ЖЫЛУ ФИЗИКАСЫ ЖӘНЕ ТЕОРИЯЛЫҚ ЖЫЛУ ТЕХНИКАСЫ
ТЕПЛОФИЗИКА И ТЕОРЕТИЧЕСКАЯ ТЕПЛОТЕХНИКА
THERMOPHYSICS AND THEORETICAL THERMOENGINEERING

A.D. Mausymbayeva[1], Ya.Zh. Baisagov[2], V.S. Portnov[1], V.M. Yurov[2], S.A. Guchenko[2], A. Amangeldikyzy[1]

[1]Karaganda State Technical University, Kazakhstan;
[2]Ye.A. Buketov Karaganda State University, Kazakhstan
(E-mail: aliya_maussym@mail.ru)

Measuring the iron oxide in Shubarkol deposit coal

Comprehensive development of mineral resources is one of the main objectives of a state. An important role for its solution is the import substitution of expensive colombian coals used in the production of industrial silicon, with shubarkol coals having similar characteristics. One of the main geological tasks is to study the distribution of iron oxide in coals, which affects to the technology of ore-thermal production of silicon. Researches have shown that expensive chemical analyzes of iron oxide, with high accuracy, do not allow them to be used promptly when forming a batch of coal at the enterprise. To solve the urgent task of an express assessment of the content of iron oxide in coal we have been developed a method and device that implements the induction principle of measuring the magnetic characteristics of coal. The method is based on the transition of the oxide of two-valence iron into a complex oxide of trivalent during ashing. The discrepancy between the measurement results according to the Kazakhstan state standard GOST 10538–87 and the developed method is within the permissible range of this standard. The device is being used at Shubarkol Komir JSC Company. It received certificate of metrological certification No. 9912 and is authorized as a measurement instrument in the Republic of Kazakhstan.

Keywords: coal, ash, iron oxides, magnetization, induction coils, concentration measurement.

Introduction

Shubarkol Komir JSC company would be interested in supplying its products to RusAl and Tau-Ken Temir LLP as a substitute for Colombian coal for silicon production. To assess this possibility, Centrgeolanalit LLP conducted a study to check the ash content of coal benches and the iron oxide content in coal ash. The findings suggest that:

1. The ash content of coal benches varies from 1.5 % to 4.0 %, and its iron oxide content varies from 0.9 to 1.5 kg/t, which enables to use Shubarkol coal as a substitute for Colombian coal;

2. Seam extension in areas where the iron oxide content is within the required limits is about 500 m in the Western Area, which is 40 % of the extension of mining, whereas in the Central Area it is about 1100 mm, which is 20 %;

3. Since mining is carried out according to the annual plan, mining in areas with low iron oxide content may not coincide with the time of coal shipment to RusAl.

4. Few samples does not give certainty about the iron oxide content over the entire seam extension as this indicator is variable both along strike and at depth.

In this regard, it is difficult to forecast the average iron oxide content in coal during mining and to quickly monitor its grade during production and shipping to consumer, which is associated with high cost of chemical analyzes and their duration. It was concluded that meeting technological requirements for the iron

oxide content in coal within the established limits (up to 1.5 kg/t) for shipment to RusAl and Tau-Ken Temir enterprises is costly and difficult.

Sources of iron oxide in coal

The main minerals in the coals of Shubarkol deposit are vitrinized matter, and to a lesser extent semi-vitrinized and fusainized matter. The reflection index of vitrinite is 0.50–0.62 %. As per Kazakhstan state standard GOST-25543, they relate to stone type, grade D (long flame), subgroup DV (long flame, vitrinite). According to ST RK ISO 11760, coals are subbituminous of low grade A, high vitrinite grade.

As per GOST 11022–95, there had been checked the ash content of coals which varies in individual seams within 4.2–20.1 % with extreme values for individual seams of 1.7–31.0 %. The ash content and mineral composition of raw coal is determined by occurrence of rock interlayers in the seams and is dependent on its impurity degree. The average ash content in the Upper Level coals varies from 8.7 to 8.9 % (Western area), 11.9–12.7 % (Central area) and 10.9–12.1 % (Eastern area).

One of the iron sources in coal are interlayers and lenses of siderite ($FeCO_3$) 62.1 % FeO and 37.99 % CO_2, which are developed mostly in the central part of the overburden rock section.

As an iron oxide carbonate, siderite is formed in reduction conditions, i.e. in conditions of oxygen deficiency and decomposition of organic residues with the formation of carbon dioxide and hydrogen sulfide due to protein substances. The source of ferruginization of weathering crust sandstones and hematite-goethite nodules in the deposit is ferric oxide (Fe_2O_3), which is formed during the siderite oxidation and forms «iron caps» (outliers), consisting of goethite (60–80 %), hematite (20–35 %) with the following chemical composition (%): Fe_2O_3 — 87–88 %, FeO < 0.25; MnO — 0.4–0.6; SiO_2 — 3.4; Al_2O_3 — 0.7; TiO_2 — 0.03; P_2O_5 — 0.2; S_{total} — 0.2.

The coal seams of the Upper and Lower Levels are characterized by interlayers of coal saturated with siderite spherolith, resulting in coals acquiring a granular structure [1].

Quite often, iron pyrite disulfide (II) (FeS_2) is found in the coals of the deposit, filling cracks and present in the form of oolites confined to gelified matter.

The Upper Horizon seams are characterized by an unusual mineral association, oolites in the form of loose formations consisting of a pelitomorphic mixture of pyrite, quartz and an amorphous organic matter represented by a gelified substance.

The average content of iron sulfides in raw coals of the Upper Level is 0.14 %, and 0.2 % in the Lower Level.

In total (excluding hydroxides), there are four natural iron oxides $2\text{-}Fe_2O_3$ (hematite), Fe_3O_4 (magnetite), $\gamma\text{-}Fe_2O_3$ (maghemite), $Fe_{1-x}O$ (wustite).

Hematite is an antiferromagnet and has weak ferromagnetism below the Néel point (948 K). In magnetite, all bivalent iron ions are in an octahedral environment, and trivalent ions are divided in half between the octahedral and tetrahedral environment $(Fe^{3+})[Fe^{2+} Fe^{3+}]O_4$. The ratio $Fe^{2+}/Fe^{3+} = 0.5$.

The values of magnetic moments are dependent on the number of uncompensated electrons in the $3d$-electron shell of iron ions, which explains ferromagnetic properties of magnetite. It acquires paramagnetic properties above the Curie temperature $T = 850$ K. With a decrease in temperature in a constant magnetic field, magnetite acquires induced and thermo-remanent magnetization, which occurs during coal ashing (1150 K). Maghemite contains only trivalent iron cations. At temperatures below $T = 840$–986 K, it is a ferromagnet. Hematite, magnetite, maghemite and wustite are practically not found in coal, but magnetite is of interest as a newly formed mineral appearing during the ashing and transition of bivalent iron to trivalent iron.

The carbonaceous type of siderite ($FeCO_3$) can have calcium, cobalt, zinc and manganite minerals. Iron oxide (III) (Fe_2O_3) 86–89 %, water (H_2O) 10–14 % are quickly eroded with transition to limonite. Oxidizing, it transfers to brown iron ore $nFe_2O_3 + nH_2O$ [1].

Goethite produces pseudomorphs in pyrite, marcasite and other sulfides, in siderite, magnetite, hematite and ferruginous silicates.

The oxygen content in coals of the deposit varies from 3 to 5 %, which indicates that they belong to the demethanization zone and the oxidation zone of iron-containing minerals (silicates, sulfides, iron minerals) which is characterized by active water-gas exchange, creating conditions for the release and transfer of oxidation products to coal seams. This is also evidenced by high nitrogen content. According to the hermetic glasses data, at a depth of 40–115 m they exceed 90 %, rising to 95–97 %, and according to core samples in

the depth interval 43–200 m it varies from 38–55 % to 95–97 %. The average methane content is 2.5 %, which confirms the conclusion about coal demethanization accross the entire deposit.

The carbon dioxide content in the Upper Level seams at depths from 40 to 100 m is 60–30 %, whereas to the basin center it decreases to 20–10 %. The hydrogen content at depths of up to 100 m does not exceed 1 %.

The average value of the moisture mass fraction (GOST 8858–76), which was estimated by the maximum moisture capacity (W_{max}%), for the Upper seam is 15.3 with extreme values of 8.0–28.4, while it does not depend on the ash content of coal.

Under such conditions, there occurs oxidation of Fe^{2+} coming into the coal seam from overlying rocks as products of decomposition of iron-containing minerals up to Fe^{3+} by reaction exemplified by iron oxide (II) both with moisture and without it:

$$4FeO + 2nH_2O + O_2 \rightarrow 2(Fe_2O_3\, nH_2O)$$

and at temperatures above 300–500º C (ashing)

$$6FeO + O_2 \rightarrow Fe_3O_4$$

Measurement of the mass fraction of iron oxide in coal ash samples according to GOST 10538–87 is done by photogrammetry with orthofentrolin, whereas measurement of iron content is carried out in ash samples after coal ashing according to GOST 11022–95 at a temperature of (815 ± 10) ºC in an air atmosphere with active interaction with oxygen.

Magnetite (Fe_3O_4) is formed in coals and their ashes, which is a complex oxide that simultaneously contains II and III valence iron. In the presence of constant magnetic field of the Earth, conditions are created for the acquisition of induced magnetization by this oxide, and during thermostatic magnetization ashing the magnetic moment arises, which is determined by the mass fraction of Fe_3O_4.

All this provides the basis for using the induction method for assessing iron oxide in coal.

There are chemical and physical methods (X-ray fluorescence, atomic emission) for determining chemical composition of coal, ash, including iron oxides (III) regulated by GOST: 10538–87, P 55879–2013, P 54237–2010 (ASTMD 6349–2008) [1].

These methods are characterized by long-term measurement process, which is unacceptable when preparing coal as a carbon reducing agent for transportation to the consumer.

Induction method in coal iron oxide test

In this regard, we have developed a device for rapid analysis of the iron oxide (III) concentration in coal by its magnetic susceptibility. Pieces of works [1, 2] on achievements in induction method for measuring the magnetic susceptibility of samples in feed-through coil by changing the introduced complex resistance enabled us to elaborate on the subject and create the device.

To measure extreme low values of magnetic susceptibility with high accuracy, it was necessary to consider many influences. A sample to be magnetically measured is placed to an inductor, while the winding inductance changes in proportion to the magnetic susceptibility of the sample [1, 2].

To measure little changes in inductance, we used a bridge method which uses two identical inductors, with the sample placed into one of them. Identical secondary coils are wound on the coils, with their windings connected in series and in opposite phases for mutual compensation of the signal induced to them in the absence of the measured sample. An equivalent chart of the measuring unit is shown in Figure 1.
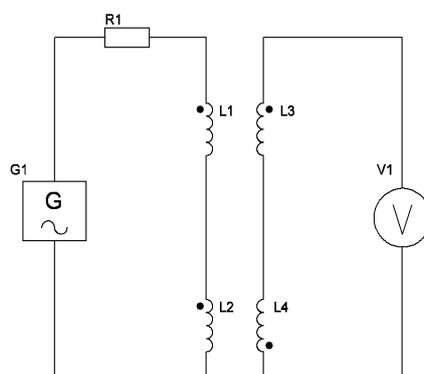

Figure 1. An equivalent chart of the measuring unit

In this circuit, generator G1 excites an alternating sinusoidal electric current in the circuit G1, R1, L1, L2, and resistor R1 displays the total active resistance of the winding wire L1 (measuring) and L2 (compensation).

As per the Kirchhoff's second law:

$$U_{G1} = IR1 + Ij\omega L1 + Ij\omega L2, \tag{1}$$

where ω is angular frequency of alternating current, I is current in the circuit of primary windings. Secondary voltages:

$$U_{L3} = Ij\omega L_1 k \; ; \; U_{L4} = Ij\omega L_2 k , \tag{2}$$

where k is transformation ratio.

As a result, a useful error signal will be:

$$\Delta U = Ij\omega L_1 k - Ij\omega L_2 k = Ij\omega k (L_1 - L_2) . \tag{3}$$

From formula (3) it follows that the error voltage depends on the difference of inductance of the measuring and compensation (reference) coils, but does not depend on active resistance of the winding, which helps to avoid problems associated with temperature dependence of the coil.

Due to extremely small size of the relative magnitude of the change in coils inductance when introducing the sample, measurement of the useful error signal appears to be a difficult task. Additional difficulty is impossibility of full compensation of the secondary voltage due to misalignment of the voltages both in amplitude and in phase due to influence of inter-turn and inter-winding capacitance. To solve this problem, it was decided to abandon exact compensation of voltages and the use of a zero indicator. Instead, the error signal is digitized using a high-precision analog-to-digital converter. The chart of the error signal processing unit is shown in Figure 2.
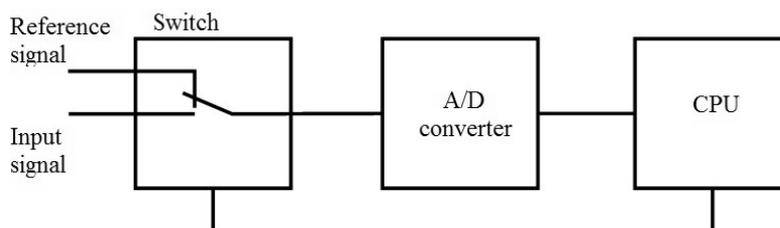

Figure 2. Error signal processing unit

Analysis of tracer amounts of heavy metals using traditional physicochemical methods (atomic absorption, polarography, photometry, etc.) requires preliminary preparation of the sample because metals in most objects are in a bound state. They form fairly strong organic complexes that hinder to accurately reproduce and determine their content. Therefore, it is necessary to deconstruct the organic component of the coal sample in order to identify the target elements in the form of stable inorganic compounds convenient for subsequent analysis [2].

Destruction of organic components is performed by ashing, i.e. burning a sample in a muffle furnace, and wet ashing, which is heating with acid oxidizing agents. Preparation for heavy metal analysis in samples of complex composition by these methods sometimes takes 8–10 hours and about 80–90 % of the total testing time. In most cases, errors of the experimental results are made at this stage [2].

To reduce the time of sample preparation, we used partial ashing process which includes:

− weighing by 10 g of coal and placing in a crucible with a lid;

− crucibles are quickly placed to the zone of stable temperature of the furnace heated to (900±5) ºC, kept for 10 minutes (the temperature that fell when the crucibles were placed to the furnace should again reach (900±5) ºC in no more than 4 min.);

− a support with the crucibles is taken away from the furnace, cooled on a metal or asbestos plate to room temperature;

− the test sample is transferred from the crucible to a sealed polyethylene container, which is placed to a flask for putting into the measuring coil of the device and analyzed in accordance with the developed procedure.

The developed PIKOZ-1 device and the method of induction-based measurement of the iron oxide content in coal are introduced in a coal mine of Shubarkol Komir JSC.

The results of measurements of the iron oxide content in coal according to GOST 10538–87 and using induction-based method are presented in the Table which suggests that the observed discrepancy in results is within acceptable limits (GOST 10538–87). The time of one measurement as per GOST 10538–87 (using chemical method) was 14 hours, and the induction method took 0.5 hours, which reduces the time of coal test for iron oxide content by 48 times. This is a crucial factor when preparing coal before shipment.

T a b l e

Results of measuring iron oxide in coal by analytical and induction methods

Certificate #	Content of Fe_3O_4, (kg/t)		Mass fraction of Fe_3O_4, (%)		Discrepancy (%) abs.
	GOST 10538–87	Induction method	GOST 10538–87	Induction method	
1453	2.08	1.78	0.208	0.178	0.03
1024	0.77	2.05	0.077	0.205	0.13
1021	1.02	2.66	0.102	0.266	0.16
1598	2.33	2.71	0.233	0.271	0.04
1239	4.36	4.23	0.436	0.423	0.01
1539	1.50	1.32	0.150	0.132	0.02
1201	2.33	2.28	0.233	0.288	0.06
1221	2.67	2.70	0.267	0.270	0.01
1454	1.63	1.74	0.163	0.174	0.01
1271	10.77	11.09	1.077	1.109	0.03
1342	8.73	8.64	0.873	0.864	0.01
191	1.47	1.48	0.147	0.148	0.001

The error of analytical measurement according to GOST 10538–57 for iron oxide from 5 to 10 % should be 0.4 % absolute or 7.7 % relative. For a mean iron oxide content of 3.35 % the resulting error is 0.2 % absolute found by analytical and induction methods.

Conclusion

For rapid measuring of the concentration of iron oxide in coal, the PIKOZH-1 method and device have been developed. The device was introduced at Shubarkol Komir JSC, Certificate No. 9912 on metrological certification as a measuring instrument with the right to be used in the Republic of Kazakhstan was received for it. It can be offered to organizations working on supplies of unique coal of the Shubarkol type in order to use it as a carbon reducing agent in the production of silicon and aluminum.

The resulting error in the measurement of iron oxide in coals meets the requirements of the Kazakhstan state standard GOST 10538–57 and is 0.2 % abs.

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А.Д. Маусымбаева, Я.Ж. Байсагов, В.С. Портнов,
В.М. Юров, С.А. Гученко, А. Амангелдіқызы

Шұбаркөл кен орны көмірлеріндегі темір оксидін анықтау

Пайдалы қазбаларды кешенді игеру мемлекеттің басты міндеттерінің бірі болып табылады. Оны шешуде маңызды рөл өнеркәсіптік кремний өндірісінде қолданылатын қымбат колумбиялық көмірлердің импортын ұқсас сипаттамалары бар Шұбаркөл көмірлеріне алмастыру болып табылады.

Негізгі геологиялық міндеттердің бірі — кремнийдің кен термиялық өндіру технологиясына әсер ететін көмірдегі темір оксидінің таралуын зерттеу. Жүргізілген зерттеулер көрсеткендей, темір оксидінің қымбат химиялық талдаулары жоғары дәлдікпен, оларды кәсіпорында көмір партиясын қалыптастыру кезінде жедел қолдануға мүмкіндік бермейді. Өзекті мәселені шешу үшін көмірдегі темір оксидінің құрамын жедел бағалау үшін көмірдің магниттік сипаттамаларын өлшеудің индукциялық принципін жүзеге асыратын әдіс пен аппарат жасалды. Бұл әдіс екі валентті темірдің оксидін ұсақтау кезінде күрделі үшвалентті тотығына айналдыруға негізделген. ГОСТ 10538–87 бойынша өлшеу нәтижелері мен әзірленген әдіс арасындағы сәйкессіздік рұқсат етілген деңгейге сәйкес келеді. Құрылғы «Шұбаркөл Көмір» АҚ кәсіпорнында қолданылады. Қазақстан Республикасындағы өлшеу құралы ретінде метрологиялық Сертификаттау туралы № 9912 куәлік берілді.

Кілт сөздер: көмір, күл, темір оксиді, магниттенгендік, индукциялық катушкалар, концентрацияны өлшеу.

А.Д. Маусымбаева, Я.Ж. Байсагов, В.С. Портнов,
В.М. Юров, С.А. Гученко, А. Амангелдыкызы

Определение оксида железа в углях месторождения Шубарколь

Комплексное освоение минеральных ресурсов является одной из главных задач государства. Важную роль для ее решения имеет импортозамещение дорогостоящих колумбийских углей, используемых при получении технического кремния, шубаркольскими углями, имеющими сходные характеристики. Одной из главных геологических задач является изучение распределения в углях оксида железа, который оказывает влияние на технологию руднотермического получения кремния. Проведенные исследования показали, что дорогостоящие химические анализы на оксид железа, при высокой точности, не позволяют оперативно использовать их при формировании партии угля на предприятии. Для решения актуальной задачи — экспрессной оценки содержаний оксида железа в угле разработаны способ и прибор, реализующие индукционный принцип измерения магнитных характеристик углей. Способ основан на переходе оксида двухвалентного железа в сложный оксид трехвалентного при озолении. Расхождение результатов измерений по ГОСТу 10538–87 и разработанной методике лежит в пределах допустимости. Прибор используется на предприятии АО «Шубарколь Комир». Получен Сертификат № 9912 о метрологической аттестации как средство измерения в Республике Казахстан.

Ключевые слова: угли, зольность, оксиды железа, намагниченность, индукционные катушки, измерение концентраций.

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