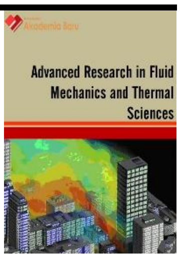
Penerbit Akademia Baru

Journal of Advanced Research in Fluid Mechanics and Thermal Sciences

Journal homepage: www.akademiabaru.com/arfmts.html
ISSN: 2289-7879



Studies on Valued Components Extraction from Titanium-Magnesium Production Wastes

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ARTICLE INFO

Article history:
Received 25 April 2020
Received in revised form 3 August 2020
Accepted 9 August 2020
Available online 25 September 2020

ABSTRACT

Based on the results of studies on the extraction of rare-earth elements from exhausted molten titanium chlorinators and the production of carnallite from chloride waste from titanium-magnesium production, the possibility to obtain REE production solution suitable for their separation and synthetic carnallite intended for chlorination of titanium slags is demonstrated. A purified water leaching solution from the exhausted molten titanium chlorinator (EMTC) was obtained to isolate synthetic carnallite with the addition of hydrochloric acid and magnesium electrolysis cell sludge up to pH 6.8-7.6. Physicochemical analysis of EMTC showed that the composition contains rare-earth elements in the form of oxides and water-soluble chlorides. The optimal EMTC water leaching mode was established: S:L ratio = 1:0.7, temperature 20-25 °C, duration — 60 min. In this case, a solution was obtained with a concentration of 0.532 g/dm^3 of the sum of rare-earth elements, 122.8 g/dm^3 of iron, pH 0.76. The separation of iron from a chloride solution during precipitation with a solution of potassium hydroxide in the range of pH 2.6-3.1 at a temperature of 80 °C. The precipitation of REEs from the solution with oxalic acid in an amount of 150% of the amount required stoichiometrically in the form of oxalates with a pulp exposure time of oxalates of 4 hours. The precipitate formed from oxalates was washed on the filter with a 2% oxalic acid solution at S:L = 1:8. Obtaining a collective REE concentrate in the processing of exhausted molten titanium chlorinators. The throughout recovery of rare-earth elements from EMTC into collective concentrate was 66%.

Keywords:
Chloride waste; REE concentrate; carnallite

1. Introduction

A global problem is the conservation and restoration of natural ecosystems, stabilization and improvement of the environment quality, solid waste processing and disposal arrangement.

Comprehensive processing of production wastes is necessary not only to reduce their negative impact on the environment but also to use them as valuable raw materials. This requires the

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https://doi.org/10.37934/arfmts.75.3.140155

characterization of waste as a raw material source of valuable components, development of optimal process flow schemes for extraction.

Krol's process is the main method to produce a titanium sponge in all countries of the world manufacturing a titanium sponge [1] involving the magnesium thermal reduction of titanium tetrachloride at 850 °C. To carry out the process, the production chain includes the production of metal magnesium by electrolysis from its molten salts. The raw material used to produce magnesium electrolysis is dehydrated carnallite, and the exhausted electrolyte is used in the chlorination of titanium slags. Natural carnallite is pre-enriched and dehydrated. A significant amount of chloride waste is formed at the stages of titanium slag chlorination and magnesium electrolysis.

According to [2,3], the production of titanium at Ust-Kamenogorsk Titanium-Magnesium Plant JSC (UKTMP), the Republic of Kazakhstan, annually generates up to 76 thousand tons of non-recyclable chloride waste, and the total amount of waste in three tailings management facilities of the enterprise accounts for more than 1.5 million tons. Chloride wastes of UKTMP JSC include as follows: exhausted molten titanium chlorinators (EMTC) 30,000 tons – 40%; exhausted molten vanadium chlorinators (EMVC) – 3,000 tons – 4%; exhausted molten potassium chloride electrolyte (EMPCE) – 30,000 tons – 39.5%; exhausted molten chlor-magnesium electrolyte (ECME) – 6,000 tons – 8%; carnallite chlorinators sludges (CCS) – 2,000 tons – 2.5%; electrolysis cells sublimates (ECS) – 500 tons – 0.5%; chlorinators' dust (sublimates) (CD(S)) – 500 tons – 0.5% and condensation system sublimates (CSS) – 4,000 tons – 5%.

Industrial wastes pose a danger to the environment, polluting soils and natural waters when they are released into the atmosphere, when industrial wastewater is discharged into water bodies, and also when solid waste is disposed in sludge storages [4].

The waste of titanium-magnesium production contains cesium, niobium, tantalum, rubidium, scandium, rare earth elements and other metals. Potassium and magnesium are also lost among others in the waste, having an average content of potassium chloride of 50-60%, magnesium 25-30% [5, 26]. At the same time, UKTMP JSC procures carnallite that is a reagent consisting of a mixture of magnesium and potassium chlorides, abroad at fairly high prices. Meanwhile, the problem of carnallite deficiency can be reduced by obtaining it by regeneration of valuable components from titanum-magnesium production wastes [6,7].

It is known that rare-earth elements practically do not form their own ore deposits, and the bulk of REEs is present in small quantities as an impurity to the main component. An example of such ores is ilmenite. The content of rare-earth elements in them ranges from 0.1 to 0.3%. Based on the chemical properties of REEs, the most probable places of their accumulation in the processing technology of ilmenite concentrates are recycled dust of ore-smelting and chloride waste.

At the same time, the lack of technology for processing chloride waste prevents the possibility of creating production of such expensive products as rare-earth concentrate. Given the volume of processing of titanium-containing raw materials, the extraction of REEs from it seems to be a long-range objective.

2. Reagents

The objects of the study were the exhausted molten titanium chlorinators (EMTC) and slurries of magnesium production, i.e. slurry of a furnace of continuous refining of magnesium (FCR), slurry of a magnesium electrolyzer of a chlorine-magnesium scheme (SMECMS), slurry of a magnesium electrolyzer of a carnallite scheme (SMECS). The composition of chloride waste is shown in Table 1.

The main waste products of titanium tetrachloride production are exhausted molten titanium chlorinators, in which, according to X-ray microanalysis, the highest content of niobium, tantalum, scandium and rare-earth elements is detected. In our work, we used high grade hydrochloric acid, high grade sulfuric acid, and KU-2-8n ion exchange resin.

Table 1
Chemical composition of titanium-magnesium production wastes of UK TMK JSC

Wastes	Component content, %										
	TiO_2	FeO	$FeCl_2$	KCl	$MgCl_2$	MgO	NaCl	Cr_2O_3	MnO	$AlCl_3$	SiO_2
EMTC	4.9	-	16.8	9.0	1.7	-	17.0	1.4	4.2	4.1	8.2
FCR slurry	0.9	1.39	-	26.3	7.48	32.5	11.8	0.04	0.009	max	<0.2
SMECMS	1.4	2.7	-	21.8	7.8	32.45	14.6	0.07	0.018	max	<0.2
SMECS	1.93	3.5	-	21.8	9.82	27.3	16.0	0.07	0.03	0.015	<0.2

3. Method of Procedure

Aqueous and acid leaching of chloride wastes was carried out in glass reactors. Intensive mixing was used to remove diffusion limitations. The agitator rotational speed was 600 rpm. REEs sorption was carried out in a dynamic mode. Chemical analysis of the samples was performed on Optima 2000 DV inductively coupled plasma optical emission spectrometer. Thermal analysis was performed on DERIVATOGRAPH Q – 1000 using STA 449 F3 Jupiter synchronous thermal analysis instrument. Before heating, the furnace space was pumped out and then purged with an inert gas. The sample was heated at a rate of 10 °C/min. in an atmosphere of highly purified argon. The volume of incoming gas was 80 ml/min. Cooling was carried out to 300 °C at a rate of 15 C/min. Processing of the results obtained using the STA 449 F3 Jupiter was performed using NETZSCH Proteus software. The IR spectrum was obtained on Avatar 370 IR Fourier spectrometer in the spectral range of 4,000-250 cm^{-1} from the preparation in the form of a tablet prepared by compression from 200 mg of CsI and 2 mg of sample; CsI spectrum was taken as a comparison spectrum. Detachable device for experiment: Transmission E.S.P. X-ray experimental data were obtained on BRUKER D8 ADVANCE using copper radiation at an accelerating voltage of 36 kV and a current of 25 mA. The pH of the solutions was measured using a pH-150MI pH meter. Mapping of the elemental and phase composition of technical calcium carbonate was carried out on JXA-8230 electron probe micro-analyzer from JEOL (Japan).

Samples in the form of powders were placed on NISSHIN EM Co double-sided adhesive conductive carbon tape. To exclude the expansion of particles during evacuation in the lock and column of the micro-analyzer, the powder particles were fixed on the tape by pressing medium force with a flat tool. Since the samples did not have sufficient electrical conductivity, a thin layer of carbon with a thickness of about 10 nm was applied to reduce the effect of image blurring due to the accumulation of an electronic charge. Scanning electron microscopy (SEM) studies and X-ray spectral microanalysis (XSMA) were carried out for each sample at several points. The most informative SEM images are those images that were taken in the backscattered electron mode (COMPO), because they allow to sort the particles by contrast. In this mode, the brightest contrast is formed from those particles that contain elements with higher atomic numbers, and accordingly, belong to the so-called heavy fraction. An additional feature of such images is the increased resolution, which makes it possible to register images of small size particles. X-ray fluorescence analysis was carried out on Venus 200 PANalytical B.V. wave dispersion spectrometer (PANalytycal B.V., Holland).

4. Result and Discussion

The main redistribution of the developed technology is the production of a salt solution with a carnallite module $KCl/MgCl_2 = 0.8-1.0$. When EMTC was leached with water under optimal conditions, the resulting solution had a carnallite module of 2.94, i.e. the content of potassium chloride was almost three times higher than necessary. In addition, the solution is contaminated with iron, silicon, manganese and aluminum. When leaching magnesium slurry with water, a third of the magnesium oxide is lost with the residual cake. For a more complete extraction of magnesium into the solution, 10% hydrochloric acid solution was used. From the data of Table 2, it is seen that the most concentrated solutions of magnesium are formed during the leaching of FCR slurry.

Table 2

Results of the magnesium sludge leaching with 10% solution of hydrochloric acid

Product	$\frac{KCl}{MgCl_2}$	Content of components, g/dm^3								Extraction into the solution, %	
		Fe(II)	Fe	K	Mg	Ti	Si	Mn	HCl	K	Mg
FCR slurry	0.35	0.0001	<0.001	29.9	41.1	<0.001	0.098	3.05	not detected	99.9	97.1
SMECMS	0.34	0.00016	<0.001	26.2	36.5	<0.001	0.12	1.48	not detected	99.3	95.1
SMECS	0.4	4.5	5.2	24.5	30.0	<0.001	0.12	55.0	26.3	99.7	99.7

When leaching FCR and SMECS slurries solutions with a high content of manganese impurities, which makes them unsuitable for further research, were obtained. It should be noted that with acid leaching, poorly filtered pulps are formed. Filtration rate does not meet industry requirements. To saturate the EMTC leach solutions with magnesium and at the same time to remove impurities, slurries of magnesium electrolyzers were used.

EMTC aqueous leach solution was obtained at pH 1.2-1.8, which was strengthened with hydrochloric acid. Then SMECMS up to pH 6.8-7.6 was introduced by batches. This technique allows precipitating impurity metals and almost completely dissolving magnesium compounds of SMECMS, which provides the required carnallite module of 0.8-1.0. The following saline solution of the composition was obtained, g/dm^3: Ti 0.0001-0.0004; Fe 0.001-0.003; Si 0.026-0.033; Mn 0.04-0.06, suitable for isolation by a known method of synthetic carnallite [8,9].

According to the most common technology at present, titanium concentrates are processed by reduction smelting and subsequent chlorination of the resulting slurries in a melt of alkali and alkaline earth metal chlorides. During chlorination, a number of elements associated with titanium (vanadium, niobium, tantalum) are removed mainly with gaseous chlorination products, while other elements (scandium, zirconium, thorium, REEs) are concentrated in the melt [10, 23-25].

A study of the distribution of rare-earth elements by chloride wastes showed that one of the potential raw materials for rare-earth elements is exhausted molten titanium chlorinators (Table 3). The composition of the rare-earth elements of EMTC is commercially attractive, since the share of dysprosium is 57%, neodymium is 8%, and non-deficient cerium is only 13%.

The mineralogical forms of occurrence of rare-earth elements in EMTC were determined by the thermal method, which is associated with their low content in the product. A weak exothermic effect at 510 °C, obtained during sample cooling and characterizing the phase transition of terbium chloride $TbCl_3$, was recorded on the DTA curve.

In order to clarify the phase composition and structure of EMTC, images were obtained in secondary electrons (Figure 1) and in backscattered electrons (Figure 2). Topographic information obtained in secondary electrons indicates the presence of aggregates and a finely dispersed phase (Figure 2). The image of EMTC sample with a magnification of 1,900 times, presented in Figure 2, illustrates the phase composition of the sample. It is seen that the gray phase is the main one, and there are dark areas and rare light spots.

Table 3
Distribution of the amount of REEs by the products of titanium tetrachloride production

Technological redistribution	Product	ΣREE share, %
Ore thermal smelting of titanium concentrate	Slurry	97
	Electrostatic precipitators dust	3
Slurry chlorination	Technical titanium tetrachloride	7.5
	Sublimates	5.7
	Exhausted molten titanium chlorinators	83.8

Calculation of the distribution of the amount of REEs was conducted relative to the content in the source raw material

The results of EMF analysis (Figure 3) of different sections of the sample (Figure 2) and X-ray phase analysis made it possible to identify the mineral phases of EMTC. At site No. 1, the presence of carbon (coak) and sodium chlorides was established, characterized by a dark color image, and impregnation of neodymium oxide in the form of a bright spot. At site No. 2, sodium, potassium, neodymium, calcium chlorides, erythrosiderite K_2FeCl_5, sodium aluminum silicate $Na_2Al_2Si_3O_9$, manganese iron oxychloride $FeMn_7O_{10}Cl_3$ were detected. The main phase is halite NaCl. At site No. 3, chlorides of potassium, sodium, calcium, manganese, iron, neodymium, lanthanum, chromium, and quartz SiO_2, complex stoichiometry titanium oxide $TiO_{0.89}$ were identified. The main phases of the site No. 4 are compounds of ferric and ferrous iron – rinneite $K_2NaFeCl_6$ and iron chloride (II) $FeCl_2$.

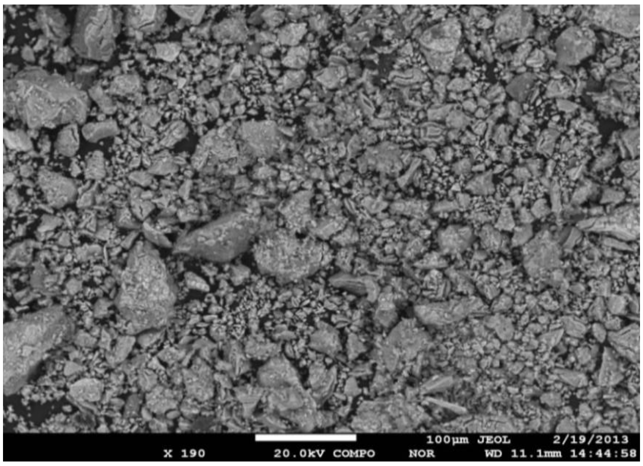


Fig. 1. Image of EMTC sample in secondary electrons

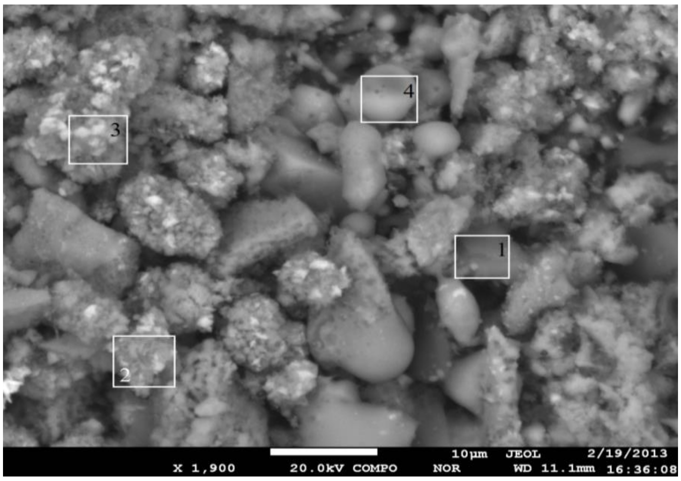


Fig. 2. Image of EMTC sample in backscattered electrons

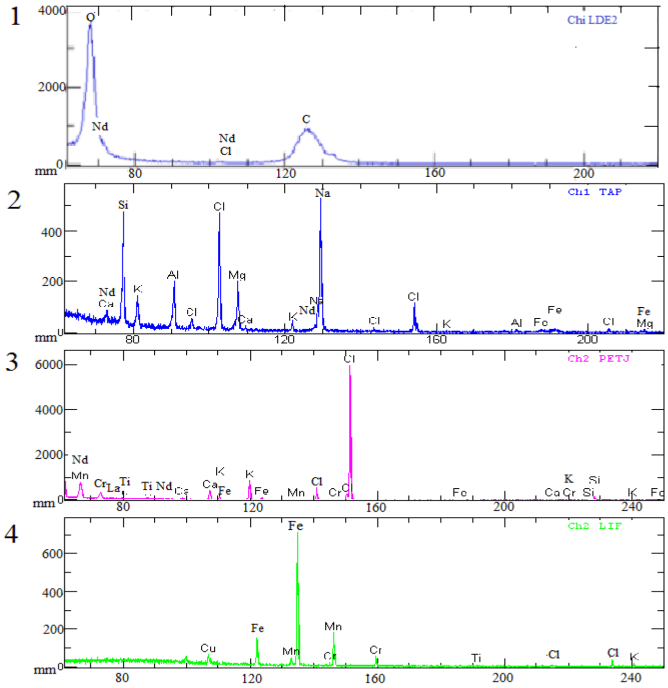


Fig. 3. Energy dispersive spectra of EMTC sample sites (Figure 2)

Thus, the physicochemical analysis of the spent melt of titanium chlorinators showed that rare-earth elements are present in the composition of the studied EMTC in the form of oxides and water-soluble chlorides, which suggests that there are no difficulties in leaching REEs.

Earlier [11] we investigated the possibility to obtain a REE production solution from the exhausted molten titanium chlorinators, in which REEs were present in the form of water-insoluble molybdates, tungstates, perrenates, for example, praseodymium molybdate $Pr_2O_3{\cdot}4MoO_3$, lanthanum tungstate $La_2O_3{\cdot}2WO_3$, terbium perrenate $Tb(ReO_4)_3$.

As follows from the above data, EMTC, studied in this work, contains rare-earth elements in a water-soluble form. In connection with this, the purpose of the first stage is to determine the conditions of water leaching of REEs. Leaching was carried out in vessels with stirrers. A certain volume of water was poured into the vessel, stirring was switched on and 100 g of EMTC was added. The duration of the experiments is 60 min, the temperature is 22 °C. At the end of the leaching process, the solid and liquid phases of the pulp were separated on a vacuum filter. The pH of the original solution was determined. Cake was analyzed for REEs and iron.

The study results showed (Figure 4) that the output of the cake strongly depends on the amount of water spent on leaching of rare-earth elements from EMTC in the range of the ratio of solid to liquid — 1:0.5-1:1.5. Under these conditions, the output of cake decreases from 72.2 to 25%. A further increase in the volume of water has little effect on the output of cake — from 25% at S:L = 1:1.5 up to 21.5% at S:L = 1:4.

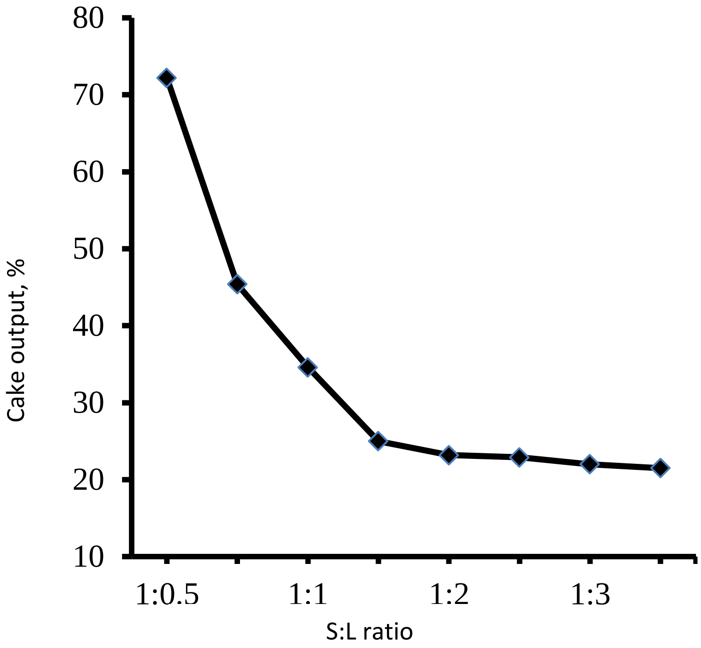


Fig. 4. Dependence of cake output on S:L ratio with water leaching of EMTC

One of the physicochemical characteristics of mineralized solutions is their stability, which is largely influenced by pH. A study of the dependence of the pH of the filtrate on the ratio of solid to liquid allowed us to establish that when EMTC is leached with small volumes of water, the final pH values are less than 1.0 (Figure 5), that is, the solutions obtained after filtration of the pulp are quite stable and the hydrolysis of iron, titanium and chrome salts is unlikely.

With an increase in the amount of water for EMTC leaching, pH of the filtrate monotonously increases to 1.76 at S:L = 1:4 and the solution becomes unstable, and with an increase in pH, the stability time of the solution decreases from 12 to 0.5 hours and sedimentation occurs.

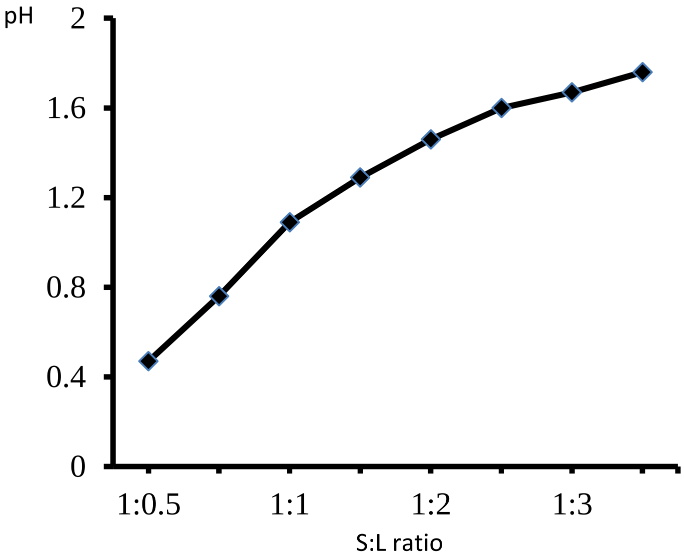


Fig. 5. Dependence of pH of the filtrate on S:L ratio with water leaching of EMTC

Studies on the leaching of exhausted molten titanium chlorinator with water according to solid to liquid ratio of 1:0.5÷4 showed that the concentration of the amount of rare-earth elements and the main harmful impurity, iron in solution, decreases with an increase in water consumption from 0.669 to 0.122 g/dm^3 of REEs and from 143.4 to 29.0 g/dm^3 of iron (Figure 6), while the degree of extraction of components increases from 46.7 to 88.9% of REEs and from 44.4 to 92.0% of iron.

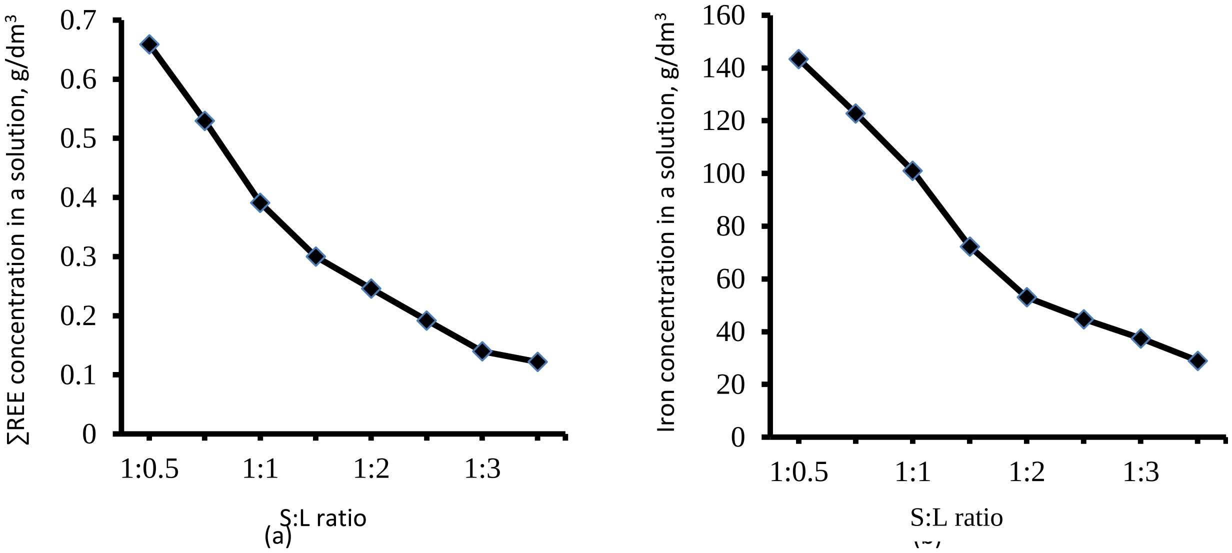


Fig. 6. Dependence of the concentration of components in the filtrate on S:L ratio during water leaching of EMTC (a) sum of rare-earth elements (b) iron

It should be noted that the ratio of iron concentrations to the sum of rare-earth elements in the filtrate remains constant, equal to 227±10, in the entire range of the studied S:L ratios.

It was experimentally established that during leaching, the degree of extraction of individual rare-earth elements into the solution differs from the average REEs amount by more than ten percent (Table 4).

Table 4
Effect of S:L ratio on the extraction of REEs in solution during aqueous leaching of EMTC. Leaching time – 50 min

S:L	Degree of extraction into solution, %										Concentration of ΣREE in solution, g/dm^3
	Lu	Dy	Y	Yb	Sm	Pr	Nd	Ce	La	ΣREE	
1:0.5	63.9	46.3	50.0	52.4	40.7	54.3	47.1	46.1	43.3	53.3	0.659
1:0.7	72.9	70.3	60.0	63.4	59.2	73,7	59.0	57.4	55.7	59.8	0.532
1:1	84.9	82.7	70.8	73.9	69.1	85.8	68.8	66.8	64.8	69.8	0.391

Therefore, when choosing the optimal ratio of solid to liquid, the conditions were taken into account under which the degree of extraction of the most sought-after elements is greatest.

Due to the fact that in order to efficiently carry out further operations to obtain REE concentrate, it is necessary to obtain a solution that is sufficiently concentrated rare-earth elements and the solid-to-liquid ratio is selected when EMTC is treated with water, which allows significant leaching of expensive elements without diluting the solution.

The analysis of the obtained and processed results showed that the optimum ratio is S:L = 1:0.7, at which the degree of extraction of REEs required in the world market of REE is quite high, the concentration of the sum of rare-earth elements in the solution satisfies the requirements of subsequent operations.

At the same time, at S:L = 1:0.5, solutions are obtained with a high concentration of not only REEs but also iron, which is accompanied by chromium, titanium, aluminum, and sodium. The most negative factor is the high content of hydrochloric acid (Figure 6).

The main disadvantage of the solutions obtained during the leaching of EMTC at S:L = 1:1 is the low concentration of lanthanides – 26% lower than in the solution obtained at S:L = 1:0.7.

A series of experiments carried out at the optimal ratio S:L = 1:0.7 of EMTC water leaching showed (Figure 7) that the degree of REEs extraction into the solution reaches a maximum in 60 minutes and practically does not change with a further continuation of the process.

Cake composition, mass. %: Fe 4.76; Ti 0.98; Al 2.45; Mn 1.16; K 2.06; Na 16.36; Ca 0.89; Cr 0.63; Si 6.13; Cl 40.54; Σ REE 0.052 from EMTC water leaching is directed to the production of carnallite for additional leaching of sodium and potassium chlorides.

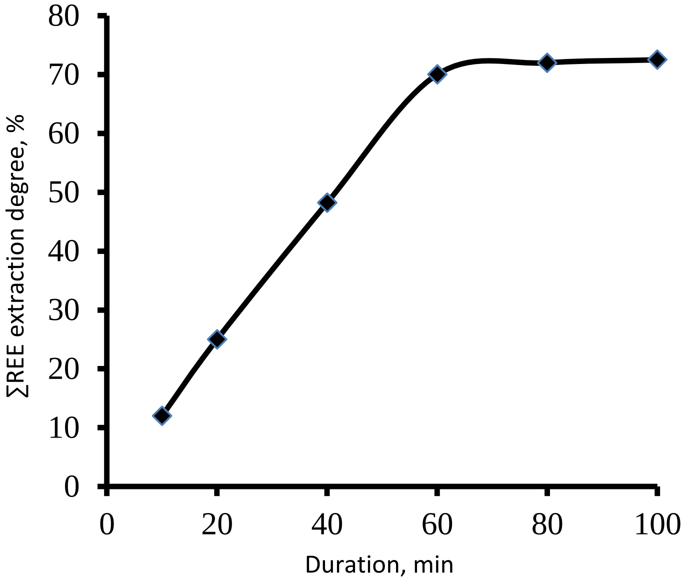


Fig. 7. Dependence of the degree of REE extraction into the solution on the duration of the water leaching of EMTC

As a result of the studies, the following optimal mode of water leaching of EMTC was established: S:L ratio = 1:0.7, temperature – 20-25 °C, duration – 60 min. In this case, a solution was obtained with a concentration of 0.622 g/dm^3 of the sum of rare-earth elements, 122.8 g/dm^3 of iron, pH 0.76. The output of cake is 45.4%.

Henceforth, studies were conducted on the purification of REE-containing solution from iron. The compounds of iron (III) and REEs are characterized by close chemical properties [12,13, 22]. In this regard, the problem of their separation arises. One of the effective methods for metals separation in solutions is the selective precipitation of one of them in the form of hydroxide.

Hydrolytic precipitation of iron hydroxide was carried out in thermostated reactors with stirring. A solution preheated to 80 °C in a volume of 100 ml was poured into the reactor and the stirrer was turned on. The neutralizing agent was administered in portions until the required pulp pH was reached and kept under the achieved conditions for 40 min. At the end of the process, the solid and liquid phases were separated by filtration through a red ribbon filter. The precipitate was analyzed for REEs and iron.

Commercial reagents were used in the studies: 44% potassium hydroxide solution of chemically pure qualification; 25% solution of ammonia chemically pure qualification.

It is known [14] that iron (III) hydroxide begins to precipitate at pH 1.6, and ends at pH 3.5. In this regard, studies on the precipitation of iron from solutions of the leaching of the exhausted molten titanium chlorinators in the form of hydroxide were carried out in the range of pH 2.3-3.1, since preliminary experiments established that trivalent chromium is precipitated with iron hydroxide at pH greater than 3.0.

Analysis of experimental data (Table 5) showed that the use of a 25% solution of ammonia as a neutralizing agent leads to an increase in the loss of rare-earth elements by 30%, which coincides with the results [15,16].

It should be noted that the chlorine ion affects the structure and properties of solutions, since the chlorine ion is not only an anion that binds free water molecules, and one of the ligands, complexes with which are stable but also a micelle stabilizer.

Table 5

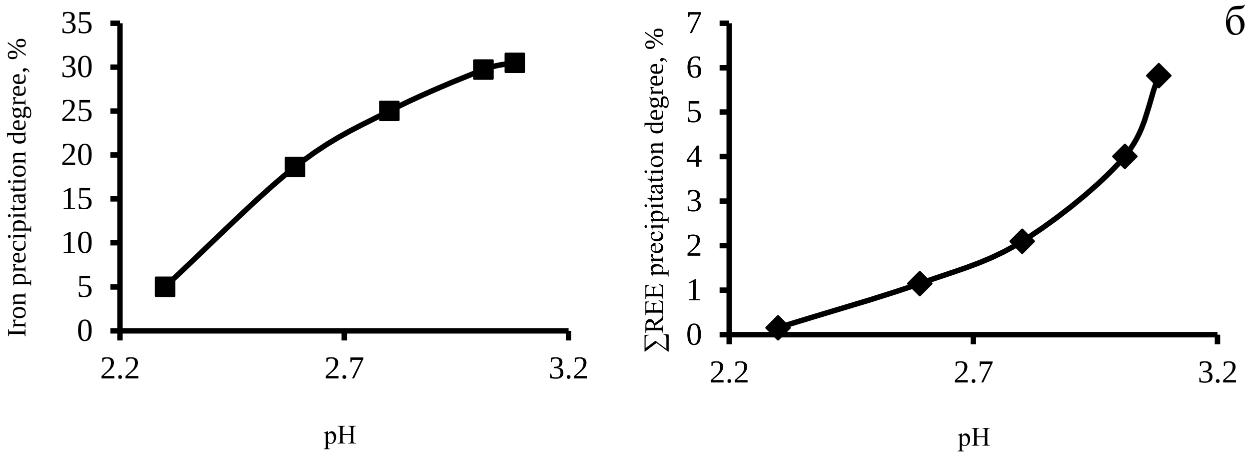
Results of experiments on the precipitation of iron hydroxide from REE-containing chloride solution

Neutralizing agent solution	Pulp pH	Density of the originalsolution, g/cm^3	Weight of sediment, g	Content in the sediment, mass. %		
				ΣREE	Fe	FeOOH
Original solution	0.76	1.442				
Potassium hydroxide, 44%	2.30	1.392	1.26	0.004	48.74	77.24
	2.59	1.361	4.58	0.008	49.97	79.25
	2.80	1.360	5.86	0.012	51.23	81.25
	3.01	1.359	7.11	0.018	51.31	81.37
Ammonia, 25%	3.02	1.360	7.23	0.036	49.89	79.12
Potassium hydroxide, 44%	3.08	1.330	8.01	0.032	51.80	82.15

By chemical analysis in solution after EMTC leaching, the concentration of chloride ions was determined to be 254.3 g/dm^3, which is sufficient for the formation of a stable colloidal form during the formation of iron hydroxide [17]. According to the results of x-ray phase analysis of the precipitate sample obtained at pH 2.80, the formed iron hydroxide is in an amorphous state and is described by the formula FeOOH.

From the data of Table 5, it can be seen that an increase in the pH of the precipitation of iron hydroxide leads to coagulation of colloidal particles and loss of adsorbed water, which is accompanied by an increase in the content of the basic substance in the precipitate. For example, when the pH of the pulp reached 2.30, the amount of hydroxide in the sample was 77.24%, and when the solution was neutralized after leaching of EMTC to pH 3.01 – 81.37%.

However, with an increase pH up to 3.08 in pulp, not only the degree of iron precipitation increases but the degree of co-precipitation of rare-earth elements also sharply increases (Figure 8). In addition, trivalent chromium hydroxide is co-precipitated and chromium chloride is occluded, which is confirmed by the results of thermal analysis (Figure 9), according to which an intense exothermic effect with a peak at 115 °C was recorded on the DTA curve. The effect developed against the background of a decrease in the weight of the sample. Probably, there is an oxidation of some organic component of the sample. Further oxidation of organics is reflected by peaks at 431 and 486.5 °C. The endothermic effect on DTA with an extremum at 254 °C and exothermic effects with peaks at 263 and 524 °C is a manifestation of iron oxide gel.



(a) (b)

Fig. 8. Dependence of the degree of components precipitation from REE-containing chloride solutions (a) iron (b) sum of rare-earth elements

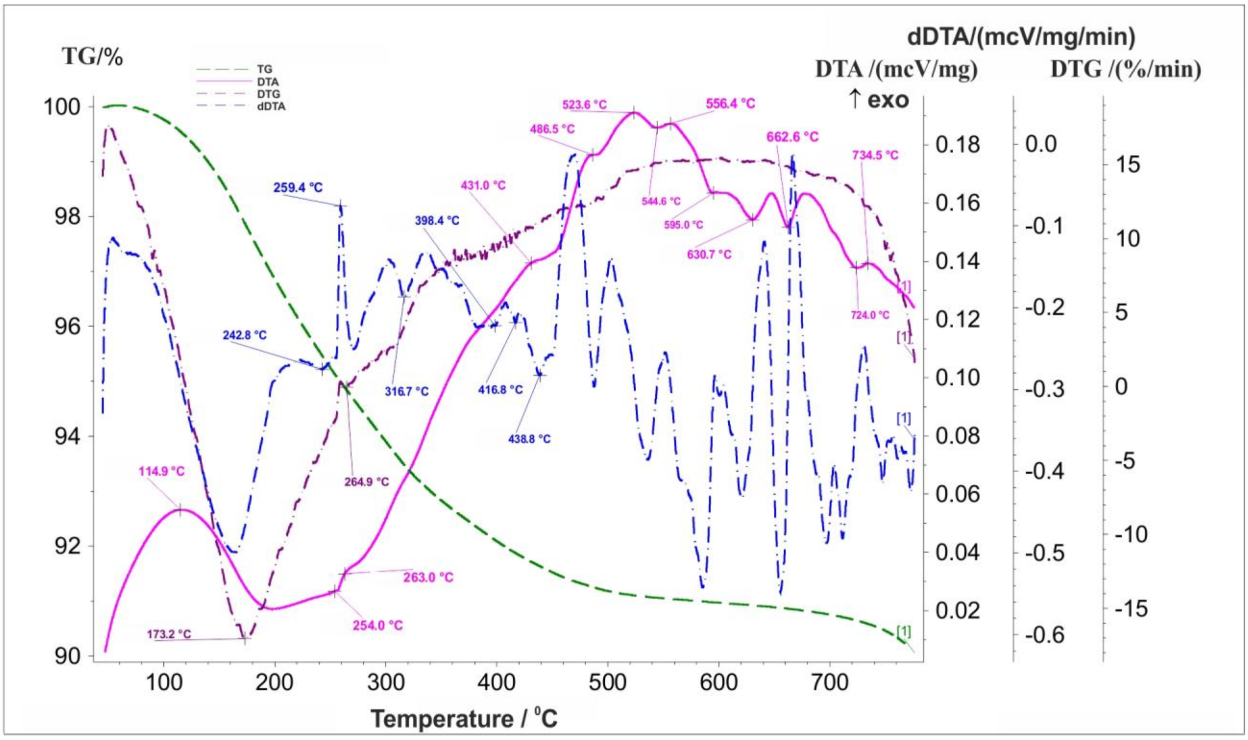


Fig. 9. Thermogram of iron hydroxide sample, obtained at pH 3.08

In addition, the minimum on the DTG curve at 173 °C in combination with the endothermic effect with an extremum at 254 °C reflects the presence of amorphous iron hydroxide. Also in the overlay, the endothermic effect with an extremum at 254 °C is a manifestation of chromium hydroxide dehydration.

Exothermic effect with a peak at 556 °C due to polymorphic transformation of maghemite – γFe_2O_3, having magnetic properties. Low-intensity endothermic effect with maximum development at 595 °C is a reflection of polymorphic transformation Na_3CrCl_6. The endothermic effect with an extremum at 631 °C characterizes the polymorphic transformation of magnetite. Magnetite could appear as a result of hematite reduction processes by products of organic oxidation. Therefore, in the overlay, the effects manifested in the temperature range 400 – 600 °C, also reflect the recovery processes. The endothermic effect with an extremum at 663 °C may be a manifestation of $FeCl_2$ melting. The endothermic effect with an extremum at 724 °C characterizes the melting of the solid solution of $FeCl_3$ – NaCl system.

The dDTA curve revealed additional effects that were not reflected in the DTA curve. Endothermic effects with extremum at 243 and 398 °C are a manifestation of the KOH impurity. IR spectroscopic studies of the iron-containing precipitate are shown in Figure 10. The obtained spectrum was not found in the special literature and spectrometer software.

The absorption bands of valence ν (OH) - 3432 cm¯1 and deformational δHOH-1627 cm¯1 vibrations of molecular water were recorded in the spectrum [17], which indicates the presence of crystalline hydrates in the sample. In the range of manifestation of characteristic vibrations of closed polyhedra $[CrO_4]^{2-}$, bands with peaks at wave numbers 852, 491 cm^{-1} and shoulders at wave numbers 937, 452 cm^{-1} are observed on the spectral curve [18]. The band observed in the spectrum with a maximum at a wave number of 695 cm^{-1} can be attributed to Fe–O bonds in ferrites with a garnet structure and other compounds with condensed iron oxygen tetrahedra [19]. A band with a maximum at a wave number of 695 cm^{-1} also falls into the region of manifestation of isolated tetrahedra AlO_4 [18].

Perhaps the presence of polyhedra of the following type: isolated tetrahedra $Fe^{2+}O_4$ – 452 cm^{-1} [19]; open octahedrons $[FeO_6]^{9-}$ – 491 cm^{-1} [18]. In the long-wavelength region of the spectrum, in the range of the appearance of Me–O, Me–Cl bonds, there is an absorption band with a maximum at a wave number of 276 cm^{-1}. As a result of IR spectroscopic studies of a sample of the precipitate obtained at pH 3.08, the presence of aluminum hydroxide was established. In order to clarify the phase composition of the chemically precipitated iron hydroxide, part of the sample was dried at 230 °C for 3 h. The result of X-ray phase analysis of the crystallized precipitate is shown in Figure 11.

An analysis at Figure 11 showed that the iron-containing precipitate obtained at a precipitation pH 3.08 consists mainly of a mixture of hematite Fe_2O_3 and a solid solution of iron and chromium oxides $(Cr,Fe)_2O_3$. In addition, a significant amount of hydrated chromium chloride $CrCl_3 \bullet 6H_2O$ was found.

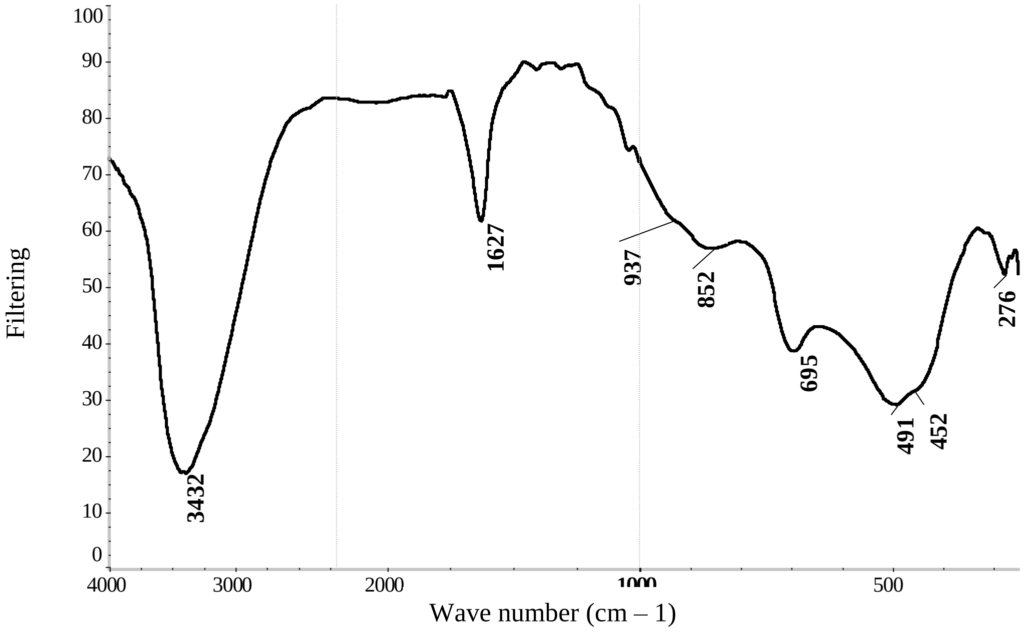


Fig. 10. IR spectrum of iron hydroxide sample, obtained at pH 3.08

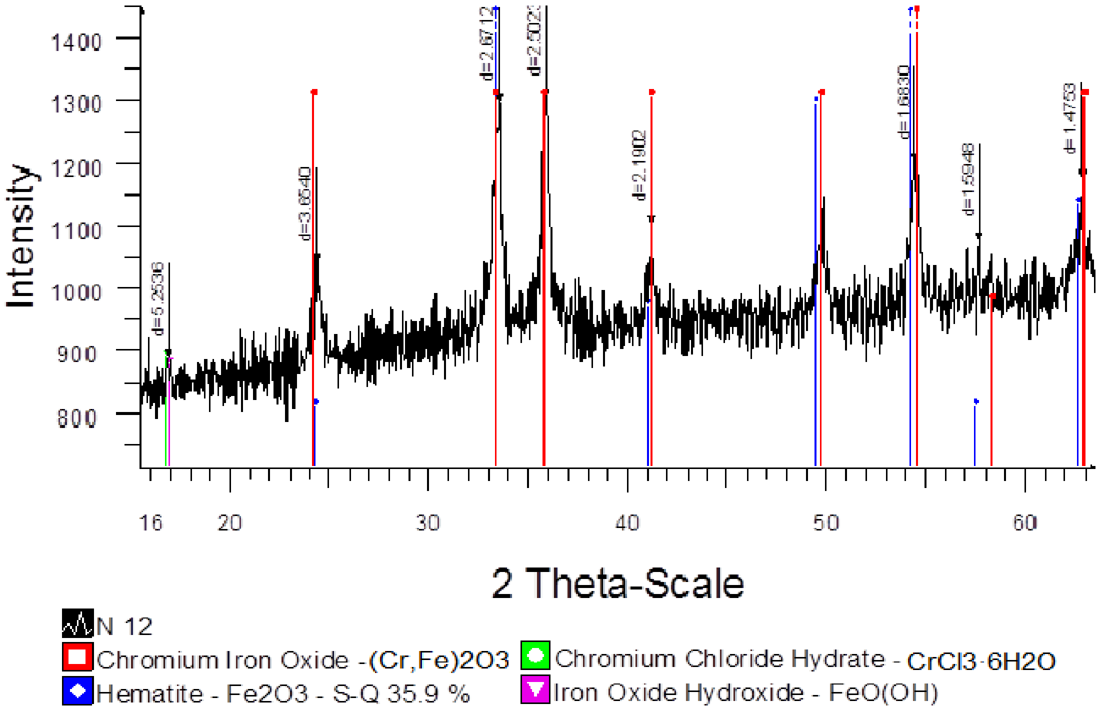


Fig. 11. Diffraction pattern of iron hydroxide sample, obtained at pH 3.08 and dried at 230 °C

According to chemical analysis, the precipitate obtained at pH 3.01 contains chromium 13.8, aluminum 1.8 and iron 31.5%, and the precipitate obtained at pH 3.1 contains chromium 21.0, aluminum 4.4 and iron 18.4%. Products of this composition can be used to produce ferrochrome.

Thus, the conducted experimental studies on the hydrolytic decrease in the concentration of iron in the chloride solution after leaching of EMTC showed the possibility of separating part of the iron in the form of hydroxide upon precipitation with potassium hydroxide solution in the range of pH 2.6-3.1 at a temperature of 80 °C.

Despite the fact that the value of the coefficient of purification from iron does not exceed 1.5 (ratio of the impurity contents in the original and purified solutions [20, 21]), the resulting solution is suitable for the precipitation of rare-earth elements in the form of oxalates. It should be noted that a favorable factor is a decrease in the density of the solution after precipitation of impurities and, as a consequence, its viscosity.

4.1 Experimental Procedure

The precipitation of REE oxalates was carried out in vessels with stirring at ambient temperature. The consumption of oxalic acid was 150% of the stoichiometrically required amount due to the low concentration of REEs in the solution. The exposure time of the oxalate pulp was 4 hours. The formed precipitate of oxalates was washed on the filter with a 2% solution of oxalic acid at S:L = 1:8.

4.2 Reagents

During the studies, commercial oxalic acid of pure qualification was used. X-ray phase analysis showed that lanthanide oxalates precipitate in the form of crystalline hydrates and are in an amorphous state (Figure 12).

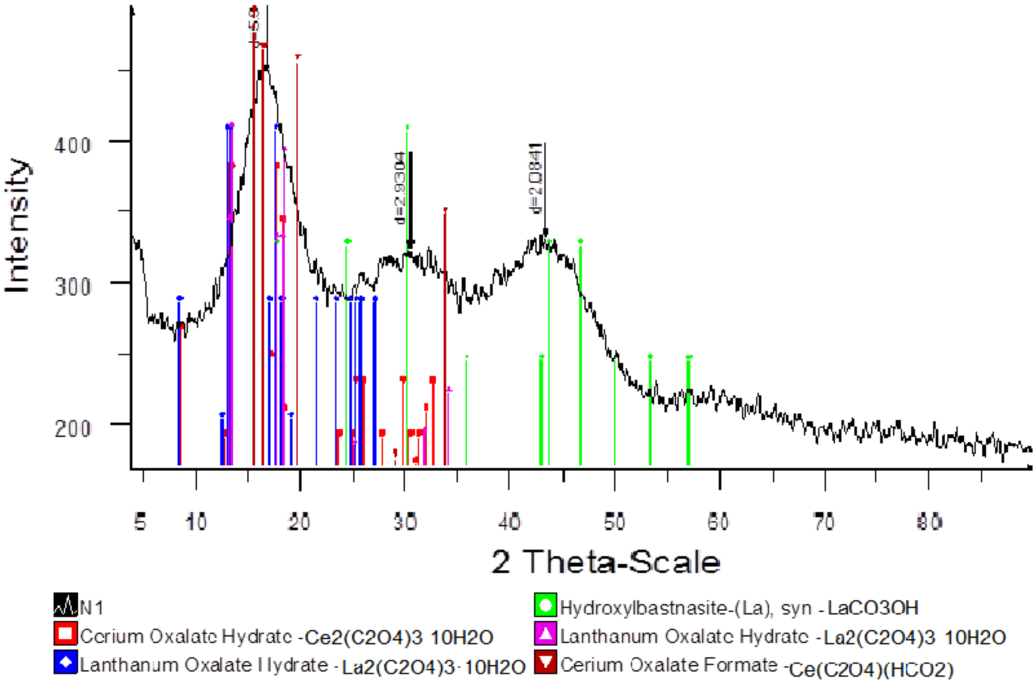


Fig. 12. Diffraction pattern of REE oxalate concentrate

After removal of crystallization water, according to chemical analysis, the content of the product of the amount of rare-earth elements in the product is 49.4%, and rare-earth oxalate is 96.0%. The main impurities are barium and iron oxalates, the total content of which is 3.1%. End-to-end extraction of rare-earth elements from EMTC into collective concentrate – 66%. The original solution after separation of REE oxalates is sent to the production of carnallite.

5. Conclusions

The studies carried out have shown the possibility of obtaining a collective concentrate of REE during the processing of EMTC. With the optimal mode of water leaching of EMTC, a solution with a concentration of 0.532 g/dm^3 of the total of rare earth elements, 122.8 g/dm^3 of iron, pH 0.76 was obtained. Separation of a part of iron in the form of hydroxide during precipitation with a potassium hydroxide solution in the range pH 2.6-3.1 at 80 °C. The consumption of oxalic acid was 150% of the stoichiometrically required amount, the holding time of the oxalate pulp was 4 h. The formed oxalate precipitate was washed on the filter with a 2% solution of oxalic acid at S:L ratio = 1: 8. After removal of the water of crystallization, according to the data of chemical analysis, the content in the product of the sum of rare earth elements is 49.4%, and the content of rare earth oxalates is 96.0%. End-to-end extraction of rare-earth elements from EMTC into collective concentrate - 66%. After separation of rare-earth oxalates, the mother liquor is sent to the carnallite production.

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