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Kinetics of magnetizing field of gravitational-magnetic concentrate in the presence of liquid hydrocarbon

Calculation of activation energy and kinetic parameters of magnetization combustion of Lisakovsk gravitational-magnetic concentrate in the presence of liquid hydrocarbons (oils of different deposits) was made. The conditions of thermo-gravitational processing were chosen. It was established that catalytic destruction of organic compounds of liquid hydrocarbons adsorbed on oolits allowed decreasing temperature of dehydration and reduction of gravitational-magnetic concentrate.

Key words: kinetics, liquid hydrocarbon, Lisakovsk ironstone gravity-magnetic concentrate, hydrocarbon feedstock, effective additive.

The scheme of thermochemical preparation of Lisakovsk ironstone gravity-magnetic concentrate (GMC) for dephosphorylation includes the process of its calcination in an oxidizing atmosphere at the temperature of 950–1050 ºC. The resulted hematite calcine undergoes leaching by 5 % solution of sulfuric acid to remove phosphorus. After leaching the product, containing 0.24 % of phosphorus and 60 % of iron, is used as a conditioning concentrate for further iron smelting [1].

To reduce the temperature of GMC calcination the method of catalytical thermal dehydration and reduction (CTDR) by oolites pretreated with a liquid hydrocarbon material was proposed [2].

It is found that a complete removal of moisture from the GMC is carried out at 600–650 ºC during 45–90 minutes at CTDR, the reaction product is highly magnetic iron oxide Fe_3O_4 [3].

Catalytic degradation of organic matter of the liquid hydrocarbon adsorbed on the oolites during the heat treatment can significantly reduce the temperature of dehydration and reduction of GMC at CTDR. As the result a carbon and molecular hydrogen are formed:

$$C_xH_y \rightarrow xC + (y/2)H_2 \qquad (1)$$

Molecular hydrogen is catalytically decomposed by the contact with oolites components FeOOH, Al_2O_3 and SiO_2 with the formation of two radicals:

$$H_2 \rightarrow H^{\cdot} + H^{\cdot} \qquad (2)$$

Iron hydroxide is thermally dissociated into iron oxide (III) and water:

$$2FeOOH + C \xrightarrow{650\ ^{\circ}C} Fe_2O_3 + H_2O \qquad (3)$$

Activated carbon reacts with iron hydroxide at high temperature with the formation of carbon monoxide, iron oxide (III) and water:

$$2FeOOH + C \rightarrow Fe_2O_3 + CO + H_2O \qquad (4)$$

Activated carbon also interacts with the hydrated moisture:

$$C + H_2O \rightarrow CO + H_2 \qquad (5)$$

Further, molecular hydrogen is dissociated on the surface of iron oxide (III):

$$H_2 \xrightarrow{MeO} H^{\cdot} + H^{\cdot} \qquad (6)$$

As a result, the radicals of hydrogen and carbon monoxide reduce iron oxide (III) to the magnetic iron oxide Fe_3O_4 by the reactions:

$$3Fe_2O_3 + 2CO \rightarrow 2Fe_3O_4 + CO_2 \qquad (7)$$

$$3Fe_2O_3 + 2H^{\cdot} \rightarrow 2Fe_3O_4 + H_2O \qquad (8)$$

The source of active hydrogen is a water vapor as well as various radicals ($\cdot CH_2$, $\cdot CH_3$, $\cdot C_2H_5$, $\cdot C_6H_5$) which act as a reducer.

In this paper the basics of the magnetisation kinetics of GMC in the presence of liquid hydrocarbon are given.

Experimental part

A representative sample of Lisakovsk gravity-magnetic concentrate (GMC) was used in experiments. 0,75 % Solution of viscous oil from Karazhanbas was used as a liquid reducer. The degree of magnetization cinder GMC (α) was determined by measuring their magnetic susceptibility. Additionally, the phase composition of combustion products was monitored by using X-ray diffraction. Experiments were carried out in the temperature range 500–650 ºC. Isothermal dwell time of experimental samples in the oven was varied from 5 to 45 minutes.

Results and discussion

Kinetic curves of magnetization MMC plotted from experimental data are shown on the figure 1 in the coordinates: the degree of conversion (α) — time (τ). Analysis of the curves shape shows that the interactions (7, 8) belong to a class with the highest initial reaction rate which means that no matter whether heterogeneous or homogeneous system is considered, the reaction starts immediately across the whole reaction surface. This is due to the high reactivity of liquid carbon reducer.

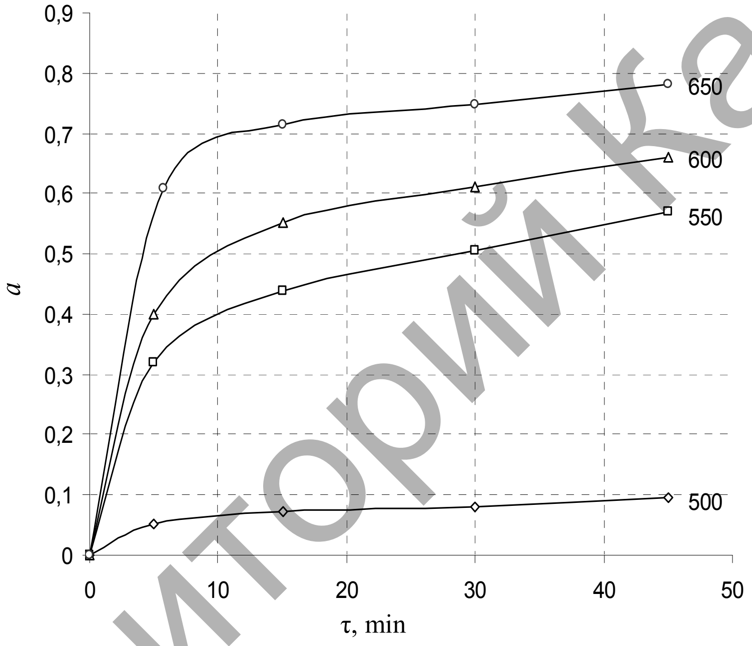

Figure 1. Kinetic curves of GMC magnetization

Induction period with the formation of embryos in this system is not observed. The reaction rate with the increasing degree of conversion decreases sharply at first and declines going on smoothly. It should be noted that this effect is weakly expressed at low temperatures. This fact indicates that the rate's maximum is due to the heating of the sample to the required temperature, and is not associated with the phenomena of autocatalysis. Furthermore, in our experiments, the magnetization process of GMC is also not limited by the rate of external diffusion.

Such reactions are described by the well-known Erofeev-Kolmogorov equation [4]:

$$\alpha = 1 - e^{-k\tau^n}, \tag{1}$$

where k and n — constants, characterizing kinetic mode of the reaction. Rate constants were calculated by using Sakovich equation (table)

$$K = nk^{1/n}. \tag{2}$$

Table

Kinetic parameters of Erofeev-Kolmogorov and Roginski equations

Temperature, ^{o}C	Model					
	$k\tau^n = \lg(1-\alpha)$ (1)			$k_1\tau^n = 1-\sqrt[3]{1-\alpha}$ (2)		
	n	k, min^{-1}	E, kJ/mol	n	k, min^{-1}	E, kJ/mol
500	–0.32	–4.96	27,77	–0.63	–0.83	18.12
550	–0.31	–1.88		–0.91	–0.60	
600	–0.27	–1.25		–0.50	–1.22	
650	–0.28	2.39		–0.44	–1.31	

Figure 2 shows the validity of the selected equation since the experimental curves are linearized in the coordinates $\lg\left[-\lg\left(1-\alpha\right)\right]-\lg\tau$ in a wide range of time. Values of the parameter *n* (table) indicate that the process occurs in a region close to the diffusion and its kinetics can be described as a model of «contracting sphere» [5].

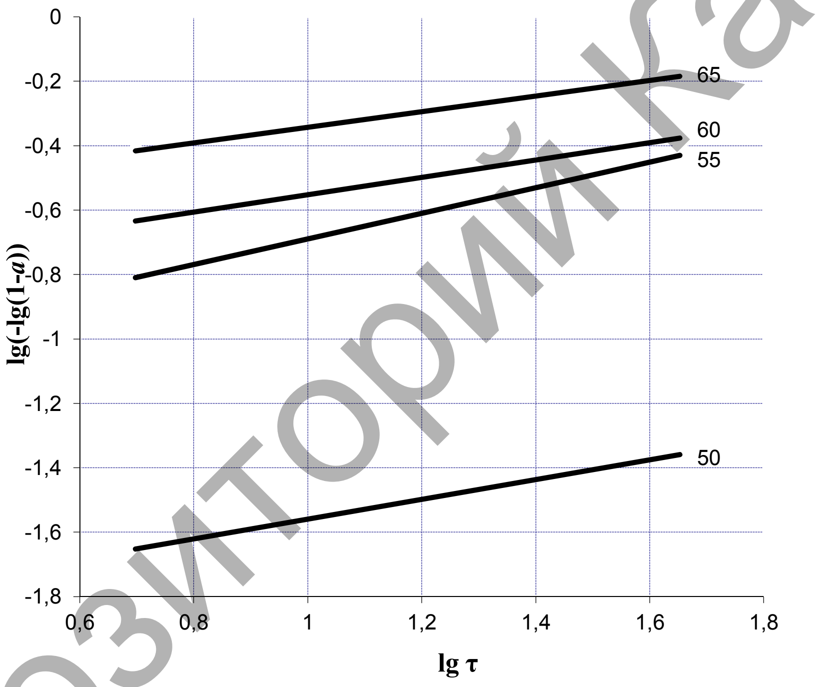

Figure 2. Calculations of kinetic parameters of GMC magnetization by using Erofeev-Kolmogorov equation

In this case, the reaction spreads from the outer geometric surface of the particle to its center to form a layer of magnetite which prevents transport of reagents in the reaction zone. The kinetic equation is used to test this model:

$$1-\left(1-\alpha\right)^{1/3} = k_1\tau^n . \tag{3}$$

Rate constant k_1 is found as the slope of lines in the coordinates $\lg\left[1-\left(1-\alpha\right)\right]^{1/3}-\lg\tau$ (Fig. 3).

For consistency of approach the Sakovich formula was used; obtained k_1 values are also given in Table. Adaption of the experimental results using two different models show that both of them quite satisfactorily describe the kinetics of the process studied.

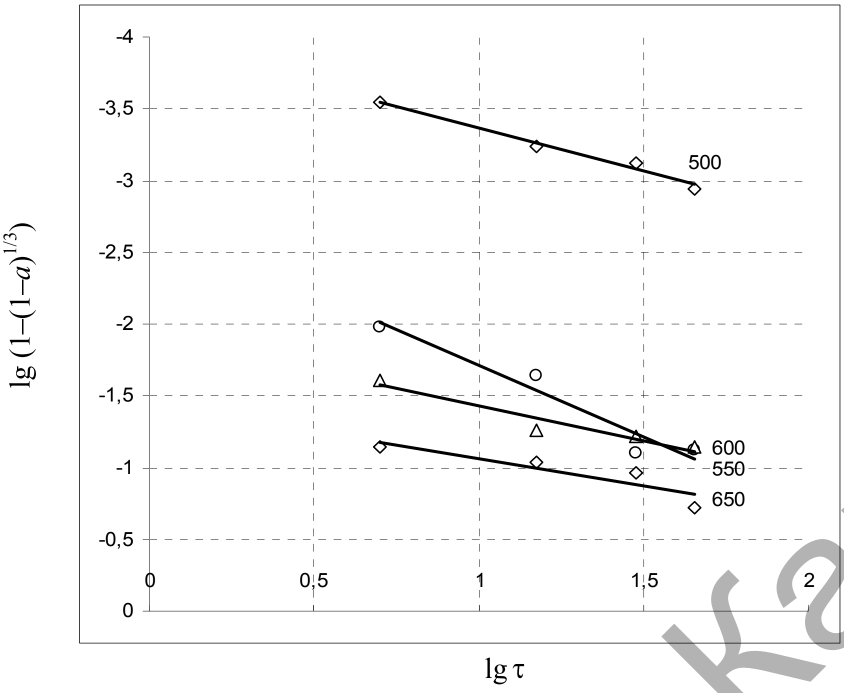

Figure 3. Calculations of kinetic parameters of magnetization ГМК by using Roginski equation

Thus, a comparison of the calculated activation energy and the kinetic parameters of the above models suggest that the process of magnetization MMC by liquid hydrocarbon is heterogeneous; the rate-limiting step of the process is diffusion at the interface $FeOOH_s$ — JUV.

References

1 *Kantemirov M.D., Bobir B.L., Levintov S.K., Namazbayev S.K.* The study of activation mechanism of phosphorous in oolite minerals in cyclic processes «calcination-alkalization» at different temperatures // Complex use of mineral raw materials. — 2007. — No. 5. — P. 72–79.

2 *Mukhtar A.A., Kochegina E.V., Baikenov M.I.* The study of liquid hydrocarbon in the process of thermal preparation of ironstone raw materials to magnetic enrichment // The News of Kazakhstan Science: Scientific-technical abstract book. — Almaty, 2006. — No. 4. — P. 56–59.

3 *Mukhtar A.A., Kim V.A., Kochegina E.V.* The research of thermocatalitic dehydration products of Lisakovsk gravitational–magnetic concentrate at the presence of liquid hydrocarbons // Complex use of mineral raw materials. — 2008. — No. 5. — P. 8–11.

4 *Baram I.I.* Macrokinetics of heterogeneous processes. — Almaty, 1986. — 206 p.

5 *Yang D.A.* Kinetic diversion of solid compounds. — Moscow, 1969. — 251 p.

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Сұйық көмірсутегі қатысындағы гравитационды-магнитттік концентратының магнетизирленген облысының кинетикасы

Лисаковск магнетизирленген күйдірудің гравитационды-магнитттік концентратының сұйық көмірсутектердің (әр түрлі кең орындарының мұнайлары) қатысында белсендік энергиясы мен кинетикалық параметрлерінің есептеулері жүргізілген. Термо-гравитациондық өңдеудің жүргізу жағдайлары анықталды. Адсорбциондық оолит бетіндегі органикалық заттардың сұйық көмірсутектердің каталитикалық деструкциясының термиялық өңдеу нәтижесінде, дегидратация температурасы мен гравитационды-магниттік концентраттарының тотықтыруларын азайтуға болады.

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Кинетика магнетизирующей области гравитационно-магнитного концентрата в присутствии жидкого углеводорода

Проведен расчет энергий активации и кинетических параметров магнетизирующего обжига лисаковского гравитационно-магнитного концентрата в присутствии жидких углеводородов (нефти различных месторождений). Подобраны условия проведения термо-гравитационной обработки. Установлено, что каталитическая деструкция органического вещества жидких углеводородов, адсорбированных на оолитах при термической обработке, позволяет снизить температуру дегидратации и восстановления гравитационно-магнитного концентрата.