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EXPRESS ANALYSIS METHOD OF ALUNITE ORE

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Abstract: *The article presents a method to determine an amount of alunite in alunite ore and technological samples by alternative method. The essence of the method is that the alunite mineral in the ore is heated to the temperature of complete decomposition (800-850^{0}C) and the degree of alunitation of the ore for the total mass loss, based on the amount of aluminum oxide and sulfur trioxide. The method was compared with other available methods (thermal, chemical, X-ray phase). The advantage of the method is that more than one sample is analyzed at a time, the analysis is completed in a short time, no preliminary preparations are made, nor chemical reagents are used. Alunite ore consists of alunite and non-alunite (kaolinite, hematite, quartz). Since the mass loss during the heating of the ore is mainly caused by the decomposition of alunite, a mathematical relationship of $a\%=2.34\omega_{loss}$ was found between the loss and the degree of alunitation. According to the degree of alunitation, for the aluminum oxide and sulfur trioxide in the ore, the expressions $\omega_{(Al2O3)}=0.8775\cdot\omega_{loss}$, $\omega_{(SO3)}=0.6888\cdot\omega_{loss}$ were obtained. Chemical, derivotographic methods of analysis experimentally confirmed the adequacy of these equations. It was established that in order to completely decompose the ore, it is necessary to heat it at 850^{0}C for half an hour and at 800^{0}C for an hour.*
Keywords: *alunite, express analysis, thermal decomposition, mass loss*
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Introduction

Physico-chemical analysis of a large number of samples should be carried out for geological exploration of mineral raw materials, field assessment, preparation of average samples and etc.. Therefore, there is a great demand for reliable analysis methods performed in a shorter period of time and with less reagent consumption.

Since the amount of aluminum in alunite ore depends on the degree of alunitation of the rock, the initial analysis of the samples is carried out to find the amount of alunite mineral. Thus, in addition to alunite, kaolinite, quartz, hematite, etc. are found in the ore.

The main method of determining the degree of alunitation is the alkaline method. Alunite ore is dissolved in 10% alkali at 80-90^{0}C for 15 minutes. The alkalinity is relatively high, so the aluminum compounds in the sample are converted to $NaAlO_2$. The aluminate solution is filtered off from the insoluble residue, hydrolyzed to obtain $Al(OH)_3$ and the amount of Al_2O_3 is determined by gravimetric methods [1]. The degree of alunitation of the ore is calculated based on the mass of Al_2O_3. As can be seen, too much time and reagent is spent on analysis.

Another proposed method for determining the degree of alunification of ore is heating samples at a temperature of 750-850^{0}C and the degree of alunitation in view of mass loss due to the release of the resulting SO_3. However, the separation of SO_3 is carried out over a wide temperature range and it turns out that the sample must first be heated to separate the water (550-600^{0}C), then re-heated at 780-850^{0}C and the mass loss for SO_3 must be studied. This also requires additional time and expens [2].

In another method, the amount of alunite in samples and technological products is determined chemically according to the amount

of sulfate in the ore. Sulfate ions combined with both Na^+ və K^+ and aluminum are calculated here. To do this, coefficients are calculated for different amounts of Na and K [3].

Recently, the amount of alunite is used to determine the amount of alunite in ore and technological samples, based on methodological recommendations for X-ray diffraction phase analysis [4]. The essence of the method is that the most intensive peak of alunite in the radiograph of the analyzed sample is compared with pre-prepared standart samples. A graph of the relationship between the mass fraction of alunite in the ore and the intensity of the peaks is constructed for reference samples and according to the graph, the amount of alunite in the ore is found. However, in this method, the most intense peak of alunite (d=2.971) may not always change linearly depending on the amount of alunite in the alunite ore due to the amount of Na and K in it and the effect of other mixtures. On the other hand, the number of technological samples can be hundreds to find only the average sample. X-ray diffraction phase analysis of so many samples is not convenient in terms of both time loss and certain difficulties.

Theoretical part

The degree of alunitation for the total mass loss is established by calculating the amount of Al_2O_3 and other components based on the calcination of the samples taken at 850^0C in the proposed method.

The difference of the method is that the incandescence is carried out only at one temperature (850^0C). It is at this temperature that the complete decomposition of alunite comes to an end. At the same time, the result is obtained by heating a large number of samples at once in a short time.

Since the method is gravimetric, it is necessary to determine the molar mass of alunite. Thus, the amount of Na and K in the alunite is calculated as 828 g/mol for potassium alunite or 812 g/mol for sodium potassium alunite taken separately [5].

Numerous studies have shown that Na and K change monotonously in the Zeylik alunite, and its empirical formula is as follows [6]:

$$Na_{0,8}K_{1,2}O{\cdot}3Al_2O_3{\cdot}4SO_3{\cdot}6H_2O$$

Then the molar mass of the alunite mineral is 815.2 g/mol and calculations were made at this value.

Alunite ore can be conventionally written as the sum of two parts:

Ore (F) = Alunite(A) + Non-alunite(Ao)

The decomposition of the alunite mineral (alunite part) can be shown as follows at 800-850^0C:

$$(Na_{0,8}K_{1,2})Al_6(SO_4)_4{\cdot}(OH)_{12} \longrightarrow (Na_{0,8}K_{1,2}){\cdot}SO_4\text{-}3Al_2O_3+3SO_3+6H_2O$$

The non-alunite part consists mainly of quartz, hematite, kaolinite (dickite). For example, X-ray phase analysis determined that the phase composition (by percentage) of one of the samples was as follows: SiO_2 – 53.4; alunite – 35.5; kaolinite – 9.8; hematite – 1.5. The mass loss during the heating of the ore may change due to the water released from the kaolinite. However, it was established that its amount does not exceed 1.5%. Also, water is mainly separated after 850^0C [7]. Therefore, the amount of water obtained from kaolinite does not affect the overall result beyond the error allowed for express analyzes.

If the degree of alunification of the ore is a%, then the alunite part is $(m_F{\cdot}a\%)/100$, where m_F – sample weight of ore, the non-alunite part is $\frac{m_F \cdot (100-a\%)}{100}$.

When heating the alunite ore, the mass loss due to the loss of SO_3 and water is expressed as follows:

$m_{loss}=m_F$ (mass left over from the decomposition of alunite + mass of non-alunite).

When alunite is heated, 1 mole (815.2 g/mol), 3 moles of SO_3 and 6 moles of H_2O (348 by mass) are lost. In percentage terms, the remaining part is 57.31%.

$$m_{loss} = m_F - \left[\frac{m_F \cdot a\% \cdot 57{,}31}{10^4} + \frac{m_F(100-a\%)}{10^2}\right]$$

$10^4 \cdot m_{loss} = 42{,}69 \cdot m_F \cdot a\%$

degree of alunification $a\% = \frac{m_{loss} \cdot 10^4}{m_F \cdot 42{,}69} = 2{,}34 \cdot \frac{m_{loss}}{m_F} \cdot 100$ in the formula $\frac{m_{itki}}{m_F} \cdot 100$ is the percentage of loss (ω). Then the degree of alunitation is a%=2,34 ω_{loss} (1).

Once the degree of alunitation of the ore is known, the amount of Al_2O_3 and SO_3 in the samples can also be calculated. Mass of Al_2O_3 in the alunitized part:

$$m_{Al_2O_3} = 0{,}00375 \cdot m_F \cdot a\% = 0{,}00375 \cdot m_F \cdot 2{,}34 \cdot \omega_{loss} = 0{,}008775 \cdot m_F \cdot \omega_{loss}$$
$$\omega_{Al_2O_3} = \frac{m_{Al_2O_3}}{m_F} \cdot 100 = 0{,}8775 \cdot \omega_{loss} \quad (2)$$

The mass of SO_3 in the ore sample, which is contained in the ore and can be separated when heated, and the mass fraction for mass loss can be calculated:

The mass fraction of SO_3 in the mineral alunite is 29.44%. Then the mass of SO_3 in the sample (m_{SO3})

$$m_{SO_3} = \frac{m_F.a\%}{100} \cdot \frac{29{,}44}{100} = 0{,}002944 \cdot m_F \cdot a\%$$

Mass fraction(ω_{SO_3}) of SO_3 in the sample (m_F)

$$\omega_{SO_3} = \frac{m_{SO_3}}{m_F} \cdot 100 = \frac{0{,}002944 \cdot m_F \cdot a\%}{m_F} \cdot 100 = 0{,}2944 \cdot a\%$$

If we replace the value of a % in the formula (1):

$$\omega_{SO_3} = 0{,}294 \cdot 2{,}34 \cdot \omega_{loss} = 0{,}6888 \cdot \omega_{loss}$$
$$\omega_{SO_3} = 0{,}6888 \cdot \omega_{loss} \quad (3) \quad \text{is obtained.}$$

Experimental part

In order to verify the accuracy of theoretical calculations, a sample of alunite ore (size 200 mesh) weighing 25.848g with the composition being established by physicochemical methods and containing 50% alunite, is heated in a muffle furnace at 850^0C for 1 hour. Mass loss is 21.53%. If we replace it in formula 1, we get

$a\% = 2.34 \cdot \omega_{loss} \rightarrow 2.34 \cdot 21.53 = 50.38\%$.

When the same alunite sample (about twice less) weighing 12,594 g was heated for the second time under the same conditions, the mass loss was 21.425%:

$$a\% = 2.34 \cdot 21.425 = 50.13\%$$

Given that the derivatographic analysis is more accurate, the above derivatographic analysis of the same sample taken for thermal decomposition was performed (Figure 1). As can be seen from the figure, the total mass loss was 21.25%. If we write the amount of loss in the formula

$$a\% = 2.34 \cdot 21.25 = 49.725$$

the error is 0.81%.

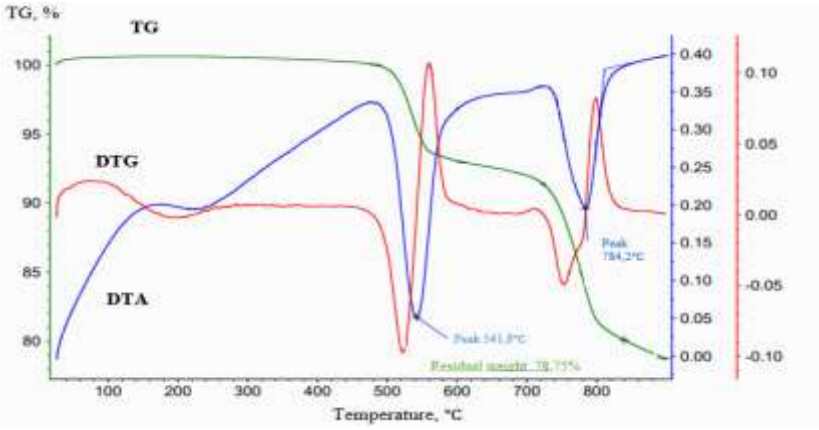

Fig. 1. Derivatographic analysis of a sample containing 50% alunite.

To determine the effect of incandescence time on mass loss, the samples were heated in an oven at 800 and 850^{0}C for 15, 30, 45, 60 minutes and brought to a constant weight after the temperature had stabilized. As can be seen from Fig. 2, the mass loss stabilizes after 30 minutes of incandescence.

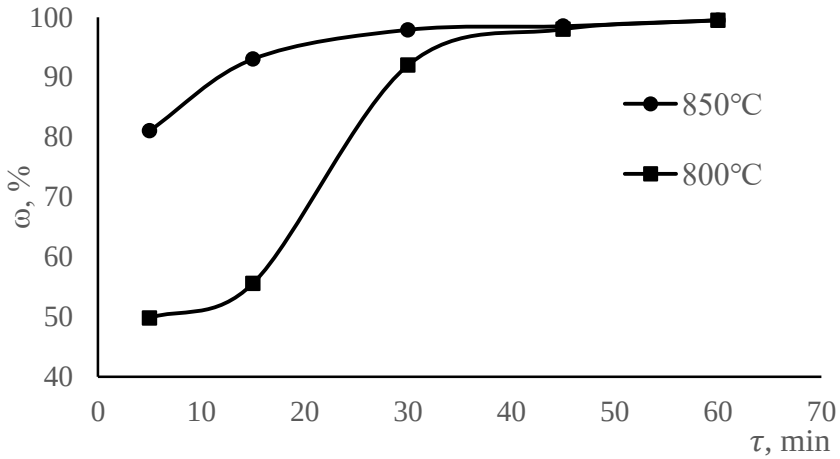

Fig. 2. Dependence of the degree of decomposition of alunite ore on its heating time

Experiments have shown that mass loss during incandescence at 800^{0}C occurs within half an hour at 850^{0}C. That is, the incandescence can be carried out at 800^{0}C. However, this takes more time.

In subsequent experiments, the results of both thermal decomposition and derivatographic analysis of samples with a predetermined degree of alunitation by chemical analysis were compared.

Table 1. Comparison of alunitation rates found by different methods

№	Found by chemical analysis	Found by derivatographic analysis	Calculated according to mass loss
1	23.7	23.4	24.66
2	36.6	36.1	35.6
3	50	49.73	50.13
4	52.02	51.55	52
5	76.93	76.54	76.50

6	90	89.99	89.78

As can be seen from the Table, the proposed method of finding the degree of alunitation for mass loss is useful as an express method.

The amount of Al_2O_3 in the kaolinite of the ore is usually taken from 2-3% in technological samples [8] and the total Al_2O_3 is found by combining the amount of alumina in the alunite.

To test the adequacy of the proposed method, a sample ore weighing 3,209g is dissolved in an excess 10% alkaline solution. The obtained sodium metaaluminate solution is diluted and hydrolyzed to precipitate $Al(OH)_3$ and the amount of Al_2O_3 is calculated by gravimetric method. 0.704g of Al_2O_3 is obtained, which is 21.93% of the total ore.

When the same amount (3.209g) is taken from the same sample and heated at 850^0C, the mass loss is 0.686g. This percentage is 22.64%. If we replace the value of the loss in the formula (2),

$$\omega_{Al_2O_3} = \frac{m_{Al_2O_3}}{m_F} \cdot 100 = 0.8775 \cdot \omega_{loss} = 0.8775 \cdot 22.64 = 19.86\%$$

As mentioned above, the amount of Al_2O_3 in the non-alunite part of the ore is usually 2-3% in technological samples. On average, if 2.5% is taken, it will be 19.86+2.5 = 22.36. The error is 1.96%.

Studies have shown that in samples containing less than 25% of the alunite mineral ("poor alunite") the error is up to 5%. Therefore, it would be more appropriate to treat such samples, most of which are made of koalinite (dikkit) and quartz, as clay, rather than as alunite ore.

Let us use formula (3) to find the amount of SO_3 obtained from the decomposition of aluminum sulphate in alunite ore for the total mass loss of the above-mentioned samples at 850^0 C.

$$\omega_{SO_3} = 0.6888 \cdot \omega_{loss}$$

When a sample of alunite with an alunitation rate of 50% is heated to 850°C, the total mass loss is 21.25%.

$$\omega_{SO_3} = 0{,}6888 \cdot 21.25 = 14.63$$

In order to verify the accuracy of the calculation of the amount of SO_3 obtained from the decomposition of alunite ore for the total mass loss, ore samples taken in the same mass were chemically analyzed. Also, ore samples dehydrated for two hours at 585^0C were preheated for one hour at a temperature of 750-850^0C. The amount of SO_3 released in the sample was calculated for mass loss.

For chemical analysis, ore samples placed inside a quartz tube are heated to 850^0C for one hour in a tubular furnace. SO_2, and SO_3 obtained by injecting nitrogen gas from a balloon are blown over the sample and passed through successively connected drexels containing hydrogen peroxide. The obtained sulfate ions are precipitated with 5% $BaCl_2$ solution. The amount of SO_3 in the sample is calculated according to the mass of $BaSO_4$. Table 2 shows the chemical values of sulfur trioxide obtained from the decomposition of alunite ore for mass loss at 780-850^0C and for the proposed total mass loss.

Table 2. Chemical values of sulfur trioxide obtained from decomposition of alunite ore for mass loss at 750-850^0C and total mass loss

Degree of alunitation of the ore	Finding ω_{SO_3} by chemical method	Finding ω_{SO_3} for mass loss at 780-850^0C	Finding ω_{SO_3} for total mass loss
33.6	10.54	9.68	10.59
50	14.28	14.05	14.63
80.12	22.51	22.4	23.52

As is evident from Table 2, the results obtained by the proposed method are adequate to other methods.

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ALUNİT FİLİZİNİN EKSPRES ANALİZ ÜSULU

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Xülasə: Məqalədə alunit filizində və texnoloji nümunələrdə termoqravimetrik yolla alunitin miqdarı tərkibinin təyin edilməsinin alternativ üsulu verilmişdir. Üsulun mahiyyəti ondan ibarətdir ki, filizdəki alunit mineralı tam parçalanma temperaturuna (850^0C) qədər qızdırılır və ümumi kütlə itkisinə görə filizin alunitləşmə dərəcəsi, onun əsasında isə alüminium-oksid və kükürd-trioksidin miqdarı tapılır. Üsul digər mövcud (termiki, kimyəvi, rentgenfaza) üsullarla müqayisə olunmuşdur. Üsulun üstünlüyü ondan ibarətdir ki, bir dəfəyə daha çox nümunə analiz olunur, analiz qısa müddətdə başa çatır, öncədən müəyyən hazırlıqlar aparılmır və heç bir kimyəvi reaktiv sərf olunmur. Alunit filizinin tərkibi alunit və qeyri alunit (kaolinit, hematit, kvars) hissədən ibarətdir. Filizin qızdırılması zamanı kütlə itkisi əsasən alunitin parçalanması hesabına baş verdiyindən itki ilə alunitləşmə dərəcəsi arasında a%=2.34 ω_{itki} riyazi asılılığı tapılmışdır. Alunitləşmə dərəcəsinə görə filizdəki alüminium-oksid və kükürdtrioksid üçün $\omega_{Al_2O_3} = 0{,}8775 \cdot \omega_{itki}$, $\omega_{SO_3} = 0{,}6888 \cdot \omega_{itki}$ ifadələri alınmışdır. Kimyəvi, qravimetrik və derivatoqrafik yolla alınmış nəticələrin təcrübi olaraq verilmiş düsturlarla adekvat olduğu təsdiqlənmişdir. Müəyyən edilmişdir ki, filizin tam parçalanması üçün 850^0C-də qızdırmanı yarım saat, 800^0C-də isə bir saat ərzində aparmaq lazımdır.

Açar sözlər: *alunit, ekspres analiz, termiki parçalanma, kütlə itkisi*

ЭКСПРЕСС МЕТОД АНАЛИЗА АЛУНИТОВОЙ РУДЫ

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Аннотация: В статье предлагается альтернативная методика определения количественного содержания алунита в рудах и технологичеких пробах термогравиметрическим методом. Сущность методики состоит в том, что алунитсодержащая руда нагревается до температуры полного разложения (850 ^{0}C). Степень алунитизации руды определяется по потере веса, и на ее основе рассчитывается количество окиси алюминия и триоксида серы в составе руды. Способ сравнивался с другими существующими методами (термический, химический, рентгенофазовый). Преимуществом метода при всей его быстроте и относительной дешевизне является возможность определения количества алунита в пробе без специальной пробоподготовки и использования химических реактивов. Данный метод позволяет в течение короткого времени анализировать большое количество технологических проб. Алунитовая руда состоит из алунита и неалунитовой (каолинит, гематит, кварц) части. При нагревании руды потеря веса происходит, в основном за счет разложения алунита. Поэтому была найдена математическая зависимость между степенью разложения алунита и общей потерей веса руды: a%=2.34 ω, где ω - общая потеря веса.

А по степени разложения найдено количество оксида алюминия и триоксида серы в составе руды: $\omega_{Al_2O_3} = 0{,}8775 \cdot \omega_{\text{потр}}$, $\omega_{SO_3} = 0{,}6888 \cdot \omega_{\text{потр}}$. Химическим, дериватографичес- ким методами анализа экспериментально подтверждена адекватность данных уравнений. Определено, что для полного разложения руды при 850 ^{0}C требуется полчаса, а при 800 ^{0}C - один час времени.

Ключевые слова: *алунит, экспресс анализ, температура разложения, потеря веса*