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I. Yu. Kozlovskaya, PhD student (BSTU);**V. N. Martsul**, PhD (Engineering), assistant professor, head of department (BSTU)**LANTHANUM EXCRETION FROM SPENT PETROLEUM
HYDROCARBON CRACKING CATALYST**

The article presents the results of the work on lanthanum excretion from spent petroleum hydrocarbon cracking catalyst by mineral acids processing. Methods of receiving lanthanum compounds in the form of insoluble compounds (carbonates and hydroxides) from acid extracts have been validated. The experimental data characterizing the structure and properties of the received sediments, and allowing to prove the possibility of using spent cracking catalyst as raw material for obtaining rare-earth elements are given.

Introduction. Compounds and the materials containing rare-earth elements (REE) are applied in petro-chemistry, glass and ceramic industry, metallurgy, in production of electronic devices. Consumption of rare-earth elements increases and it is connected with development of high-technology industries and emergence of new spheres of their application. According to estimations of Industrial Mineral Company of Australia, demand for rare-earth oxides by 2015 will have increased by 50% (in comparison with 2010) and will have reached 200 thousand tons a year [1].

The main raw materials for receiving REE are minerals: bastnasite, a monacite, loparite (elements of cerium group prevail), and also xenotime, evxenite (elements of yttrium group prevail). The composition of REE in them changes in limits from 3 to 75% (in terms of oxides) [2]. Now monacite and bastnasite deposits are generally developed. Acid and alkaline ways of their processing are used in practice.

The production technology REE is the multi-stage process including decomposition of crushed raw materials by acid or alkalis solutions, isolation of radioactive elements (mainly thorium and uranium) and the bulk of ordinary impurities, division of REE into groups, production of individual REE compounds and special purpose products [2].

These processes are power- and labor-consuming and demand the use of the concentrated acids and alkalis, they are connected with the formation of a waste of rock dirt and a radioactive concentrate.

The search of alternative sources of REE such as production wastes (phosphorus- [4], slurries of aluminous productions [5], an ash-slag wastes [6]) is actual.

However it is very difficult to get products of high purity from these raw materials because of multi-component structure and formation of a large number of secondary wastes.

The perspective raw material which can be used for production of rare-earth element compounds is a spent petroleum hydrocarbon cracking catalyst but it has not enough been studied. The content of REE in it is higher, than in wastes listed above (Table).

**Content of rare-earth elements
in a waste used for their production**

Waste	Contents REE, %
Spent cracking catalyst	1.7–2.0
Phosphor-gypsum	0.3–0.6
Slurry of aluminous productions	Less than 0.1
Ash-slag waste	0.5–0.9

Main part. In the spent catalyst which is the object of research REE are presented by a lanthanum which quantity is 2%.

Besides rather high content of REE, the spent catalyst is also characterized by a number of such peculiarities as the constant composition of a small number of elements; lanthanum ions are included into catalyst structure according to the ion-exchange mechanism.

The conditions of rare-earth elements extraction from the spent petroleum hydrocarbon cracking catalyst have already been studied by us [7]. It is established that when using nitric acid as the leaching agent the extent of lanthanum extraction is 85.0–99.9%, in case of sulfuric acid it is 45–53%.

The purpose of this article is separation of lanthanum compounds from the spent petroleum hydrocarbon cracking catalyst in the form of the concentrates suitable for further application.

Various ways of separation of REE from acid extracts are known: sedimentation in the form of almost insoluble compounds (hydroxides, carbonates, phosphates, fluorides), a three-N-butyl phosphate extraction, selective oxidation reduction, a sorption on ion-exchange material with the subsequent elutriation [2, 3].

Extraction division methods are multistage, but allow receiving products of high purity degree. The ion-exchange method is characterized by low productivity, need of multiple repetition of sorption-desorption cycles. The method of selective oxidation reduction is used only for extraction of Ce, Eu and Yb [2].

In the article REE concentrate extraction was carried out from extracts (extra agent – solutions of sulfuric and nitric acids), received under the condi-

tions described in [7]. Here the lanthanum was presented by the corresponding salts (nitrate, sulfate). Concentrates were received in the form of a solid phase (deposit) by sedimentation in the form of hydroxides and carbonates. Ammonia solution with concentration of 25% and saturated solution of sodium carbonate were accordingly used as a precipitator.

The choice of such division variant is caused by simplicity of realization, availability of reagents used, and also possibility of receiving lanthanum oxides when heating hydroxides and carbonates.

La_2O_3 (TU 48-4-523-90 with the content of the main substance of 99.9%) was processed for determination of the concentrate structure features caused by presence of aluminum, silicon, micro impurities at a catalyst under the conditions similar to an acid leaching and sedimentation of a lanthanum in the form of carbonates and hydroxides. Thus solutions of lanthanum nitrate and sulfate were received.

The structure of precipitated concentrates was determined by the method of X-ray fluorescence analysis on a scanning electronic microscope of JSM 5610 LV with the system of the chemical analysis of EDX JED of 2201 JEOL. Identification of crystalline phases was carried out by means of the X-ray-phase analysis on the D8 ADVANCE Bruker AXS device. The thermo gravimetric analysis of samples was carried out on the TGA Standard device with TGA V5.1A software and differential thermogravimetric curves were received, besides thermal effects of decomposition reactions of lanthanum compounds precipitations were studied.

In concentrates received by sedimentation from solutions by ammoniac water Al : La ratio is 5.8 : 1 for nitrate solutions, and 12 : 1 for sulphate solutions (in the spent catalyst this ratio is equal to 15.3 : 1).

X-ray patterns of the deposits received from nitrate solutions showed existence amorphous and crystalline phases in them. Comparison of X-ray diffractograms of lanthanum concentrate precipitated from the spent catalyst and of lanthanum hydroxide received from lanthanum nitrate (Fig. 1), confirms existence of aluminum ions in the deposit.

Crystalline phases received at sedimentation from nitrate extract of the spent catalyst are of complex lanthanum structure. They are formed by nitrate hydroxolanthanum $\text{La}(\text{OH})_2\text{NO}_3$, hydrate of this salt $\text{La}(\text{OH})_2\text{NO}_3 \cdot \text{H}_2\text{O}$, and also by hexohydrate of hexonitroaluminium and $\text{LaAl}(\text{NO}_3)_6(\text{H}_2\text{O})_6$ lanthanum.

According to available data [8], lanthanum hydroxide evolves in the form of an amorphous, volume deposit under the effect of water (gase-

ous) ammonia or alkalis on salts solutions of lanthanum hydroxide in the range $\text{pH} = 7.28\text{--}8.16$ ($\text{SP} = 1 \cdot 10^{-19}\text{--}0.9 \cdot 10^{-22}$). During sedimentation from nitrates and sulfates solutions deposits evolve in the form of average salts and only at surplus of hydroxide groups gradual anions exchange and transition into hydroxides take place. Micro quantities of REE coprecipitate together with aluminum hydroxide (its sedimentation occurs in range $\text{pH} = 3.5\text{--}5.2$).

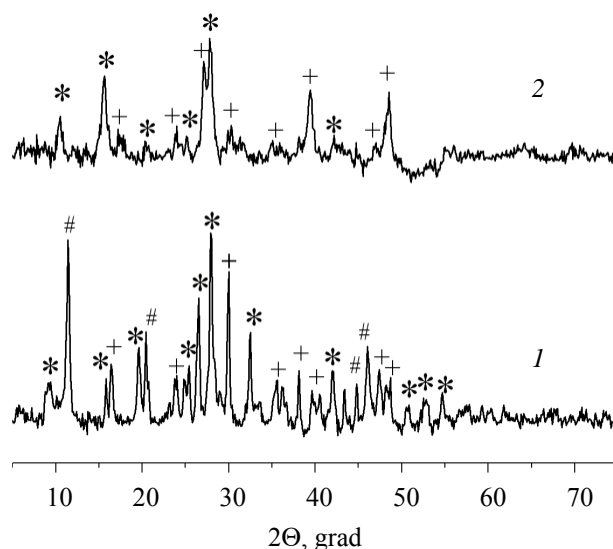


Fig. 1. X-ray patterns of the deposits received from an acid concentrate of spent catalyst (1) and lanthanum nitrate (2) by sedimentation by ammoniac water:

- * – the phase $\text{La}(\text{OH})_2\text{NO}_3 \cdot \text{H}_2\text{O}$;
- + – the phase $\text{La}(\text{OH})_2\text{NO}_3$;
- # – $\text{LaAl}(\text{NO}_3)_6(\text{H}_2\text{O})_6$

Data on concentrate structure received from the spent catalyst agree with the standards. Formation of complex aluminum and a lanthanum salt is explained by features of raw materials used for receiving REE, and by the high content of aluminum in the extract.

Curves of the thermogravimetric analysis of lanthanum concentrate received under the influence of ammonia water solution (Fig. 2), testify to prevalence of endothermal processes.

Considerable loss of sample weight is observed in three thermal ranges and is connected with decomposition of the main salt and a water pinching ($265\text{--}351^\circ\text{C}$), decomposition of $\text{LaAl}(\text{NO}_3)_6(\text{H}_2\text{O})_6$ ($380\text{--}480^\circ\text{C}$) and lanthanum hydroxide ($504\text{--}567^\circ\text{C}$).

During heating a deposit sample received from lanthanum nitrate, the greatest loss of weight (7.3%) is fixed in the range of temperatures $515\text{--}567^\circ\text{C}$. It is possible to draw a conclusion that decomposition of lanthanum hydroxide occurs in the temperature interval $500\text{--}570^\circ\text{C}$.

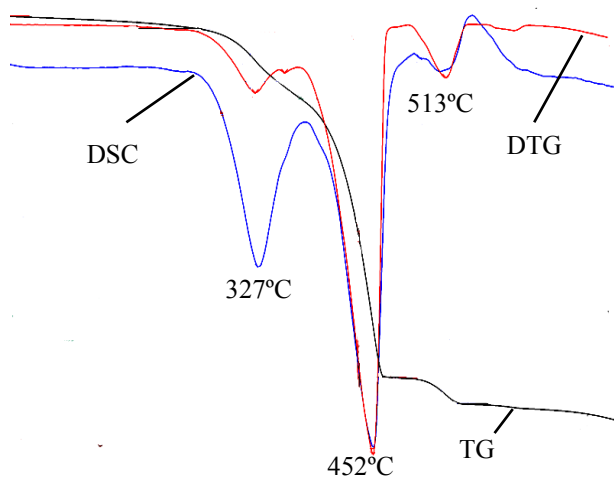


Fig. 2. Curves of the thermogravimetric analysis of lanthanum concentrate (sedimentation by ammonia solution)

In the concentrates received by sedimentation from solutions by saturated solution of sodium carbonate, ratio Al : La for nitrate solutions is 3.20 : 1, for sulfate solutions is 4.85 : 1. The precipitations received from acid extracts are an amorphous substance with inclusions of a crystalline phase – an eight-water lanthanum carbonate of $\text{La}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}$, which is consistent with data provided in literature [9], and also a lanthanum oxide carbonate of $\text{La}_2\text{O}_2\text{CO}_3$. The concentrate deposited from sulfate is the hydrated lanthanum carbonate (Fig. 3).

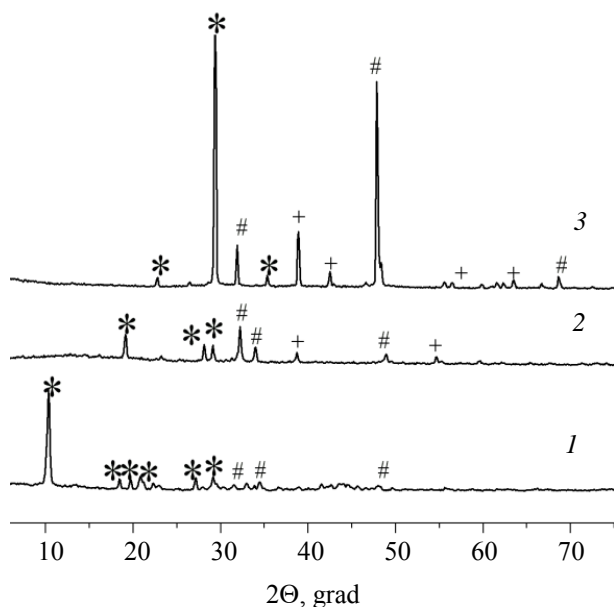


Fig. 3. X-ray patterns of the precipitations received from lanthanum sulphate (1), sulphate (2) and nitrate (3) concentrates of the spent catalyst at sedimentation by sodium carbonate: * – the phase $\text{La}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}$; # – the phase $\text{La}_2\text{O}_2\text{CO}_3$; + – impurity phase

Compounds of such a structure with lanthanite type structure form light REE and lanthanum refers to them in the temperature interval 20–80°C. Complete lanthanum sedimentation is reached at mole ratio $\text{CO}_3^{2-} : \text{La} = 1.5$. It is necessary to avoid large surplus of a precipitator and the conditions promoting carbonates hydrolysis (higher temperatures, much time for carrying out a process). In the presence of aluminum large amounts the extent of carbonates sedimentation can be changed within 90–99% at increasing pH from 5 to 6 [9].

Curves of the thermogravimetric analysis of the hydrated lanthanum carbonate show that loss of hydrate moisture occurs in the range of temperatures from 64 to 180°C, decomposition of lanthanum carbonate takes place at 378–510°C.

For a concentrate received from lanthanum sulphate, ranges of temperatures of weight reduction coincide with given above data: temperature for carbonate decomposition is 365–535°C, for water removal is 56–200°C (Fig. 4).

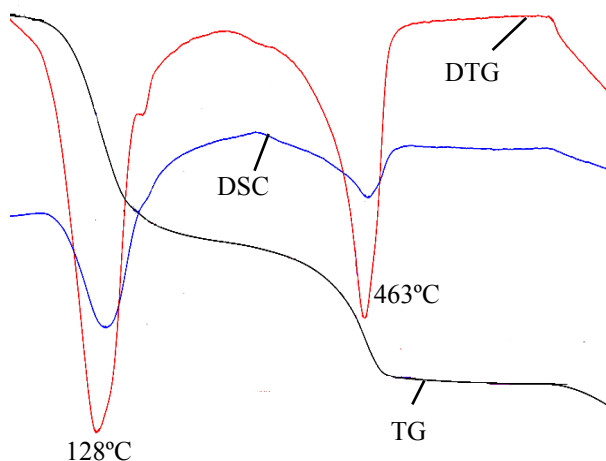


Fig. 4. Curves of the thermogravimetric analysis of lanthanum concentrate (sedimentation by solution of sodium carbonate)

Conclusion. Possibility of receiving concentrates of REE from the spent cracking catalyst has been established. The content of lanthanum in these concentrates is as higher as 5 times, than in initial waste. Data of quantitative and qualitative structure of precipitations testify that more homogeneous concentrate can be received at lanthanum sedimentation in the form of a carbonate (in comparison with hydroxide).

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