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UDC 669.243/25

HYDROMETALLURGICAL TECHNIQUE OF OXIDIZED NICKEL ORE TREATMENT IN THE URALS

SUMMARY: The hydrometallurgical technique for the oxidized nickel ore treatment in the Urals is developed. It is based on the sulfuric acid leaching of ore. It is found that adding 5-7 kg of CaF₂ per ton of ore results in enhancing the nickel recovery from the ore by 10-12 % at the leaching stage. The nickel recovery into the solution reaches 94.2-94.6 %. Further, it is reasonable to recover the nickel hydroxide concentrate after removing iron and aluminum from the solutions by the hydrolytic deposition at 3.5-4.5 pH followed by the filtration. The nickel concentrate containing 35-40 % of nickel can be recovered from the derived solutions at 7.0-7.5 pH with the magnesium oxide suspension. It is a high-quality raw material for pyrometallurgical industry. The throughout nickel recovery degree into the concentrate reaches 94.0 %. The problems of removing the magnesium impurities in the master solutions are solved by the magnesium hydroxide deposition at 10.5-11.0 pH with the limestone pulp. This enables the water recycling to be arranged in the technological cycle.

KEY WORDS. Leaching, sulfuric acid, calcium fluoride, deposition.

The purpose of the study. The pyrometallurgical technique is widely used to treat the oxidized nickel ores in the Urals. The smelting-down costs reach about half material expenses and, when the low-metal content ores are involved into the treatment, the cost effectiveness of the pyrometallurgical technique is decreasing [1-2].

It is known from [3] that in some cases, the attempts of the nickel and cobalt sulfuric acid leaching from the oxidized ores at the atmospheric pressure can give high results in the nickel recovery. Such attempts were made for the ores containing high contents of magnesia ($\geq 15\%$), the primary consumer for sulfuric acid [4-5]. Sometimes, the acceptable metal recovery (80%) was obtained; however, the process ran slowly and was accompanied by the increased consumption of sulfuric acid and the high iron yield [6-7].

The technique of the oxidized nickel ores treatment by leaching at the atmospheric pressure proves to be promising. This work describes the experiments on the sulfuric nickel recovery from the oxidized nickel ores at the ambient pressure with the further development of the technique for the nickel concentrate recovery as a hardly soluble compound.

The experiment. The sulfuric acid leaching experiments were carried out at the liquid-to-solid ratio (m³:t) equal to 2:1 for all the tests, in the thermostatically-

controlled reaction vessels equipped with the mechanical stirrers. On completing the experiment, the non-leached residue was separated from the liquid phase on the vacuum filter, then the nickel, iron, and sulfuric acid contents were determined in the filtrate obtained.

Based on the analysis results, the nickel recovery, the yield of major impurities, and the specific acid consumption for leaching were calculated.

Results and discussion. The samples from one of the Urals nickel deposits are tested. According to its mineralogical properties, this ore is referred to the semi-oxidized type specific to the middle part of the deposit profile, i.e. the most common ore type in the Urals. The mineralogical analysis confirms that the main nickel-containing mineral in the sample is nontronite, which accounts for up to 60-70% of the total nickel. The remaining nickel is associated with the isomorphic inclusions in the serpentinite structure.

The nickel content (1.05 %) enables the ore to be classified as the low-metal content one, unsuitable for the pyrometallurgical processing and pressure treatment [8]. However, the sulfuric vat leaching technique may be economically sound [9].

Initially, we studied the temperature effect on the leaching process under the leaching conditions during 4 hours and at the initial concentration of H_2SO_4 in the solution equal to 200 kg/m^3 . The results are presented in Table 1.

The data from Table 1 demonstrate that the leaching at low temperatures is extremely ineffective. In the meanwhile, the increase in temperature results in the process intensification. Thus, the rise in temperature from 60 to 80 °C results in the monotonic increase in the nickel recovery rate from 70.9 to 82.9 %. The specific acid consumption also increases from 317 to 345 kg/t. These data indicate that the optimum value of the process temperature is likely to be at the level of 80 °C.

Table 1

The results of the ore leaching depending on the process temperature

Parameter	Unit	Test No.			
		1	2	3	4
Pulp temperature	°C	20	60	70	80
Specific acid consumption	kg/t	137.2	316.7	336.3	345.0
Residual acid concentration in the solution	kg/m ³	125.6	41.7	31.9	27.4
Ni concentration in the solution	kg/m ³	1.37	3.9	4.29	4.56
Fe concentration in the solution	kg/m ³	3.63	12.29	14.80	4.80
Ni recovery into the solution	%	24.91	70.91	78.0	82.91
Fe yield into the solution	kg/t	7.26	24.58	29.60	29.60

The next step was to study the effect of the leaching time on the process parameters under the optimum temperature conditions (80 °C). The time effect was studied at the

H₂SO₄ concentration of 200 kg/m³. The results are presented in Table 2. The table demonstrates that the optimum leaching is 3-4 hours. The further increase in time is pointless, as it does not affect the increase in the nickel recovery.

Table 2

The results of the ore leaching depending on the time

Parameter	Unit	Test No.			
		9	10	4	11
Leaching time	hours	2	3	4	8
Specific acid consumption	kg/t	302.00	331.40	345.0	352.0
Residual acid concentration in the solution	kg/m ³	49.00	34.30	27.4	24.0
Ni concentration in the solution	kg/m ³	3.30	4.36	4.56	5.15
Fe concentration in the solution	kg/m ³	10.44	11.2	14.8	15.1
Ni recovery into the solution	%	58.93	77.84	82.91	83.93
Fe yield into the solution	kg/t	20.88	22.4	29.6	30.2

The usage of calcium fluoride as an activating additive for the nickel silicate mineral leaching was studied. The leaching experiment results with calcium fluoride added are presented in Table 3.

The table demonstrates that the usage of the fluoride additives increases the nickel recovery by 6-12 %, however, it is accompanied by the increase in the ore acid consumption from 345 to 373-385 kg/t. The optimum additive consumption is about 5-7 kg/t. The further increase in the consumption is pointless, as it results in the excessive reagent consumption.

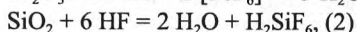
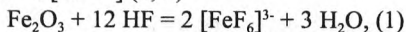
Table 3

The results of studying the effect the CaF₂ additives have on the ore leaching parameters

Parameter	Unit	Test No.				
		4	12	13	14	15
CaF ₂ additive	kg/t	0	1	5	7	10
Specific acid consumption	kg/t	345.0	352	360	373.5	385
Residual acid concentration in the solution	kg/m ³	27.4	20.8	16.5	13.23	10.5
Ni recovery into the solution	%	82.91	88.1	94.2	94.64	94.5
Fe yield into the solution	kg/t	29.60	32.51	45.85	47.2	48.1

The positive effect of the fluoride additives confirms the hypothesis on the chemistry of the fluorides – silicates interaction mentioned above. It follows from the

data presented in Table 3 that adding the fluorides to the reaction mass results in the sharp rise in the iron yield into the solution. If calcium fluorides are added, the reactions with the ionic complexes $[\text{FeF}_6]^{3-}$ and soluble fluosilicates are likely to occur, as follows [10-11] (1, 2):



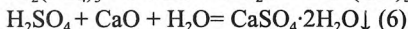
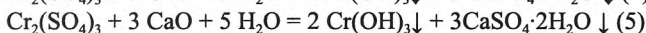
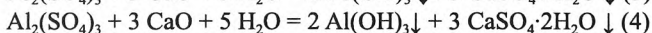
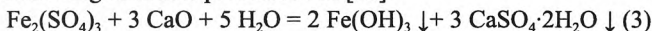
which facilitates the exposure of nickel mineral grains for their contact with sulfuric acid. It is obvious that, under the nickel isomorphism conditions, the increase in its recovery into the solution correlates to the increase in the ferrous mineral dissolution rate (Table 3).

The optimum leaching conditions are the following: the temperature is 70 °C, the acid concentration is 200 kg/m³, and the time is 6 hours.

Then the processing of such solutions for the recovery of the nickel concentrate as the final product was investigated.

The occurrence of the significant iron content in the solution indicates the need for deironing, followed by producing a nickel concentrate by the chemical deposition. It is known from the technology of the solution neutralization and deironing that this operation is carried out best by the finely ground limestone pulp [12-14]. In this basis, the solution obtained after leaching was treated by 20% limestone pulp to determine the optimum pH value for deironing.

At this stage, iron is deposited together with some other interfering cations, and the following chemical processes run [15]:

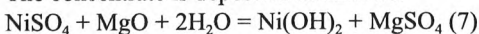


The pH neutralization value was varied in the range from 3.0 to 5.5. The solution temperature was 80 °C. The results on determining the optimum neutralization pH value are presented in Fig. 1 as the dependence of the element deposition rate on the medium pH.

It follows from Fig.1 that the optimum area is the pH range from 3.5 to 4.5. In this pH area, the nickel losses with the hydrated iron gypsum residuum do not exceed 4-5 %. It is pointless to increase pH above 4.5, as it results in the sharp rise in the nickel losses due to the nickel hydrate deposition, up to 10 % and more. The decrease in pH below 3.0 is also undesirable, as in this case, the aluminum and iron separation is incomplete, which results in the final concentrate quality loss.

At the next stage of the ore processing, the final nickel concentrate is separated from the deironing filtrate. For economic reasons, calcinated magnesia (MgO) suspension was chosen as a precipitator.

The concentrate is deposited as follows:



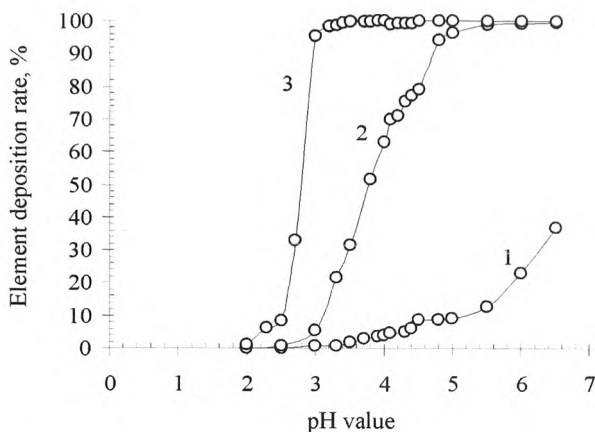


Fig.1 The dependence of the element deposition rate on the neutralization pH value: nickel (1), aluminum (2), iron (3).

It is stated that the deposition at the pH values ranging from 7.0 to 7.5 provides the nickel recovery from the deironing filtrate into the concentrate at the level of 99.1-99.7 %

The obtained nickel hydrate pulps are well condensed and filtered. The final concentrate contains about 35-40 % of nickel per dried substance, therefore, it is a high-quality raw material for the pyrometallurgical processing.

After separating nickel, it is reasonable to use the master solutions containing mainly magnesium sulfate for the magnesium hydrate deposition by the limestone pulp for magnesium to be removed from the bypass solutions. It is proved by the experiment that, according to the reagent specific consumption, it is reasonable to carry out this procedure at the pH value of 10.5-11.0.

In this case, the magnesium deposition occurs according to the reaction

$$\text{MgSO}_4 + \text{CaO} + 2\text{H}_2\text{O} = \text{Mg}(\text{OH})_2 + \text{CaSO}_4(8)$$

The master solution containing no harmful toxicants except for calcium and magnesium (at the level of 0.3-0.4 and 0.2-0.5 kg/m³, respectively), can be used as the industrial washery water. The obtained residuum being a rather pure mixture of gypsum and magnesium hydrate can be used as a raw material in the production of construction materials or it can be stored in the dumping site with the deironing residuum.

This procedure was practiced in large laboratory scale using the real processing media obtained by the nickel ore leaching according to the described technique. The experimental amount of the concentrate was produced.

It is stated that implementing this procedure provides the total nickel recovery from ores at the level of about 94.0 %.

Conclusion. The technique for the treatment of the oxidized nickel ores with the sulfuric acid leaching followed by the removal of impurities from the solutions and the deposition of the final nickel concentrate is considered.

The kinetic regularities of leaching the nickel from the oxidized iron ores are studied. It is determined that the temperature, leaching time, and intensifying additive (calcium fluoride) consumption have a significant influence on the recovery values. It is demonstrated that the usage of fluorides as additives for the leaching solution can increase the maximum nickel recovery from 80-83 to 94.6%, i.e. by more than 10%. The final nickel concentrate containing up to 40% of nickel is produced. The total nickel recovery from the ore into the concentrate can reach 94%.

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