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DEVELOPMENT OF TECHNOLOGY FOR CHROMITE CONCENTRATE FROM THE SLURRY TAILINGS OF ENRICHMENT

Abstract. The exploration results of manmade residues retreatment – slurry tailings of chromite ore enrichment of Donskoi Ore Mining and Processing Plant of the Republic of Kazakhstan are performed in the article.

The technology of chromite concentrate extraction by chemical enrichment and centrifugal separator methods has been developed. The technology includes preliminary activation processes of chromite-containing tailings in sodium hydro-carbonate solution, leaching in ammonium bisulfate solution and gravity concentration in a centrifugal separator. The preliminary activation process is required to increase enrichment degree of chromite-containing tailings when leaching by means of accompanying elements removal – magnesium, silicium, ferrum. Quantitative composition of samples is changed insignificantly as a result of activation. At the same time, the phase composition of samples is changed, calcium oxides phases and ratio of magnesium-containing phases are disappearing.

Prime results through researches when choosing reagent to slurry tailings leaching have been achieved by using 30%NH₄HSO₄solution. Out of data of X-ray phase and chemical analysis, follows that when leaching slime tailings, the rock-forming minerals mainly go to solution, while chromium and chromite-containing minerals, kaolinite and amorphous silica remain in the cake-the rough concentrate.

Chromite concentrate has been received at rough concentrate treatment using centrifugal separator KNELSON consisting of chromite mineral - (Fe_{0.52}Mg_{0.48})(Cr_{0.76}Al_{0.24})₂O₄ with Cr₂O₃ 59,2% content when ejecting Cr₂O₃ into 86,8% concentrate. Technology engineering of chromite slurry retreatment contributes to solve an environmental problem and also to increase chromite concentrate production.

Key words: slurry tailings, activation, ammonium bisulfate, centrifugal separator, and chromite concentrate.

Introduction. Processing of accumulated and newly formed manmade waste, including chromite tailings, is an actual task of the present.

The importance of solving the problem of involving in the processing of wastes of enrichment products is associated not only with ecology but also with the need to increase the production of chromium. For the period from 2005 to 2012, the world production of chromium, according to the International Chromium Development Association (ICDA), increased from about 18 million tons to 24 million tons [1].

Donskoy Ore Mining and Processing Plant is the enterprise that extracts and enriches chromium raw materials in Kazakhstan. Gravitational technology for chromium ore enrichment makes it possible to obtain a chromium concentrate from large and medium fractions. At the same time, the fine-grained tailings are practically not enriched because of the difficulty of separating complex minerals into chromium concentrates and empty rock [2, 3].

Research in Physics and Chemistry. Slurry tailings of chromite ores enrichment of the Donskoy Plant were used in the work. Chemical analysis of slurry tailings is given in table 1.

The results of X-ray diffraction analysis of slurry tailings of the Donskoy Plantare presented in table 2.

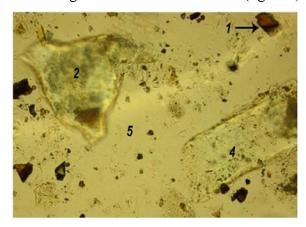
Name	Content, %	Name	Content, %
Cr ₂ O ₃	25,47	Cu	0,008
Fe ₂ O ₃	9,1	Pb	0,05
SiO ₂	21,53	As	0,025
AI_2O_3	1,51	Sb	0,23
H ₂ O(bound)	7,8	K	0,05
CaO	0,75	Na	0,05
MgO	29,4	P	0,008
MnO ₂	0,053	C	< 0,2
S_{com}	0,1	Ag g/t	< 2,0
$S_{ m sulf.}$	< 0,1	Au g/t	< 0,05
Zn	0,1	Ni	0,28
Со	0,02		

Table 1 – Chemical composition of thechromiteoreslurrytailings

Table 2 – Phase composition of the slime tailings

Name	Formula	%
Antigorite	$Mg_3Si_2O_5(OH)_4$	41,8
Aluminum-ferruginousmagnesite	MgFeAlO ₄	29,7
MagnesiumChromite	MgCr ₂ O ₄	12,5
Clinochlore	$Mg_6Si_4O_{10}(OH)_8$	5,1
CalciumIronOxide	CaFe ₂ O ₄	4,8
Aluminous Iron Oxide Of Calcium	$Ca_{2}Fe_{1.28}Al_{0.72}O_{5}$	3,9
Brownmillerite	Fe _{1.33} A _{1.67} Ca ₂ O ₅	1,7
AluminumCalciumSilicate	Ca ₄₆ (Al ₉₂ Si ₁₀₀ O ₃₈₄)	0,3
AluminumMagnesiumCalciumSilicate	$Ca_{23.20}Mg_{22.4}(Al_{92}Si_{100}O_{384})$	0,3

Mineralogical analysis of the samples was carried out using the microscope MIN-8 at 320x magnification, and using the OLYMPUS microscope at 200x, 400x magnification in transmitted light in an immersion medium and in polished sections in reflected light under an inverted Leica microscope. The photomicrographs of the samples in reflected light were made at 300x magnification using an inverted Leica microscope, in transmitted light with the help of the OLYMPUS microscope at 200x, 400x magnification using the StreamBasicR software (figure 1).



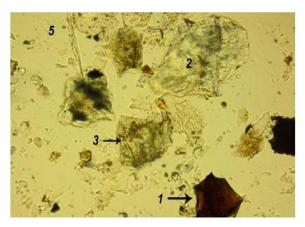


Figure 1 – Mineralogical composition of the slime tailings: 1 – shungit; 2 – spinel minerals chlorite group; 3 – aluminum-magnesium spinel; 4 – antigorite; 5 – immersion environment

The spinel of minerals of the chlorite group is represented by chamosite (Fe, Mg, Al) (Si, Al) 4O10 (OH) 8 - yellowish-green lamellar grains with pleochroism (pleochroism from green to light yellow).

Aluminum-magnesian spinel - Fe, Mg, Al, Cr - grains from brown to reddish brown, isotropic, fractured shell.

Antigorite Mg3Si2O5 (OH) 4 - anisotropic colorless grains with a fibrous structure. Optically biaxial negative 2V (-), with refractive index $N \sim 1,550$.

The thermal analysis of the tailings was carried out using a synchronous thermal analysis instrument STA 449 F3 Jupiter. Before heating, the oven space was pumped out and then purged with an inert gas. Heating of the samples was carried out at a rate of 10°C/min, in an environment of highly purified argon. The volume of incoming gas varied depending on the chemical analysis of the sample and was maintained in the range of 80-90 ml/min. Cooling was carried out to 300°Cat a speed of 15°C/min. The processing of the results obtained with the STA 449 F3 Jupiter was performed using the NETZSCHProteus software (figure 2).

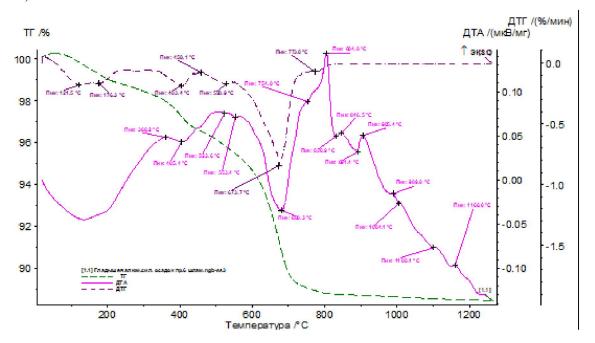


Figure 2 – Thermogram of slurrytailings

The most intense effect on the IITA curve is endothermic, with maximum development at 680 °C accompanied by a decrease in weight of the sample. In combination with exothermic peaks at 805 °C and 1160 °C this effect may reflect the manifestation of serpentine. At680°C, the structure of the mineral breaks down with the simultaneous removal of the OH group, and the formation of new mineral phases, crystalline forsterite, and X-ray amorphous enstatite. The exothermic peak at 805°C reflects the ordering of the forsterite structure, and the peak at 1160°C shows the crystallization of X-ray amorphous enstatite. At a minimum of 403°C on the curve of DTG reflects the manifestation of dehydration of iron hydroxide, magnesium, and chromium oxyhydroxide. A weak maximum on the same curve at 458°C may show the oxidation of ferrous iron in magnetite or chromite by residual oxygen. The combination of an endothermic effect with an extremum at 680°C, an endothermic effect with an extremum at 831°C, and an exothermic effect at 847°C can be interpreted as a manifestation of some magnesian chlorite - pennin, cammererite, clinochlore. The combination of an exothermic effect with a peak at 360°C, endothermic effects with extremums at 680°C and 745°C, and an exothermic effect with a peak at 905°Capparently reflects the presence of a margariteCaO₂Al₂O₃2SiO₂H₂Oin the sample of the mineral. At 360°C, oxidation of the ferrous iron impurity takes place, at 680°C and at 745°C the removal of hydroxyl water and lattice failure occurs, at 90°C crystallization of the decomposition products proceeds. It is known [5] that heating of chlorite to temperatures exceeding the temperature of the exothermic effect leads to the formation of spinels. In [4] it is reported that after dehydration of several hydroxides, a solid solution of spinels is formed. The process is displayed on the thermogram with an exothermic effect. Based on these data, it can be assumed that exothermic effects, in addition to the processes described above, also show the formation of solid solutions of chromospinelides from thedehydration products of the phase constituents of the sample.

The results and its discussion. A technology for processing slurry tailings has been developed to produce chromite concentrate, which includes preliminary activation in sodium hydrogen carbonate solution, leaching in a solution of ammonium hydrogen sulfate and gravitational enrichment with the use of a centrifugal separator.

The preliminary activation is necessary to increase the degree of enrichment of chromite-containing tailings during leaching by the removal of the accompanying elements - magnesium, silicon, iron.

The possibility of activation of slurry tailings by treatment with sodium hydrogen carbonate solution of 120 g/dm^3 concentration at temperatures of $100\text{-}240^{\circ}\text{C}$, T:F = 1.0:10.0 and a duration of 90 minutes were studied.

Chemical analysis of the activated tailings showed (table 3) that, as a result of the activation, the quantitative composition of the samples changes insignificantly, except for a decrease in the calcium content. At the same time, as follows from the data of X-ray phase analysis, the phase composition of the samples changes (Table 4), the phases containing calcium oxide are disappearing; the quantitative ratios of the magnesium-containing phases are also changing.

Name	Cr_2O_3	MgO	SiO ₂	Fe ₂ O ₃	AI_2O_3	CaO
Initial tailings	25,47	29,4	21,53	10,4	2,97	1,95
Tailings after activation at 100°C	25,4	29,49	21,73	10,28	2,96	0,864
Tailings after activation at 120°C	25,52	29,53	21,69	10,56	2,99	0,812
Tailings after activation at 150°C	25,42	29,5	21,4	10,5	2,91	0,8
Tailings after activation at 200°C	25,48	29,39	21,35	10,46	2,8	0,794
Tailings after activation at 240°C	25,5	29,38	21,38	10,5	2,75	0,641

Table 3 – Chemical composition of the slurry tailings after the activation

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Table 4 -	Phase comb	osinon o	i ine ia	mmes am	er activation

		Composition, %								
Name	Antigorite-8M Mg _{3-x} (Si ₂ O ₅) (OH) _{4-2x}	Clinochrysotile - Mg ₃ Si ₂ O ₅ (OH) ₄	Lizardite - 1M (Mg,Fe) ₃ Si ₂ O ₅ (OH) ₄	Aluminum-ferruginous magnesite - MgA1. ₆ Fe _{1.4} O ₄	Chromite- (Fe _{0.52} Mg _{0.48}) Cr _{0.76} AI _{0.24}) ₂ O ₄	Clinochlore - Mg ₆ Si ₄ O ₁₀ (OH) ₈	Aluminum magnesium silicate - Ca _{23.20} Mg _{22.4} (AI ₉₂ Si ₁₀₀ O ₃₈₄₎	Quartz SiO ₂		
Initial tailings	41,8	5,1	12,5	8,7	15,3	5,6	11,0	_		
Tailings after activation at 100°C	21,8	20,9	20,4	7,6	15,8	5,6	0,8	1,2		
Tailings after activation at 120°C	21,8	21,6	20,6	15,3	15,7	5,2	0,8	1,4		
Tailings after activation at 150°C	22,0	21,3	20,6	15,9	15,4	4,2	0,6	1,0		
Tailings after activation at 200°C	22,4	21,4	19,7	15,7	15,8	5,0	-	_		
Tailings after activation at 240°C	23,7	21,0	21,5	18,2	15,6	5,2	_			

The analysis of the given data for the preliminary activation of tailings shows that practically all main changes in the phase composition are terminating at the temperature of 120°C.

After activation, the slurry tailings were processed by leaching at a temperature of 95-100°C in the regenerated solution of ammonium hydrogen sulfateNH₄HSO₄.

The carried out study in the process of leaching of slurry tailings, a solution of ammonium hydrogensulfate with a concentration of 30.0% was used. Leaching was carried out at a temperature of 95°C for 60 minutes.

For comparison,in addition to the ammonium hydrogen sulfate solution, a solution of $5\% H_2SO_4$ and a solution consisting of $30\% NH_4HSO_4+1\% H_2O_2$ were used for leaching.

The obtained results of leaching are shown in table 5.

The best results were obtained using a leaching solution consisting of 30% NH₄HSO₄, in this case, the content of chromium in the cake (rough chromite concentrate) was 38.4% Cr₂O₃at cake output of 65.5% of the weight of the initial slurry tailings.

Name	С	Cr ₂ O ₃		Fe ₂ O ₃		MgO		SiO ₂		₂ O ₃	Cake	
Name	%	ε, % *	%	ε, %	%	ε, %	%	ε, %	%	ε, %	output, %	
Initial tailings	25,47	100	10,5	100	30,0	100	22,7	100	2,74	100		
Cake form leaching with 5% H ₂ SO ₄	32,1	95,4	9,94	69,9	18,8	46,3	30,7	100	3,04	82,1	75,0	
Cake form leaching with 30% NH ₄ HSO ₄	38,4	96,8	9,25	39,9	7,08	10,7	34,0	70,0	4,56	75,0	65,5	
Cake form leaching with 30% NH ₄ HSO ₄ + 1 % H ₂ O ₂	36,9	95,5	7,47	33,5	8,07	12,06	40,8	84,6	3,2	55,7	67,1	
ε, % * – extraction of the component in the cake (rough concentrate).												

Table 5 – Cake (rough concentrate) from the leaching of slurry tailings

For the regeneration of a solution of ammonium hydrogen sulfate, a method [6] of thermal decomposition of ammonium sulfate into hydrosulfate and ammonia according to reaction (1) is known:

$$(NH_4)_2SO_4 = NH_4HSO_4 + NH_3$$
. (1)

1947,68

291,7

2239,38

Extraction,% Cr₂O₃

86,8

13,2

100.0

Cakes from leaching were dispatched to enrichment using gravity separator KNELSON.

As a result of the centrifugal separation of cakes, chromite concentrates with the following content, mass% were obtained:

- from the cake after leaching in $(30\% \text{ NH}_4\text{HSO}_4 + 1\% \text{ H}_2\text{O}_2)$ solution 53,4 Cr_2O_3 ; 9,8 MgO; 19,1 SiO₂; 13,1 Fe₂O₃; 4,1 AI₂O₃; 0,14 CaO. The output of the concentrate accounted 32.4% of the weight of the initialtailings. The extraction of Cr_2O_3 into the concentrate accounted for 76.2%;
- from the cake after leaching in 5% H₂SO₄solution– 42,6 Cr₂O₃; 18,7 MgO; 23,0 SiO₂; 11,0 Fe₂O₃; 3,67 AI₂O₃; 0,2 CaO. The output of the concentrate accounted 36.9% of the weight of the initialtailings. The extraction of Cr₂O₃ into the concentrate accounted for 72.7%;
- from the cake after leaching in 30% NH_4HSO_4 solution 59,2 Cr_2O_3 ; 9,1 MgO; 12,4 SiO_2 ; 13,05 Fe_2O_3 ; 4,63 AI_2O_3 ; 0,21 CaO. The output of the concentrate accounted 32.9% of the weight of the initialtailings. The extraction of Cr_2O_3 into the concentrate accounted for86.8%. The material balance of cake enrichment under these conditions is given in table 6.

in a 30% NH ₄ HSO ₄ solutionusing KNELSON centrifugal separator								
Product name	Out	put	Content, %	Production				
r roduct name	g g		Cr ₂ O ₃	Cr ₂ O ₃				

32,9

67,1

100.0

49,35

100,65

150

Concentrate KNELSON

Tailings KNELSON

Total

Table 6 – Material balance of cakeen richment after leaching in a 30% NH₄HSO₄ solution in KNELSON centrifugal separator

X-ray phase analysis of cake enrichment products after leaching in 30% NH₄HSO₄ solutionis presented in tables 7, 8.

59,2

4,35

Table 7 – X-ray phase analysis of tailingsenrichment of cake after leaching in a 30% NH₄HSO₄ solution

Name	Formula	%
Kaolinite	$Al_2Si_2O_5(OH)_4$	44,9
Clinochlore	(Mg,Fe,Al) ₆ (Si,Cr) ₄ O ₁₀ (OH) ₈	44,5
Chromite	$(Fe_{0.52}Mg_{0.48})(Cr_{0.76}Al_{0.24})_2O_4$	10,6

Table 8 – X-ray phase analysis of chromite concentrate

Name	Formula	%
Chromite	$(Fe_{0.52}Mg_{0.48})(Cr_{0.76}Al_{0.24})_2O_4$	100

The data of X-ray phase and chemical analysis shows that leaching of slurry tailings with a 30% NH₄HSO₄ solution of ammonium hydrogensulfate, the rock-forming minerals commonlyconvert into solution, and chromite and chromite-containing minerals, coalitol and amorphous silica remain in the cake-the rough concentrate. The amorphous silica resists the X-ray phase analysis.

When enriching the rough concentrate using the centrifugal separator KNELSON, a chromite concentrate consisting of a chromite mineral - $(Fe_{0.52}Mg_{0.48})(Cr_{0.76}Al_{0.24})_2O_4$ was obtained.

Thus, in the process of slurry tailings enrichment, using the technology including the operations on the preliminary activation of the chromite-containing tailings in a solution of sodium hydrogen carbonate; leaching in a solution of ammonium hydrogen sulfate, and gravitational enrichment using centrifugal separator, a chromite concentrate with a 59.2% content of Cr_2O_3 was obtained with the extraction of Cr_2O_3 into a concentrate of 86.8%.

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БАЙЫТУ ҮРДІСІНІҢ ШЛАМ ҚАЛДЫҚТАРЫНАН ХРОМ КОНЦЕНТРАТЫН АЛУ ТЕХНОЛОГИЯСЫН ЖАСАУ

Аннотация. Техногенді калдықтарды – Қазақстан Республикасының Дондық тау-кен байыту комбинатының (Дондық ТКБК) хромитті кенін байытқандағы шлам қалдықтарын қайта өңдеудің зерттеу нәтижелері келтірілген.

Орталықтан тепкіш бөлгіші және химиялық байыту арқылы хром концентратын алудың технологиясы жасалынды. Бұл технология құрамында хром бар қалдықтарды гидрокарбонат натрий ерітіндісінде алдын ала белсендіруді, аммонийдің бисульфат ерітіндісінде шаймалау және орталық тепкіш бөлгішінде гравитациялық байытуды қамтиды. Алдын ала белсендіру үрдісін жүргізу — шаймалау кезінде қосымша элементтердің (магнии, кремний, темір) жойылу есебінен, құрамында хром бар қалдықтарды байыту дәрежесін жоғарлату үшін керек. Алдын ала белсендіру нәтижесінде үлгілердің құрамы сәл өзгереді. Сонымен қатар,

үлгілердің фазалық құрамы өзгереді, құрамында магний бар фазалардың қатынасы, құрамында кальций оксиді бар фазалар жойылады.

Жүргізілген зерттеу жұмыстарында шлам қалдықтарын шаймалау үшін реагентті таңдағанда – 30% NH₄HSO₄ ерітіндісін қолданғанда өте жақсы нәтижелер алынды. Рентгенфазалы және химиялық талдаулар нәтижесінен шлам қалдықтарын шаймалағанда жыныстартүзегіш минералдар негізінен ерітіндіге өтеді, ал кекте – алғашқы концентратта хромит және хромитті минералдар, коалин, аморфты кремний диоксиді қалатынын көруге болады.

KNELSON ортадан тепкіш бөлгішінде алғашқы концентратты байытқанда хромит минералынан тұратын - $(Fe_{0.52}Mg_{0.48})(Cr_{0.76}Al_{0.24})_2O_4$ құрамындағы $Cr_2O_3 - 59.2\%$ - хромитті концентрат алынды. Cr_2O_3 концентрақа алынуы 86,8%.

Хром қалдықтарын өңдеу технологиясын жасау экологиялық мәселелерді шешіп қана қоймай, сонымен қатар хром концентратының шығысын арттырады.

Түйін сөздер: шлам қалдықтары, белсендіру, аммоний бисульфаты, орталық тепкіш бөлгіші, хром концентраты.

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РАЗРАБОТКА ТЕХНОЛОГИИ ПОЛУЧЕНИЯ ХРОМИТОВОГО КОНЦЕНТРАТА ИЗ ШЛАМОВЫХ ХВОСТОВ ОБОГАЩЕНИЯ

Аннотация. В статье приведены результаты исследований переработки техногенных отходов - шламовых хвостов обогащения хромитовой руды Донского горно-обогатительного комбината Республики Казахстан.

Разработана технология получения хромитового концентрата методом химического обогащения и центробежной сепарации. Технология включает операции предварительной активации хромитсодержащих шламов в растворе гидрокарбоната натрия, выщелачивание в растворе гидросульфата аммония и гравитационное обогащение на центробежном сепараторе. Проведение операции предварительной активации необходимо для повышения степени обогащения хромитсодержащих шламов при выщелачивании за счет удаления сопутствующих элементов — магния, кремния, железа. В результате активации количественный состав проб изменяется незначительно. В то же время меняется фазовый состав проб, исчезают фазы, содержащие оксид кальция, соотношения магнийсодержащих фаз.

В проведенных исследованиях при выборе реагента для выщелачивания шламовых хвостов наилучшие результаты получены при использовании раствора с 30% NH₄HSO₄. Из данных рентгенофазового и химического анализов следует, что при выщелачивании шламовых хвостов, породообразующие минералы в основном переходят в раствор, а в кеке - черновом концентрате остаются хромит и хромитсодержащие минералы, коалинит и аморфный кремнезем.

При обогащении чернового концентрата на центробежном сепараторе KNELSON получен хромитовый концентрат, состоящий из минерала хромита - $(Fe_{0.52}Mg_{0.48})(Cr_{0.76}Al_{0.24})_2O_4$ с содержанием Cr_2O_3 59,2% при извлечении Cr_2O_3 в концентрат 86,8%

Разработка технологии переработки хромитовых шламов позволит не только решать экологическую проблему, но и увеличить выпуск хромитового концентрата.

Ключевые слова: шламовые хвосты, активация, гидросульфат аммония, центробежный сепаратор, хромитовый концентрат.