, differential thermal analysis, endothermic transformation, exothermic transformation, thermal conductivity, electrical resistivity.*

Introduction

One of the main determinants of the development of a country's mining and metallurgical complex is the quality of its ore base and its reserves. Kazakhstan has large coal reserves and is one of the top ten countries in terms of coal production. Information about coal reserves of Kazakhstan is given in many open sources [1, 2].

Approximate reserves of coal in Kazakhstan are estimated at 93 billion tons. The main reserves are concentrated in the Karaganda, Pavlodar and Kostanay regions, i.e. in Central Kazakhstan [3]. Extracted coal is used for the energy industry (51%) and for export (31%), while the rest is used for the needs of industry and the population of the country. The main share of Kazakh coal is exported to the Russian Federation (about 30.5 million tons per year), where coal is used for power generation plants. However, as stated by the generating companies in the Russian Federation, in the future there is a question of reducing coal exports from Kazakhstan and switching the power plants to Russian coal. Also, China is reducing the reported demand for Kazakh coal. This is due to the fact that China is reducing the share of imports by rail. Currently, China prefers to import coal from Australia and Indonesia transported by sea [4]. The pessimistic forecasts of the coal industry in Kazakhstan push for a new vector of development, and the question of expanding the use of coal is raised. Scientists of CMI named after Zh. Abishev actively develop the idea of involvement in metallurgical processing of coals of Kazakhstan. Positive results have been achieved in this direction: new technologies have been developed, technological tests have been conducted in industrial conditions, pilot batches have been developed, and protection documents have been obtained.

According to the existing technology for smelting ligatures and ferroalloys, carbonaceous materials with high resistivity and favourable porous structure should be chosen as reducing agents. More detailed studies of the physical and chemical properties of carbonaceous reducing agents for the carbothermic process are considered in the monograph by V.G. Mizin and G.V. Serov.

High ash coal from the Saryadyr deposit was selected for ligature and ferroalloy smelting by the carbothermic method. The coals of Saryadyr deposit belong to the Teniz-Korzhunkol basin in Ereymentau district (170 km from Nur-Sultan city). Ash content of coals reaches up to 55% [5].

Purpose of work

Metallurgical evaluation of qualitative and quantitative characteristics of high-ash coal of Saryadyr deposit for smelting of ligatures and ferroalloys by carbothermic method.

Experimental part and discussion of results

The first question is the content of the main components in the material. For this purpose, X-ray diffractometric analysis was carried out on an X-ray diffractometer DRON-2, which allows it to be carried out quickly and with high accuracy. The X-ray diagram of high ash coal of the Saryadyr deposit is shown in Figure 1.

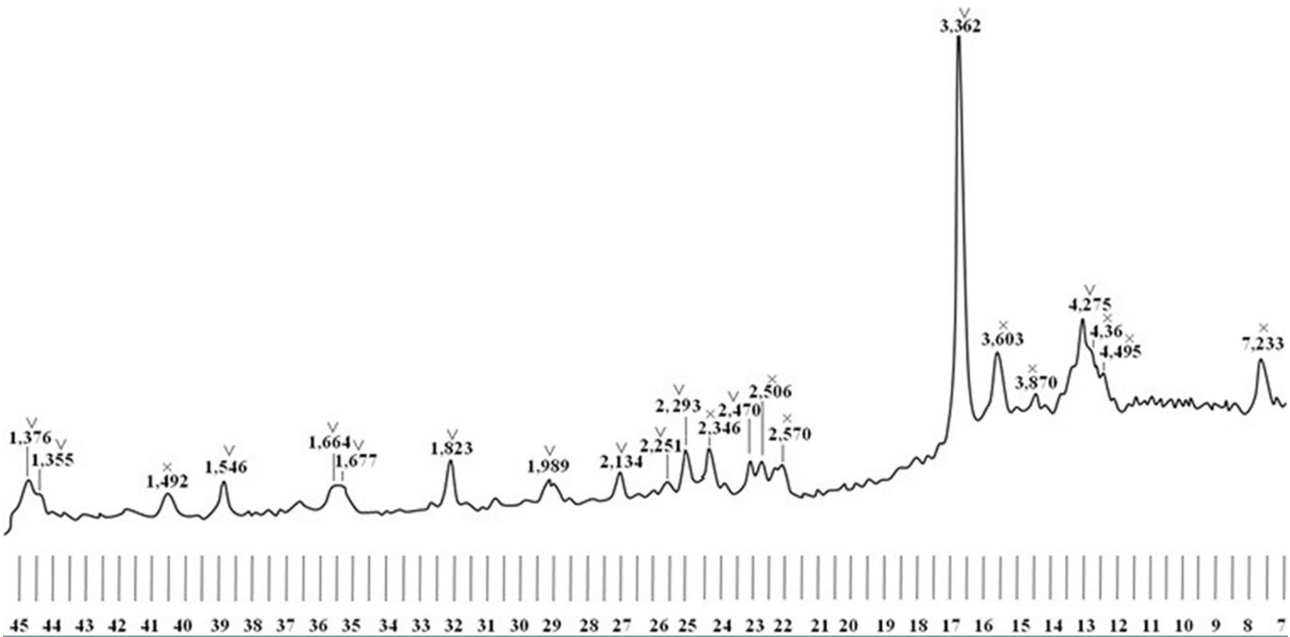
X-ray phase analysis has established that the main oxide phases in the high-ash coal of the Saryadyr deposit are in the form of quartz (ά-SiO_2) and kaolinite ($Al_2Si_2O_5(OH)_2$). These minerals can be used as complex raw material sources of aluminium and silicon.

In the process of electric melting, charge materials, under the influence of high temperatures, undergo a number of physical and chemical transformations that significantly change their original properties. In particular, under the influence of high temperature their structure, the nature of the porous structure of coal, the decomposition of organic compounds and the removal of volatile substances are altered.

Since the mentioned processes are combined in time by interaction of carbon with oxides of the non-carbon part of the charge and are interconnected to a large extent, the general picture of physical and chemical transformations is very complex and, therefore, insufficiently studied. One of the methods to study the processes occurring successively at increasing temperature, which are widely spread, is the method of thermal analysis. In the course of research, differential thermal analysis of the initial charge materials was carried out. Thermal methods of analysis are used to study chemical reactions and physical transformations occurring under the action of heat in chemical compounds or in multi-component systems between separate compounds. Thermal processes (chemical reactions, state changes or phase transformations) are always accompanied by a more or less significant change in internal heat content. A conversion entails an absorption (endothermic conversion) or a release of heat (exothermic conversion). Such thermal effects can be detected by differential thermal analysis. Transformations in many cases are connected with a change of weight, which can be determined with great accuracy by the thermogravimetric method.

Differential thermal analysis was carried out in an oxidizing air atmosphere on a derivatograph of the system F. Paulik, I. Paulik, L. Erdey, which allows to record the mass change (TG) and mass change rate (DTG) of the sample as well as the temperature difference (DTA) between the test and inert samples during continuous heating at a given rate. The temperature and differential curve were recorded using a platinum-platinum-rhodium thermocouple. The heating rate was 10 to 15 degrees per minute. The sensitivity (DTA) of the derivatograph was 1/10. Samples of the materials under study were placed in a corundum crucible of diameter 10 and height 12 mm in powder form. The duration of experiments was 100 minutes. The results of the experiments are shown in Figure 2.

Samples of the materials under investigation were placed in a corundum crucible with a diameter of 10 mm and a height of 12 mm in powder form. The



v – quartz ά-SiO_2 (1.376; 1.355; 1.546; 1.664; 1.677; 1.823; 1.989; 2.134; 2.251; 2.293; 2.470; 3.362; 4.275),
× – kaolinite $Al_2Si_2O_5(OH)_2$ (1.492; 2.346; 2.506; 2.570; 3.603; 3.870; 4.36; 4.495; 7.233)

Figure 1 – X-ray diagram of high-ash coal «Saryadyr» deposits

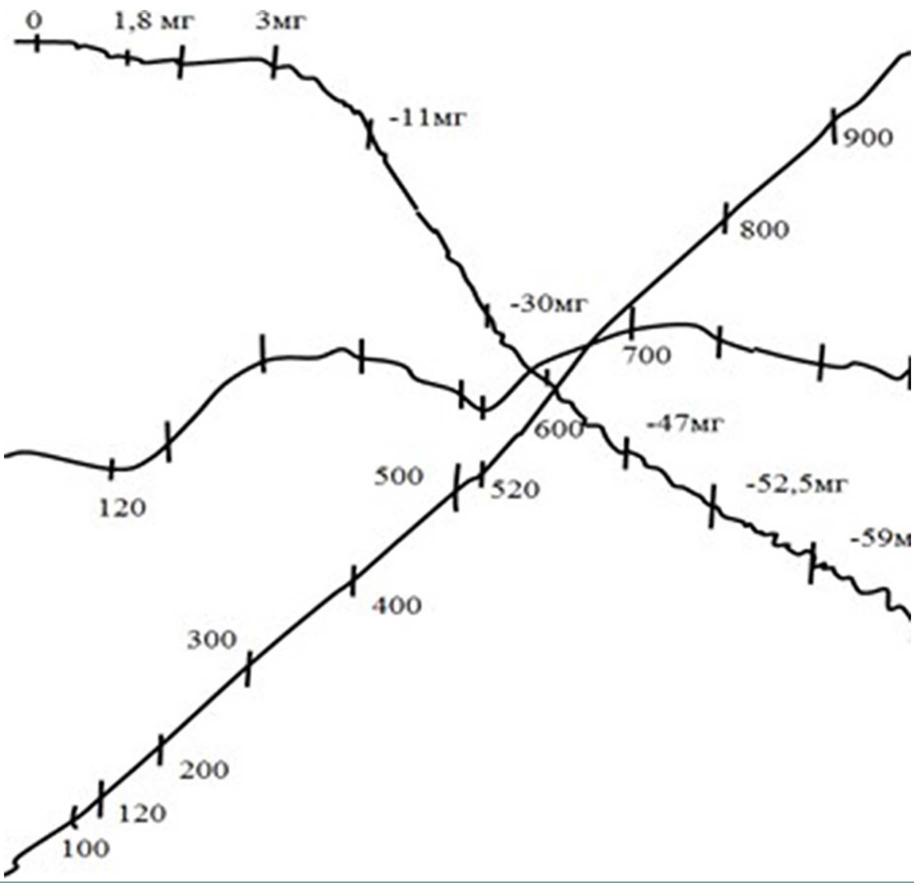


Figure 2 – Derivatogram of «Saryadyr» high ash coal (sample weight 1560 mg)

duration of the experiments was 100 minutes.

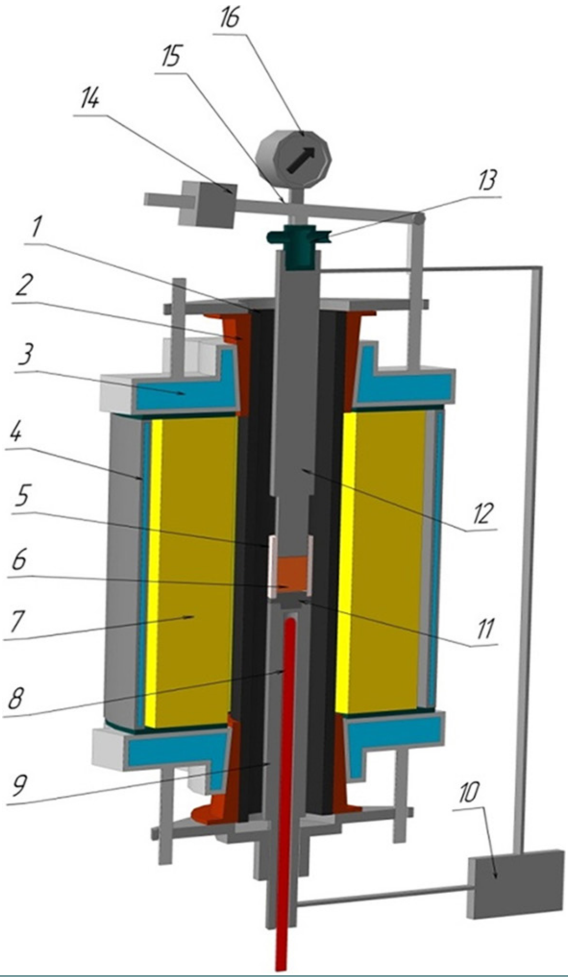
«Saryadyr» high ash coal has several thermal effects. The first endothermic effect with a maximum at 120°C indicates the loss of hygroscopic moisture, commonly referred to as the drying peak. There is a direct correlation between the depth of this peak and the moisture content of the coal. The structure remains unchanged and the mass of the sample decreases by 1.8 mg. After the end of moisture extraction from the coal, starting from about 280°C, an exothermic effect accompanied by thermal destruction of the organic mass of the coal begins, resulting in the formation of gaseous products. Somewhat later, at 500-520°C, the release of volatile substances begins. A. Boyer and P. Payen believe that the exothermic effect results from the increase in thermal conductivity of coal during its transition to the plastic state. A sharp jump at 520°C indicates an increase in the thermal conductivity of the coal.

One of the main characteristics of charge materials is the change in electrical properties when heated. The charge mixture for smelting ligatures and ferroalloys in a carbothermal process consists of 60-80% carbonaceous reducing agent and 20-40% «ore» mixture. Therefore, the electrical properties of the mixture can be judged from the carbonaceous reducing agent used in alloy smelting [6-9].

As part of this research work, experimental studies were carried out to determine the electrical resistivity of coal when heated. A schematic diagram of the installation to determine the electrical resistivity of the material is shown in Figure 3.

A sample of 3-4 mm fraction of coal from the Saryadyr deposit was used for the experiments to measure electrical resistivity. The measurements were carried out in Tamman high-temperature electric furnace. Studies on measuring the electrical conductivity of coal were carried out in the temperature range of 25-1500°C, the heating rate of 0-25 grad/min. This methodology differs from the well-known Agroskin and Shumilovskaya methods. According to their methodology, the resistance was measured after 50°C, which reduces the informative value of the data obtained. The method used by us to measure the data after 30 seconds automatically saves the information in digital format in the computer memory, allows us to avoid the disadvantages of the method described above. The method proposed by V.I. Zhuchkov is the most widespread in experimental practice [9].

The experimental setup consists of a Tammann furnace in which the material is heated. The starting material, 8 cm high, is placed in an alundumina beaker (5) (beaker diameter 4 cm) installed in the Tammann furnace. The data coming from the thermocouple (8), electrodes (9, 12) and electronic device were recorded using signal transducers. A graphite electrode (9, 12) was mounted on both sides of the material to provide voltage with an opening for the thermocouple (8). The lower electrode is fixed permanently, the upper one has the possibility to be lowered when the material



1 – carbon-graphite tube; 2 – copper crimp ring; 3 – water-cooled lid; 4 – water-cooled casing; 5 – alundumina cup; 6 – charge to be examined; 7 – protective lining; 8 – thermocouple; 9 – bottom electrode; 10 – Ohm meter digital; 11 – graphite bottom for alundumina cup; 12 – top electrode; 13 – water cooling; 14 – weight; 15 – lever; 16 – electronic shrinkage measuring device

Figure 3 – Installation for determining electrical resistivity and shrinkage (sectional view)

shrinks under the action of the weight. The weight (14) permanently presses the upper electrode to the material, thus ensuring a tight contact. The pressure on the material was 0.02-0.04 MPa. A thermocouple in an alundumina tube was placed through the lower electrode to insulate it from electricity. The results of the temperature-dependent variation of the electrical resistivity values are presented as a graph in Figure 4.

Figure 4 shows the dependence showing the effect of temperature on the change in the resistivity of coal. The curve can be divided into three temperature sections. The first is from 50 to 120°C where a slight drop in resistivity is noticed, the second is from 200 to 600°C and the last section is from 600 to 1000°C.

The kink of the curve in the 50 to 120°C region is due to the presence of a large amount of moisture in the sample, which contributes to an increase in conductivity, and at higher temperatures, as the moisture is removed, the resistance evens out. The resistance of coal decreases slightly from 200 to 600°C. This is due to the release of volatile substances, which have a slightly increased electrical resistance. At 600°C, a sharp drop in electrical resistance can be seen. Differential thermal analysis (DTA) of coal showed that at temperatures of 600-650°C there is a rearrangement of the coal substance towards an ordered structure, which contributes to a decrease in the electrical resistivity of coal.

Conclusion

Thus, the study of physical and chemical properties of charge materials determined that the main oxides of the material are represented by quartz ($\acute{\alpha}$-SiO_2) and kaolinite ($Al_2Si_2O_5(OH)_2$), the specific electrical resistance of coal when heated is relatively high. Such characteristics of coals satisfy the processes of melting of ferroalloys and ligatures in the ore-thermal furnace with deep immersion of electrodes with stable current load.

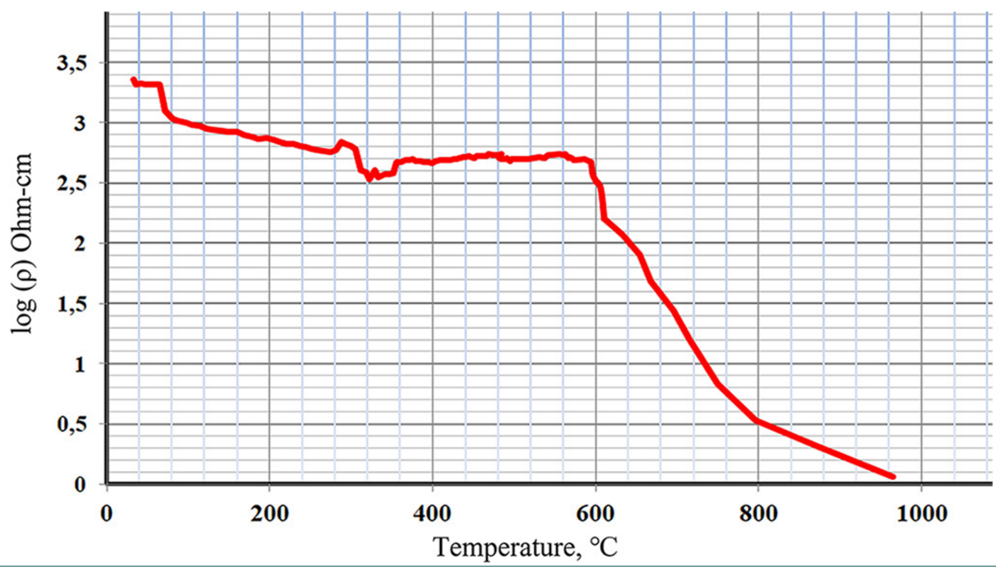


Figure 4 – Electrical resistivity of coal in depending on temperature

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«Сарыадыр» кен орнының жоғары күлді көмірінің физика-химиялық қасиеттерін зерттеу

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Аңдатпа. *Мақалада «Сарыадыр» кен орнының жоғары күлді көмірінің физика-химиялық зерттеулері нәтижелері келтірілген. ДРОН-2 рентгендік дифрактометрінде рентгенофазалық талдау әдісімен «Сарыадыр» кен орнының жоғары күлді көміріндегі тотықтардың негізгі фазалары кварц және каолинит түрінде екендігі анықталды. Зерттеу барысында көмірге дифференциалды-термикалық талдау (ДТА) жасалды. ДТА Ф. Паулик, И. Паулик, Л. Эрдей жүйесінің дериватографында жүргізілді. Бұл үлгі массасының өзгерісі мен массасының өзгеріс жылдамдығын анықтауға мүмкіндік береді. Зерттеу жұмысы шеңберінде қыздыру кезіндегі көмірдің меншікті электр кедергісін анықтау бойынша эксперименттік зерттеулер жасалынды. Өлшеу жоғары температуралы Тамман электр пешінде жүргізілді. Көмірдің электр өткізгіштігін өлшеу бойынша зерттеулер 25-1500°С температура аралығында жүргізілді, қыздыру жылдамдығы 25 град/мин. Зерттеуді Қазақстан Республикасы Білім және ғылым министрлігінің Ғылым комитеті қаржыландырады (грант № AP13068023).*

Кілт сөздер: *жоғары күлді көмір, карботермия, лигатура, ферроқорытпа, рентген-дифрактометриялық талдау, дифференциалды-термиялық талдау, эндотермиялық ауысу, экзотермиялық ауысу, температура өткізгіштігі, меншікті электр кедергісі.*

Изучение физико-химических свойств высокозольного угля месторождения «Сарыадыр»

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Аннотация. *В статье приведены результаты физико-химических исследований высокозольного угля месторождения «Сарыадыр». Методом рентгенофазового анализа на рентгеновском дифрактометре ДРОН-2 установлено, что основные фазы оксидов в высокозольном угле месторождения «Сарыадыр» представлены в виде кварца и каолинита. В ходе исследований выполнен дифференциально-термический анализ (ДТА) угля.*

ДТА проводили на дериватографе системы Ф. Паулик, И. Паулик, Л. Эрдей, который позволяет фиксировать изменение массы и скорость изменения массы образца. В рамках исследовательской работы были проведены экспериментальные исследования по определению удельного электросопротивления угля при нагревании. Измерения проводились в высокотемпературной электропечи Таммана. Исследования по измерению электропроводности угля проводили в интервале температур 25-1500°С, скорость нагрева 25 град/мин. Исследование финансируется Комитетом науки Министерства образования и науки Республики Казахстан (грант № AP13068023).

Ключевые слова: *высокозольный уголь, карботермия, лигатура, ферросплав, рентгено-дифрактометрический анализ, дифференциально-термический анализ, эндотермическое превращение, экзотермическое превращение, температуропроводность, удельное электросопротивление.*

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