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KINETICS OF THERMAL DECOMPOSITION OF DASHKASAN COBALT ORE

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Kinetics of thermal decomposition of Dashkasan cobalt mineral in the temperature range of 973-1123 K was studied. Activation energy was determined. According to the value of activation energy (236,5 kJ/mol) it revealed that the decisive stage of ore processing is the decomposition of ore depending on temperature. Note that the enrichment of ore was performed due to the use of pyrometallurgy method by melting of ore at 1673 K. When melting ore, 5% of carbon was added into furnace burden to form a reductive medium. The resultant alloy contains 15-20% of cobalt. Rate constants of thermal decomposition of cobalt ore at different temperatures were calculated. Kinetic parametrs of the decomposition processing of cobaltine were calculated using generalized topokinetic Kolmoqorov-Erofeev equation. Unlike well-known works the study was performed with natural mineral of cobaltine.

Keywords:*Cobalt ore, activation energy, mineral, kinetics, thermal decomposition, cobaltine*

INTRODUCTION

Cobalt ores have different mineralogical and chemical compositions and are many-colored. In ores the amount of cobalt may change in a wide range – from 100% to several percents. When amount of cobalt is 0.15% or less in non-oxidized complex ores (with sulfide and arsenyl), the production of it is economically profitable. In Azerbaijan, the main reserves of cobalt are located in the South Dashkasan deposit. The main mineral of this deposit is cobaltine. The work shows that as ore contains hard-melting cobalt and alumosilicate compounds cobalt cannot be fully yielded. When processing mineral with 20% of chloride acid, the yield of cobalt is 77.4%; with 2N sulfate acid it makes up 76.7%; in the dissolution of sulfatized mass in water it stands at 973K 88.52% of Co yields. When processing the primary sample with ammonia solution, more than 51% of cobalt does not go into solution[1-5]. The reason of partial extraction of cobalt from ore is the poor solubility of ore minerals in water, acid and alkali solutions. To make cobalt into maximum soluble form, first crystal cage of minerals in ores must be destructed. This process was performed in two manners - thermal decomposition of ore samples in inert medium and oxidization of ore samples by atmospheric air. These operations had first been carried out in 1935-1938 at the Giredmet Institute where the pyrometallurgical enrichment process of floatation concentrate of Dashkasan deposit performed. During the process, metals and cobalt were generated from "speiss" obtained at 1573-1613K. As the paper [6] shows, 15-20% Co alloy (speiss) is generated from floatation of Dashkasan ore while 3-4% of cobalt containing concentrate, reductive melting of concentrate as compared with primary raw material cobalt becomes condensed 200 times. The next process is performed by processing an alloy using hydrometallurgy method. Since dissolution of alloy in acid goes weakly or partially, considerable emission of toxic (AsH_3 and H_2S) gases is observed. Note that 98% of cobalt can be separated from raw material by floatation-pyrological enrichment method. Since the process is multi-stage, the use of high energy comsuming equipment, and the emission of arsenium containing toxic gases into

atmosphere poses ecological danger, we examined a new way of Dashkasan cobalt ore processing. To find extraction condition of Dashkasan cobalt ore, it is necessary to study kinetic laws of thermal decomposition of cobaltite mineral in ore. Kinetic results of thermal decomposition of ore cobaltine can be a theoretical basis for revealing technological parameters of Dashkasan ore processing. Since cobalt ore has a complex and multi component composition, different parallel-consistent reactions which are determined by kinetic and diffusion, or various factors, can be occured. Since the research of real kinetic laws of separate stages of the process is experimentally complex, we studied formal kinetics of the process. Study of kinetic laws is important for selection of optimum mode of ore burning and explanation of its mechanism.

The paper [7] examined the thermal decomposition of synthetic cobalt which was generated from powdery elements. It should be stated that mechanical and chemical properties of synthetic cobaltite differs from properties of the mineral of natural cobalt. As mentioned above, cobalt can be found in ore both together with separate minerals and in crystal cage of Fe, Cu, Al minerals. Unlike well-known known works, all the processes were analyzed, and natural cobalt mineral and kinetic parameters calculated. Kinetic parameters of experimental results were calculated through the use of generalized topokinetic Kolmoqorov-Erofeev equation:

$$\alpha=1-x=1-C/C_0=1-\exp(-k\,\tau^n) \quad [1],$$

where:

α- conversion degree of purposeful component,
x-non-conversion degree of purposeful component
k- rate constant of reaction,
τ- time of experiment,
n- kinetic parameter shows reaction composition,
C_0 and C express relevant densities of purposeful component at τ=0 and τ.
Twice logarithm of equation (1) gives the following expression:

$$\lg[-\lg(1-\alpha)]=n\lg\tau+\lg k$$

Tangent of inclination of line to abscissa axis equals to "n" kinetic parameter, when lgτ=0 intersection point of it with axis of ordinatesequals to lgk.

Using $K=nR^{1/n}$ equation we calculate rate constant (lnK) of the reaction.

$$\lg K=\lg n+1/n\lg R.$$

According to graphic method detection, of K and n demands many experiments and since kinetic parameters are not obtained precisely, kinetic parameters in the Kolmogorov-Erofeev equation were performed by the simplex method of I.N.Beloglazov [8]. This method reduces the volume of experimental results unlike graphic method and simplifies calculation method. Detection of precise parameter values of K, n and C_o is performed through the use of the simplex method of analytical equation. Thus, when using the simplex method the equation of the kinetic curve goes over into the dimensionless form of the equation corresponding to the experimental values of C_i and τ. In any time for time interval we can refer to $\Delta\tau_1$.

$$\Delta\tau_1=\varphi_{i+1}-\tau i=\varphi_1(C_i;C_{i+1}) \text{ and } S\tau=\tau i+1/\tau_i=\varphi_2(C_i;C_{i+1})$$

Where $\Delta\tau_i$ is a time interval for two τ_i and τ_{i+1}moments; $S\tau$-simplex of time similarity.

Through the resolving $\Delta\tau_1=\varphi_1(C_i;C_{i+1})$ and $S\tau=\varphi_2(C_i; C_{i+1})$ equation, we can determine measurement indications of dependences which conform to the Erofeev-Kolmogorov equation and clarify kinetics of chemical process.

According to this method, the equation (1) can be expressed for two different time moments τ_i and τ_{i+1} ($\Delta\tau_1 = \tau_{i+1} - \tau_i$) by the following equations:

1) for time moment τ_i: $\ln^{1/n}(C_o/C_i)=k^{1/n}\cdot\tau_i$ (2)

2) for time moment τ_{i+1}: $\ln^{1/n}(C_o/C_{i+1})=k^{1/n}\cdot\tau_{i+1}$ (3)

According to the simplex method reaction, the composition (n) and rate constant k are found by the following formula:

$$n=\frac{\ln(\ln S_{c,i+1}/\ln Sc,i)}{\ln S\tau} \quad (4)$$

$$k=\frac{1\ln Sc,i}{\tau_i^n\cdot(S_\tau^n-1)} \quad (5)$$

where $S_{c,i}=\frac{C_i}{Ci+1}$ and $S_{c,i+1}=\frac{C_{i+1}}{Ci+2}\Delta\tau_i$ and $\Delta\tau_{i+1}$($S_{\tau,i+1}=S_{\tau,i}=S_\tau$)

is the simplex of density similarity in time interval for two moments $\Delta\tau_i$ - τ_i and τ_{i+1}.

RESULTS AND DISCUSSIONS

Influence of temperature and experimental time on thermal decomposition of Dashkasan cobalt ore in inert medium are given in Table 1.

Table 1. Influence of time and temperature on thermal decomposition.

Temperature, K	Thermal decomposition of ore, %			
	300 sec	600 sec	1200 sec	2400 sec
973	4.9	5.7	7.9	14.5
1023	6.8	12.5	27	56.0
1073	9.5	15.2	34.5	65.5
1123	11.4	21.5	39.8	81.2

According to experimental results in Table 1 we define n and k parameters which conform to Kolmogorov-Erofeev equation.

Value of n parameter in $\Delta\tau_1$, $\Delta\tau_2$ and $\Delta\tau_3$ time moment at 700°C temperature is calculated as follows:

$$\text{Then } n=\frac{\ln(\ln Sc,3/\ln Sc,2)}{\ln S}=\frac{\ln(\ln 1{,}077/\ln 1{,}0238}{\ln 2}=\frac{\ln 3{,}26989}{\ln 2}=\frac{1{,}18475}{0{,}6931}=1{,}7$$

Value of K constant is found according to formula [5]:

$$K=\frac{1}{\tau_1^n}\cdot\frac{\ln Sc,1}{(S_\tau^n-1)}=\frac{1}{300^{1{,}43}}\cdot\frac{\ln 1.00848}{(2^{1{,}43}-1)}=0{,}000001429=0{,}1429\cdot10^{-5}$$

Table2. Rate constants of thermal decomposition of Dashkasan cobalt ore at different temperatures.

T, K	K	lgK	k· 10^{-5}, san^{-1}
973	10.277	-5.8453	0.1428
1023	9.7775	-5.24916	0.5634
1073	9.319	-4.7099	1.95
1123	8.9047	-4.259	5.5

Depending on temperature the values of K are shown respectively by Arrhenius equation (Fig. 1).

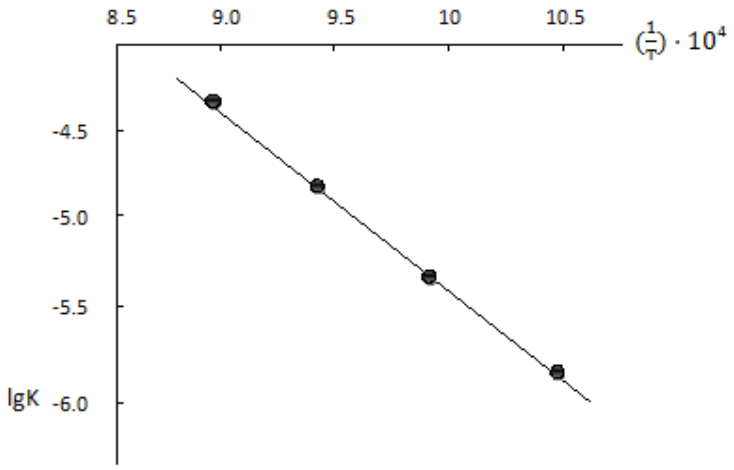

Fig. 1. Dependence of logarithm of rate constant of thermal decomposition of cobalt ore on temperature.

$$\mathrm{tg}\,\alpha = \frac{E_{ak}}{2{,}303 \cdot R \cdot \xi}$$

Activation energy is calculated using the following equation [9-12]:

$$E = 2{,}303 \cdot R \cdot [\mathrm{tg}\alpha] \cdot \xi$$

Where α –inclination of line to abscissa axis, ξ-ratio of scale in abscissa axis to scale in axis of ordinates, is called correction constant.

As to Arrhenius coordinates in Fig.2 according to rate constant curve of thermal decomposition of Dashkasan cobalt ore, the value of tgα is 1.235.

$$\xi = (1:0{,}5 \cdot 10^{-4}):(1:0{,}5) = 10^4$$

Where $E = 2{,}303 \cdot 8.314 \cdot 1{,}235 \cdot 10^4 = 236467C \cdot mol = 236{,}5kC \cdot mol$

Value of activation energy (236.5 kJ/mol) and size of kinetic parameter ($n > 1$) show that thermal decomposition of cobaltite mineral in Dashkasan cobalt ore takes place in kinetic regions at 973-1123 K temperatures.Value of activation energy, comparison of dependence curve of lgK on $^1/_T$

with Arrhenius curve of V.D. Chunaeva went to show that the decisive stage in the decomposition of ore cobaltite is the decomposition stage where cobaltite depends on temperature.

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DAŞKƏSƏN KOBALT FİLİZİNİN TERMİKİ PARÇALANMASININ KİNETİKASI

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Daşkəsən kobalt filizindəki kobaltin mineralının 973-1123 K temperatur intervalında termiki parçalanmasının kinetikası tədqiq edilmişdir. Aktivləşmə enerjisi təyin edilmişdir. Aktivləşmə enerjisinin qiymətinə (236,5kc/mol) görə müəyyən edilmişdir ki, filizin işlənməsində təyinedici mərhələ filizin temperaturdan asılı olaraq parçalanmasıdır. Filizin zənginləşməsi prosesi pirometallurgiya üsulu ilə filizi 1673 K temperaturda əritməklə aparılmışdır. Filizi əridərkən reduksiyaedici mühit yaratmaq üçün şixtaya 5% karbon əlavə edilir. Alınmış ərintinin tərkibində 15-20% kobalt olur. Müxtəlif temperaturlarda kobalt filizinin termiki parçalanmasının sürət sabitləri hesablanmışdır. Kobaltinin parçalanma prosesinin kinetik parametrləri Kolmoqorov-Yerofeyevin ümumiləşmiş topokinetik tənliyinin

köməyi ilə hesablanmışdır. Məlum işlərdən fərqli olaraq bütün proseslər təbii kobaltin mineralı üzərində aparılıb.
Açar sözlər: *kobalt filizi, aktivləşmə enerjisi, mineral, kinetika, termiki parçalannma, kobaltin.*

КИНЕТИКА ТЕРМИЧЕСКОГО РАЗЛОЖЕНИЯ ДАШКЕСАНСКОЙ КОБАЛЬТОВОЙ РУДЫ

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Исследована кинетика термического разложения в температурном интервале 973-1123 K минерала кобальтина в составе Дашкесанской кобальтовой руды. Определена энергия активации. По значению энергии активации процесса (236.5 kДж/моль) установлено, что при разработке руды определяющей стадией является разложение руды в зависимости от температуры. Процесс обогащения руды проведен методом пирометаллургии расплавлением руды при температуре 1673 K. При расплавлении руды для создания восстановительной среды в шихту добавлено 5% углерода. Полученный расплав содержит 15-20% кобальта. Рассчитаны константы скорости разложения кобальтовой руды при различных температурах. Кинетические параметры процесса разложения кобальтина рассчитаны с помощью обобщенного топокинетического уравнения Колмогорова-Ерофеева. В отличие от известных работ все процессы проведены с природным минералом кобальтином.
Ключевые слова: *кобальтовая руда, энергии активации, минерал, кинетика, термическоге разложение, кобальтин.*