

RESULTS OF STUDIES ON EXTRACTION OF NICKEL SALTS FROM REFRACTORY NICKEL-CHROMIUM STEEL AND SPENT CATALYSTS

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Abstract. *The article is devoted to the study of optimal technological parameters of extraction of nickel salts from stainless steel and industrially used catalysts by anodic melting and hydrometallurgy method, recycling of extracted nickel oxide.*

Keywords: *nickel, used, catalyst, steel, acid, refractory, nitrate, sulfate, carbonate.*

Limited reserves of non-ferrous metals, increasing pollution of the environment resulting from their processing, corrosion and structural damage of metals indicate that non-ferrous metallurgical products are not expected to be widely used in the future.

Only the processing of secondary raw materials of non-ferrous metals on an industrial scale can cover the human need for non-ferrous metals and reduce environmental pollution.

The development of metallurgy and chemical industry led to a sharp increase in the need for non-ferrous metals, including nickel. For example, by the end of the 20th century, nickel production reached 1 million tons per year.

The largest reserves of copper-nickel sulfides are in Norilsk, Monchegorsk (Russia), Sudbury and Thompson mining fields (Canada), Kambal (Australia), more than 2.3 million tons of nickel are mined worldwide. [1]

Major nickel metal producing countries include Indonesia, the Philippines, Russia, New Caledonia, and Australia.

Currently, the increased production of nickel-containing steel alloys, nickel-plated machine and mechanism parts, alkaline batteries, nickel catalysts, and various salts of nickel has led to a significant increase in the demand for nickel.

It is known that in Uzbekistan there are no ores containing nickel, i.e., there are no nickel reserves, but there are nickel wastes: nickel alloys, copper-nickel alloys, scraps from their mechanical processing, expired nickel alloy pipes, accumulators, catalysts, etc., from which nickel can be extracted. retrieval and reuse is one of the pressing issues.

The increase in the deficit of nickel led to the increase in the price of this metal on the world commodity-raw exchanges. At the beginning of 2024, the price of 1 t of tin on the London exchange was 17392 US dollars.

The demand for nickel and its price in the world market require cost-effective recycling of nickel-containing waste.

These studies are devoted to the extraction and recycling of nickel wastes of the chemical industry of Uzbekistan.

The furnace for primary reforming of natural gas, one of the main processes of the chemical industry, consists of more than 500 tubes made of iron-nickel alloy, the total weight of which is 176.4 tons, which is about 32-35% nickel. Such stoves are being used in "Navoiazot" JSC, "Fergonazot" JSC, "Maksam-Chirchik" JSC, and will be replaced with new ones after the expiration date.

Catalysts used in steam reforming of natural gas: GIAP – 19, Reformax – 210, Reformax – 330, R – 67, GIAP – 8 and methanation catalysts: NKM, TO – 2 it contains nickel from 6-8% to 34-35%.

Used catalysts containing nickel belong to the IV class of danger according to the Hygienic Classification of Uzbekistan, are stored on the territory of production enterprises and are used to extract nickel. [2]

It is known that the use of nickel-containing metals, scrap metal and other industrial wastes, including spent catalysts, as secondary raw materials satisfies the demand for nickel to a certain extent.

Processing of refractory steel alloys containing nickel and chromium to nickel nitrate and nickel carbonate.

Composition of pipes of the reforming furnace, % mass: C – 0,4÷0,45; Mn – 0÷1,5; Si – 1,2÷2; P – 0÷0,03; S – 0÷0,03; Ni – 32÷35; Cr – 23÷27; Mo – 0÷0,50; Fe – 32,23 ÷ 43,4.

Iron is partially or completely oxidized to Fe (III) when a refractory nickel-chromium steel alloy is dissolved in sulfuric acid to the basic nickel carbonate and iron-chromium residue and precipitates in the form of hydroxides at different pH environments. In the presence of basic Fe (III) hydrate and (or) Fe (II) in the solution, as a result of the formation of nickel hydroferrites (secondary hydrates of nickel and iron), nickel precipitates with iron in the form of nickel (II) hydrate. This causes the nickel to leave the system and be lost. In nickel hydrometallurgy, this situation is eliminated under two conditions [3-7]:

- 1) When the melting process of the alloy is carried out in an inert atmosphere;
- 2) When nickel (II) ion is masked in a solution containing Fe (II) and Fe (III).

Anodic melting of Fe-Ni-Cr alloy in sodium chloride solution.

When an iron-nickel-chromium alloy is dissolved in a sodium chloride solution by electrolytic method, metals turn into soluble chlorides and form hydrates in an alkaline environment.

Studies of this process were studied in artificial alloys of Fe – Cr – Ni, and the polarization curves of the current density from 50 to 700 A/m² taken when changed.

Current density 50 A/m² potential jump was observed in the interval from 100 to 700 A/m² the potential changed uniformly when changing to . An increase in the temperature of the electrolyte led to a decrease in the anode polarization.

When iron-nickel-chromium alloy is electrolytically dissolved in sodium chloride solution, it was observed that nickel, iron and chromium hydrates precipitate in the form of hydrates.

In the electrolyzer, an increase in the pH of the solution was observed, and in the continuous process, the concentration of the curd did not change, and it was pH = 11.5.

Current density of the electrolysis process 200 – 1000 A/m² studied for 3-6 hours when changing to

Estimated power consumption varied from 2.27 W-h/g (current density 400 A/m²) to 3.16 W-h/g (current density 800 A/m²) depending on the current density.

Dissolving nickel, chromium and iron oxide hydrates in an ammoniacal solution of ammonium salts.

The reaction of metal hydrates with an ammonia solution of ammonium chloride proceeds according to the following general scheme:



At high concentrations of ammonia and ammonium salts, the hydrolysis of iron (II) salts is 90-93% [3]. In order to prevent the formation of nickel hydroferrites during the transfer of nickel from iron and chromium hydrates to the solution, the smelting process was carried out in the presence of ammonium salts in a neutral atmosphere. The results are presented in Table 1, and it was observed that the rate of nickel transfer to the solution was higher than 90% even when using ammonium carbonate or ammonium sulfate.

Table 1.

Changes in the composition of the alloy in the transition of nickel to solution in ammonia melting

Alloy content, % (rest Cr)		Dissolving in ammonium carbonate		Dissolving in ammonium sulfate	
Ni	Fe	Ni concentration in the solution, g/l	Dissolve,% Ni	Ni concentration in the solution, g/l	Transfer to solution, % Ni
92	1	11,0	96	10	96,9
23	61	2,0	97	3,1	98,0
18	75	1,10	95	0,7	97,0
6	88	2,8	90	0,5	93,0

According to the results of the dependence of the transfer of metal hydrates to solution in the presence of ammonium chloride on the concentration of NH₄Cl (Table 2.), 99% of nickel passes into solution when the concentration of NH₄Cl is 40 g/l. When the concentration of ammonium chloride in the solution is high (104 g/l), hexamine chloride is formed, causing a part of the nickel to pass into the iron precipitate, reducing the transfer of nickel to the solution.

Table 2.

Variation of nickel transfer into solution with NH₄Cl concentration

NH ₄ Cl concentration, g/l	Ni	
	concentration	Transfer to solution, %
16	5	97,5
32	3,69	99,0
40	3,96	99,0
48	4,13	86,0
56	4,65	90,0
104	2,2	79,6

When the concentration of ammonium chloride in the solution is reduced (16 g/l), the transfer of nickel to the solution is 97.5%.

The optimal concentration of ammonium chloride in the solution of nickel is 30-40 g/l, and 99% of nickel is transferred to the solution of ammonium chloride with this concentration.

The transition of nickel into the solution is 98.5 – 99% without significant change when the melting time is changed from 30 to 180 minutes.

Solutions formed during the transfer of nickel from the Fe-Ni-Cr alloy to a solution in the presence of ammonium salts are used to obtain nickel products.

As a result of the research, the technology of extracting nickel salts from Fe-Ni-Cr alloy was developed. The main stages of technology are as follows:

Degreasing and washing of metal waste;

Dissolving the metal in the anode in an inert atmosphere: formation and precipitation of hydrates of Fe, Ni, Cr (precipitation);

Cleaning the precipitate from chlorides by washing it in an inert atmosphere;

Treatment of the precipitate cleaned of chlorides with an ammonia solution of ammonium carbonate in an inert atmosphere. Preparation of the solution: 150 - 200 l of a solution containing 2 - 15% NH₃, 4 - 12% (NH₄)₂CO₃ is added to 250 - 300 liters of wet sediment volume of 100 kg;

Fe₂O₃ in the ammonia solution of ammonium carbonate is oxidized to Fe(OH)₃ in oxygen or air flow: Fe and Cr are precipitated, and nickel remains in the ammonia solution of ammonium carbonate;

6. The solution is filtered from iron and chromium deposits;

7. An ammonia solution of ammonium carbonate is boiled and ammonia is expelled, nickel (II) salts are hydrolyzed and precipitated. The precipitate is nickel hydroxycarbonate, which is formed by the decomposition of an ammoniacal solution of nickel;

8. The resulting precipitate containing Ni₂CO₃(OH)₂ · H₂O is separated by decantation and filtration methods;

9. If the precipitate remaining in the filter is dried at 40°C, variable hydroxycarbonate of nickel is formed, containing up to 35% nickel. Alternatively, nickel nitrate is produced by recycling the precipitate with 15-20% nitric acid to pH = 2.2, evaporating the solution, crystallization, and drying at 100-150 °C. Contains 35% Ni.

Experience - industrial tests were conducted in workshop 62 of "Maksam - Chirchik" JSC. Refractory steel pipes of 20 x 23 H 18 grade - l = 1400 mm, CD 115 mm, were processed into 5 types of nickel products by separating the nickel (II) compound from ammonia and ammonium carbonate and Fe (III) - Cr (III) from the anodized melt (Table 3.)

20 x 23 H 18 Grade Refractory Steel Processing Products

Product and item	Ni (II)hydroxycarbonate		Ni (II)nitrate			Ni chloride
	№ 1: PAB* dry residue formed by evaporation of	№ 2 PAB hydrolysis product, dried, %	№ 3 – np. № 2 HNO ₃ melted and evaporated, %	№ 4 – np. № 2 850 °C calcined, dissolved in HNO ₃ and	№ 5 – PAB KY – 28, HNO ₃ obtained from evaporation	№ 6: mixture of nickel chloride and nickel oxide, %
Actual, % wt	GOST 4466-78					

		(carbonate), %			evaporated, %		
Previous form	$\text{Ni}_2\text{CO}_3(\text{OH})_2 \cdot \text{H}_2\text{O}$			$\text{Ni}(\text{NO}_3)_2$	NiO_x	$\text{Ni}(\text{NO}_3)_2$	$\text{NiO} - \text{NiCl}_2$
The last form	$\text{Ni}_2\text{CO}_3(\text{OH})_2 \cdot \text{H}_2\text{O}$			$\text{Ni}(\text{NO}_3)_2$	$\text{Ni}(\text{NO}_3)_2$	$\text{Ni}(\text{NO}_3)_2$	
Ni	38	42	35 – 38	22,5	34	35	35 – 40
Fe	0,01-0,05	0,002	0,05	0,01-0,05	0,01-0,05	0,02	0,02
Co	0,005	0,100	0,005	0,005	0,005	-	-
Cu	0,01-0,05	0,01	0,03	0,01-0,05	0,01-0,05	0,01	0,01
Cr	0,01-1,50	-	0,08	0,01-1,50	0,01-1,50	0,01	0,01
Zn	0,1	0,01	0,1	0,1	0,1	-	-
Na	2,0-2,5	0,3	0,7	0,8	1,0	-	-
Ca+Mg	0,1	-	0,1	0,1	0,1	0,05	-

*PAB – nickel-containing solution from ammonia washing; nickel content - 0.5 g/l.

Experiment - as a result of industrial tests, it was confirmed that the components of refractory steel (Ni, Fe, Cr) can be anodically transferred to the precipitate, nickel from the deoxygenated precipitate is transferred to a solution in the presence of ammonium salts, and then it is possible to separate 90% of nickel from Fe (III) in the presence of oxygen.

Nickel hydroxycarbonate and nickel nitrate salts were extracted from the ammonium solution containing 0.5 g/l nickel. The properties of isolated nickel nitrate and nickel hydroxycarbonate were studied.

As a result of laboratory and experimental - industrial tests, a technological regulation was developed and recommended for implementation on an industrial scale.

Recycling of spent nickel-containing catalysts.

The brands, manufacturers, composition of catalysts used in the chemical industry, in which process they are used and methods of preparation are summarized in Table 4.

Table 4.

Content, %	NiO	Al ₂ O ₃	Cr ₂ O ₃	Fe ₂ O ₃	MgO	A process where a catalyst is used	Catalyst preparation method	Normative document, spectral analysis,...
Mark								
GIAP – 8	6 – 10	90-94	-	-	-	conversion with steam and air	soak	Ts 00203068-15-2014

GIAP – 16	23–26	44–52	Ca 6 - 13	Ba 0,6-1,2	13-17	conversion with par and SO ₂	mixed	[22]
NKM – 1	35,5	39,1	8,45	0,11	-	metan	mixed	spectral
TO – 2	34,7	44,4	7,77	0,10	-	metan	mixed	spectral
Reforma x–330	14,3	67,7	0,014	0,52	0,435	primary reforming	mixed	spectral
Reforma x–210	12,3	66,4	0,05	0,80	0,38	primary reforming	mixed	spectral
R – 67	>15	-	-	-	-	primary reforming	mixed	document firm Xoldor - Tonsoe
Content, %	NiO	SiO ₂	K ₂ O	Fe ₂ O ₃	MgO			
Katalco 57-4Q	16	0,15	-	-	-	primary reforming	mixed	Document firm Xoldor - Tonsoe
25 – 4Q	18	0,15	1,8	-	-	primary reforming	
GIAP–K	-	-	-	-	-	primary reforming	mixed	TY 113-03-2006-92
GIAP–3 – 6H	-	-	-	-	-	conversion with steam and air	soak	TY 113-03-313-85

One of the main methods of extracting nickel compounds is the hydrometallurgical method, which uses acids or ammonium-ammonia solutions.

When extracting nickel from spent catalysts with acids, nickel is in the form of acid salts. Nitric [8 – 10], sulfuric [11 – 15], and chloride [16 – 20] acids are used in the extraction of nickel. The selection of inorganic acids is based on their relatively cheap prices and availability of production capacity. In addition, the high solubility of inorganic salts of nickel in water ensures a high nickel content in the solution, for example, Ni(NO₃)₂ – 30.2, NiSO₄ – 29.7 g/l.

One of the disadvantages of dissolving in acids is that the metals included in the used catalysts: Al, Cr, Fe, Mg, etc., go into solution together with nickel.

Extraction of the pure salt of nickel from such solutions presents additional technological problems.

Ni(NH₃)_n and mono- and hexa-complexes are formed when nickel is dissolved using ammonia instead of acid solution [21]. When metals other than nickel are present in the solution, pure salt of nickel can be isolated from such complexes. But this situation also leads to the use of additional technological processes. That is, the resulting complex is separated from the solution by dissolving it in acid and then evaporating or precipitating it from the solution.

Disadvantages of using an ammonia solution of ammonium salts to extract nickel from spent catalysts include the release of ammonia into the gas phase during the process and the lack of a simpler solution for extracting nickel from ammonia solutions.

Based on the analysis of the literature, the following can be stated: the number of types of used nickel catalysts, the differences in their production technologies, and their specific characteristics, such as the fact that they are not of the same size, show that there will not be the same technological solution for all of them.

The technology to be created must take into account acid types, concentrations, process duration, temperature, and catalyst sizes.

Another drawback here is that if the catalysts are ground, the surface area increases and the nickel ion is adsorbed from the solution onto the catalyst carrier. As a result, the nature of the dependence of the degree of nickel dissolution into the solution on the technological parameters changes. If the catalysts are used without grinding, it leads to a decrease in the consumption of the cocktail and an intensification of the filtration process.

Extraction and recycling of nickel from spent GIAP-8 catalyst.

GIAP-8 catalyst is used in the chemical industry to obtain synthesis gas by converting natural gas with steam. 28 t are loaded on the mine-shaped converter in one-stage conversion sections, and 50 t in two-stage conversion sections (AM – 76).

Alumina in the production of catalyst ($\gamma - Al_2O_3$) it is mixed with nitric acid and special shavings and brought to the shape of a cylinder, dried and 1400 – 1450 °C at $\alpha - Al_2O_3$ is transferred to corundum, and $Ni(NO_3)_2 + Al(NO_3)_3$ solutions are added to it and heat treated again.

The service life of the catalyst is from 6 months to 7 years. Nickel salt was extracted from the spent GIAP-8 catalyst obtained from the methane conversion workshop of "Maksam-Chirchik" JSC in experiments related to the amount of sulfur compounds coming with natural gas, catalyst activity, strength.

The level of nickel transformation into solution was studied in the hydrometallurgical method at concentrations of nitric acid from 10% to 70% for 4-8 hours.

Researches were carried out at 60-70 °C, with the ratio of catalyst to acid being 1:1.5.

The results are presented in Table 5.

Table 5.

Variation of nickel dissolution rate from used GIAP-8 catalyst with technological parameters

Used GIAP - 8 weight, g	HNO ₃ concentration, %	Acid volume, ml	Melting time, hours	Amount of NiO dissolved in solution, g	Extraction rate of Ni, %	Acidity residual, g/dm ³
100,0	20	800	4	38	53,50	25,20
100,0	10	800	4	20,6	29,06	26,50
100,0	20	800	8	37,65	53,02	27,10
100,0	20	800	8	38,73	54,50	32,80

200	20	200	4	10,5	76,1	-
200	70	200	6	11,1	78,3	57,5
220	20	300	4	12,5	80,1	-
Second boiling in acid or water						
100	20	130	4	1,9	92,07	-
100	70	200	6	1,1	78,3	57,5
100	0 (cyB)	0 (130)	4 (without boiling)	1,35	88,8	-
100	0 (cyB)	0 (130)	4 (without boiling)	1,1	85,5	-

The results presented in Table 5 showed that 86-90% nickel was converted to solution by boiling the solution in 20% nitric acid for 4 hours and washing the residue with boiling water.

After boiling the spent, unground GIAP-8 catalyst in nitric acid solution for 4 hours, the residue was separated and boiled in water for 1 hour. Then it was cooled, the amount of $\text{Ni}(\text{NO}_3)_2$ was determined by titrimetric method by combining the first and second solutions.

The mass concentration of nickel in the solution was 200-550 g/l, and that of sulfate salts was 400-500 mg/l, calculated in relation to SO_4 . The amount of nitric acid that did not react in the solution was 20-30 g/l.

The resulting nickel nitrate salt solution was evaporated to a concentration of 387 g/l, leaving HNO_3 residue at 53.5 g/l and SO_4^{--} at 550 mg/l.

In order to clean the solution from SO_4 , it was neutralized to pH - 7 - 7.5 with sodium carbonate solution of 140 - 165 g/l, and NiCO_3 precipitate was obtained. The neutralization process was carried out at a temperature of 65-70°C. The precipitate was stirred in the solution for 2 hours, filtered, dried at 100 – 125 °C and calcined at 300 – 350 °C to form a black powder (NiO).

This powder was dissolved in nitric acid, $\text{Ni}(\text{NO}_3)_2$, and the resulting solution was diluted to 500 g/l and used to prepare the catalyst.

The composition of the obtained $\text{Ni}(\text{NO}_3)_2$ solution was analyzed according to GOST 4055-78. According to the results presented in Table 6, the $\text{Ni}(\text{NO}_3)_2$ solution meets the standard requirements for the amount of SO_4 — and Cl — and can be used for catalyst preparation.

Table 6.

Description of nickel nitrate solution isolated from spent GIAP-8 catalyst

Indicator name	Requirement according to GOST 4055 – 78 (brand – 4), not more than %	Actual data on experience, %
1. Mass fraction of water-insoluble substances	0,005	0,005
2. Mass fraction of sulfates (SO_4)	0,01	0,01
3. Mass fraction of chlorides (Cl)	0,003	0,003
4. Mass fraction of iron (Fe)	0,001	0,11
5. Cobalt mass fraction (Co)	0,02	0,003
6. Mass fraction of copper (Cu)	0,005	0,003
7. Cadmium mass fraction (Cd)	Without norm	

8. Mass fraction of lead (Pb)	Without norm	
9. Mass fraction of zinc (Zn)	0,002	0,010
10. Mass fraction of potassium, sodium, calcium and magnesium (total).	0,08	0,38

The spent GIAP-8 catalyst was dissolved in nitric acid, and the separated and purified Ni(NO₃)₂ solution was soaked with a mixture of Al(NO₃)₃ solution on a ready-made alumina carrier. Dimensions of the carrier: d= 15 – 16 mm; N = 14 – 16 mm; strength 20.3 MPa; bulk weight 1.23 kg/dm³.

TU Uz. Meets the requirements of 6.3 – 67 – 99.

Table 7 shows the results of the obtained catalyst activity in the process.

Table 7.

Catalyst activity characterized by volume fraction of residual methane in the gas leaving the converter

T, °C	Used GIAP-8 catalyst		Catalyst obtained from Ni(NO ₃) ₂ according to GOST 4055 – 78	TU Uz. Requirements for 6.3 – 67 – 99
	№ 2	№ 3	№ 4	
1	2	3	4	5
500	62,9	21	27,1	Not more than 35.0
	78,1	23,4	26,9	
	78,1	22,5	27,6	
	78,1	23,2	27,1	
	71,6	23,4	27,9	
800	29,8	4,3	0,4	Not more than 1.0
	26,6	4,2	0,4	
	40,4	6,9	0,5	
	36,7	6,9		
	28,0	7,0		

Thus, it is possible to convert 90-92% of nickel from the used GIAP-8 catalyst with a 20% solution of nitric acid for 4 hours at 65-70 °C; on the basis of this solution, it was shown that it is possible to produce a new GIAP-8 catalyst that meets the standard requirements.

Extraction of nickel from catalysts of GIAP-16, R-67, Reformax-330 brands used in the primary reforming of natural gas.

The table below shows the composition of industrially used GIAP-16 and R-67 catalysts.

Table 8.

Content of used catalizators *

№	Components, % mass	GIAP – 16	R – 67
1.	NiO	21,6 – 26	15,7 – 16,69
2.	Al ₂ O ₃	65,0 – 68,8	61,65
3.	CaO	0,15 – 0,21	-

4.	MgO	0,09 – 1,08	21,6
Additives, %			
5.	Fe	0,2	0,13
6.	Cu	0,24	0,16
7.	Zn	0,75	0,4
8.	Na	2,5	2,75
9.	K	5,0	50
10.	Cr	0,05	-

* Analyzes were performed in the central laboratory of Maksam-Chirchik JSC.

Extraction of nickel from used catalysts was carried out by the hydrometallurgical method using 5-40% solutions of nitric acid at 100-105 °C for 4-6 hours.

The 2-3 mm fractions of the used catalysts were separated by filtration and dried at 100-110 °C without washing. The contents of filtrate and insoluble residue were determined by complexometric titration method.

The insoluble residue was retreated with 5% nitric acid to remove undissolved nickel.

The results are summarized in Table 9.

Table 9.

Results of extraction of nickel from used GIAP-16 and R-67 catalysts by hydrometallurgical method $t = 100 - 110$ °C.

Indicators	GIAP – 16				R – 67				Note
	№ 1	№ 2	№ 3	№ 4	№5	№ 6	№ 7	№ 8	
HNO ₃ , % mass	30	40	40	30	30	40	30	40	The amount of NiO in 25 g GIAP-16 is 5.4 g.
Catalyst mass, gr	25	25	25	25	25	25	25	25	
Mass of undissolved residue, gr	12,96	13,83	13,2	12,6	20	22,9	20,0	20,2	
Melting time, hours	6	6	4	4	6	6	4	4	The amount of NiO in 25 grams of R-67 is 3.93 grams.
NiO in the filtrate, gr	4,32	4,1	3,55	2,80	2,86	2,2	2,65	2,67	
NiO in the residue, gr	0,71	0,82	0,79	0,90	0,96	0,88	0,80	1,31	
Separation rate, %	80,0	75,9	65,7	51,8	72,8	56,0	67,4	68,0	

The results presented in the table show that it is possible to dissolve 75.9-80% NiO with 30-40% nitric acid at 100-110° C for 6 hours using GIAP-16 catalyst.

In this case, 13.15-15.18% of NiO remains in the residue.

In order to extract NiO from the undissolved residue, when it is processed in a 5% nitric acid solution at a temperature of 100-110° C for 2 hours, the total extraction rate is 100%.

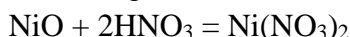
From this it can be concluded that the undissolved catalyst NiO in the small pores completely passes into the dilute acid. One of the reasons for this is that the viscosity of the diluted acid is small, so the diffusion process is complete.

The concentration of nitric acid is 10; 15; The degree of transition of NiO into solution during processing with 30% solutions was studied with the amount of acid. When the amount of 30% acid compared to the catalyst changed from 1.5 to 2.5, the degree of release of NiO into the solution increased from 70.8 to 99.2%.

When R-67 catalysts were treated with 30 and 40% nitric acid, the degree of NiO extraction was observed to change from 56.0% to 72.8%.

Table 10 shows the results of changing nickel oxide in the form of nickel nitrate solution with the amount of nitric acid.

According to the reaction of NiO with nitric acid



The average stoichiometric amount of nitric acid with a density of 1.31 g/cm³ for 10 g of catalyst and the amount used in the experiments are as follows

Table 10.

Acid concentration, mass %	GIAP– 16, cm ³		R – 67, cm ³	
	steheomet.	in experience	steheomet.	in experience
5	-		4,15	70
10	30,53	70	20,76	70
15	20,38	70	13,82	80
30	10,17	15	6,95	25

Table 11 shows the results of the change in the degree of extraction of nickel oxide from the catalyst depending on the concentration of nitric acid, the amount used for the experiment and the amount of water used for washing the residue.

Table 11.

Change in the degree of extraction of nickel oxide from the used catalyst.

Indicators	GIAP – 16				R – 67				
	№ 1	№ 2	№ 3	№ 4	№5	№ 6	№ 7	№ 8	№ 9
HNO ₃ , % mass	10	15	30	30	30	15	10	15	5
Amount of catalyst, gr	10	10	10	10	8,8	10	10	10	10
Acid consumption, cm ³	70	70	15	25	40	80	70	70	70
Volume of filtrate and washing water, cm ³	81	82	87	105	120	119	82	80	95
NiO in the filtrate, gr	2,07	2,09	1,84	2,58	2,24	2,59	1,34	1,42	1,09

Resolution level,%	79,6	80,3	70,8	99,2	97,8	99,6	80,2	85,0	65,3
Time consumption, hours	4	4	6	6	6	6	4	4	4

As can be seen from the given results, the extraction rate of nickel from the used GIAP-16 and R-67 catalysts can be up to 99.2-99.6%, depending on the concentration of nitric acid, consumption, and the amount of water used for washing.

In the process of extracting nickel from the used GIAP-16 and R-67 catalysts, Al₂O₃, CaO, MgO in their composition were also studied. When processing 25 g of the catalyst, it was seen that 0.02-0.04% of GIAP-16 and 0.007% of R-67 Al₂O₃ passed into the solution, and the rest remained in the residue.

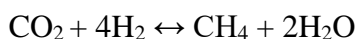
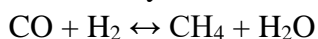
It was observed that magnesium oxide did not go into solution in the studied technological parameters, and calcium oxide went into solution at 0.61-1.12% of GIAP-16, and the rest remained in the residue.

Thus, as a result of research, the following conclusions were reached:

1. Nickel can be extracted from used GIAP-16 and R-67 catalysts by hydrometallurgy with nitric acid.
2. Optimal conditions of the extraction process: concentration of nitric acid - 15-30% by mass; temperature 100 – 105 ° C; time - 6 hours.
3. 97.8% nickel from GIAP-16 and 85% nickel from R-67 can be extracted once in the above optimal conditions.
4. The NiO in GIAP-16 can be completely extracted by recycling the residue with 5% nitric acid.

Extraction of nickel from TO-2 brand catalyst used in methanation of carbon oxides in synthesis gas.

TO - Catalyst 2 is used to convert oxygen compounds in synthesis gas into methane gas.



47,912 t are loaded into the methanator reactor in ammonia synthesis plants, the duration of operation depends on the amount of sulfur compounds in the synthesis gas.

Active aluminum oxide, nickel carbonate and chromium anhydride are used in the production of the catalyst.

The components are mixed, heated at 340 - 360 °C, ground to a powder state, mixed with 2% special graphite powder and made into tablets.

The results of spectral analyzes of the composition of the used TO-2 catalyst are presented in Table 12.

Table 12.

Composition of used TO-2 catalyst.

Components	Al ₂ O ₃	SiO ₂	SO ₃	Cr ₂ O ₃	NiO	CuO	ZnO
Spectrophotometer Rigaku NEX,	44,4	0,494	0,26	7,77	34,7	2,28	2,62

Analyzed by FP method by dilution of the catalyst, ppm	33700	1870	301	270	38400	-	783
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The analysis results show that the used catalyst contains 34.7-38.4% nickel oxide.

In the experiments, nickel nitrate and sulfuric acid salts were extracted from the used TO-2 catalyst samples taken from the methanators of "Maksam-Chirchik" JSC and "Fergonazot" JSC.

The rate of nickel dissolution with mineral acids was studied by the hydrometallurgical method.

Researches were carried out in concentrations of nitrogen and sulfuric acid from 5% to 20%, at temperatures from (20 – 25) °C to (80 – 90) °C, for 2 – 6 hours, catalyst particles (- 0.5 + 1) mm to (- 5 +6) was carried out when it was up to mm.

The amount of NiO in the solution and its optical density were determined in the FEK-56 photocalorimeter in cuvettes with a thickness of 5 cm when the wavelength of the green photofilter was 440 nm. [24-25]

The amount of acids was obtained 1.2 times more than the stoichiometric consumption.

The degree of transition of NiO into the solution (X) was also determined by spectral method in the content of the used catalyst and the amount of NiO in the residue.

$$X = \left[\frac{(GNiO)_{\text{бошл}} - (GNiO)_{\text{қолдик}}}{(GNiO)_{\text{бошл}}} \right] * 100 \%$$

Processing with nitric acid.

The results of the study are presented in tables 13 and 14.

Table 13.

The change in the degree of transition of nickel oxide to solution with the concentration of nitric acid.

$\tau = 2$ hour; $d_u = - 0,5+1$ mm.

C_{HNO_3} , %	Residual spectral analysis, %			NiO (Phacoe mulsification), gr	The level of separation, %	
	NiO	Al ₂ O ₃	Cr ₂ O ₃		spectrum analysis	Phacoemulsification
5	31,3	51,3	9,29	3,9	9,8	22,4
10	31,4	49,2	9,37	4,74	9,5	27,31
15	30,3	48,2	9,44	6,06	12,7	34,92
20	24,5	56,4	10,8	6,48	29,4	37,34

Table 14.

Change in the degree of transition of nickel oxide to the solution with the size of the catalyst particle.

$C_{HNO_3} = 20$ %; $\tau = 2$ hour; $T = 20 - 25$ °C.

d_u , mm	Residual spectral analysis, %			Resolution level, %
	NiO	Al ₂ O ₃	Cr ₂ O ₃	spectrum analysis
- 0,5+1	24,5	56,4	10,8	29,4

- 5+6	24,8	54,1	11	26,5
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From the results of the research presented in the tables, it is known that when the concentration of nitric acid changes from 5% to 20%, at room temperature, the rate of NiO transition into the solution for 2 hours is not more than 29.4 - 37.34%.

The change in the size of TO-2 catalyst particles does not significantly affect the rate of NiO transfer into the solution, i.e. 29.4% of NiO from (- 0.5+1) mm particles is transferred to the solution, and 26.5% of NiO from (- 5+6) mm particles. goes into solution.

When the separation of NiO from TO-2 used on an industrial scale is introduced, there is no need to grind it to small particles.

When the catalyst is crushed to small particles, the highly dispersed carbon in its content adversely affects the rate of diffusion of the acid into the oxides.

When the catalyst was processed at a temperature higher than room temperature, the release of brown nitrogen oxide from nitric acid in solution was observed. In order to put such a process into practice, it is required to develop the issue of returning nitrogen oxides to the process.

Table 15 shows changes in the amount of nickel, aluminum and chromium oxides in the used TO-2 catalyst.

Table 15.

Variation of residue composition with acid concentration when NiO is extracted from the catalyst.

$\tau = 2 \text{ hour}; d_u = - 0,5+1 \text{ mm}; T = 20 - 25 \text{ }^\circ\text{C}.$

Concentration HNO ₃ , %	Al	Cr	Ni	Al ₂ O ₃	Cr ₂ O ₃	NiO	NiO separation rate, %
5	26,7	6,25	24,3	51,3	9,29	31,3	11
10	24,6	6,03	23,4	49,2	9,37	31,4	14,5
15	28,6	7,38	28,3	48,2	9,44	30,3	-
20	28,9	7,54	20,3	56,4	10,8	24,5	26
Initial content	27,5	6,42	27	44,4	7,77	34,7	

As can be seen from the results, there is no significant change in the relative amount of aluminum and chromium oxides when the catalyst is treated with a 5-20% solution of nitric acid at room temperature, indicating that they pass into the solution in very small amounts under the experimental parameters. As a result, it is possible to extract nickel carbonate from the solution, which meets the standard requirements of aluminum and chromium oxides.

Thus, extraction of nickel oxide from the used TO-2 catalyst with a 5-20% solution of nitric acid at temperatures of 20-25 °C and 50-90 °C did not give satisfactory results. (Table 16)

Table 16.

Temperature variation of NiO extraction from TO-2 used catalyst.

$C_{\text{HNO}_3} = 20 \text{ } \%; d_u = - 5+6 \text{ mm}; \tau = 2 \text{ hour}.$

T, °C	Results of residual spectral analysis, %			Extraction rate of NiO, %	
	NiO	Al ₂ O ₃	Cr ₂ O ₃	specr	Phacoemulsification
50	22,1	63,9	9,73	36,3	49,39
60 – 70	21,9	63,0	12,4	36,9	57,63

80 – 90	18,4	69,4	9,70	46,97	66,4
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Comparing the results of the extraction of nickel oxide from GIAP-8, R-67, and GIAP-16 catalysts, it can be seen that the degree of extraction of nickel oxide depends somewhat on the composition and preparation method of the catalyst.

Results of treatment with sulfuric acid.

Researches were conducted in the concentration of sulfuric acid 5-20%, temperature 50-90 °C.

The rate of extraction of nickel oxide from the catalyst with 5-20% solutions of sulfuric acid at room temperature was 11.89%. (Table 17)

Table 17.

Variation of NiO release from TO – 2 used catalyst with H₂SO₄ concentration at room temperature.

τ = 2 hour; d_u = - 5+6 mm; T = 20 – 25 °C.

CH ₂ SO ₄ , %	5	10	15	20	
Separation rate, %	7,6	9,14	11,89	11,35	Phacoemulsification results

With the increase in temperature, the rate of transition of nickel oxide to the solution increases and it is 97% at 60-90 °C. (Table 18)

Table 18.

Temperature variation of NiO extraction from TO–2 used catalyst.

τ = 2 hour ; d_u = - 5+6 mm; C_{H₂SO₄} = 20 %.

Temperature, °C	20	50	60 - 70	80 – 90	
The level of separation, %	11,35	79,45	97,34	97,7	Phacoemulsification results

Thus, 97% of nickel oxide can be extracted from the used TO-2 catalyst with a 20% solution of sulfuric acid at a temperature above 60°C for 2 hours.

Obtaining nickel oxide from nickel nitrate and nickel sulfate solutions.

In order to clean the solutions from aluminum and chromium ions, nickel carbonate was precipitated with sodium carbonate. A 170-180 g/l solution of sodium carbonate was added to nickel nitrate and sulfate solutions at 70 °C with little mixing until the pH was 6.5-7. In this case, nickel carbonate salt formed in the precipitate and was separated on a filter, washed in distilled water and dried at 120-130 °C.

Aluminum and chromium residues in dried nickel carbonate were investigated using qualitative analysis. [23]

According to the results of the experiments, no turbidity was formed in the aqueous mixture of nickel carbonate, indicating Al and Cr residues.

By heating nickel carbonate at 300-350 °C, nickel oxide was obtained.

Spectral analysis of nickel oxide formed by heating washed and dried nickel carbonate at 300-350 °C was carried out. The results showed that the nickel carbonate and nickel oxide separated from the used TO-2 catalyst can be used as raw materials in the production of a new catalyst.

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