Research of Possibility of Processing of Oxidized Nickel Ore by Chloride Sublimation Roasting Technology

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Abstract. Oxidized nickel ores (ONO) contain most of the world’s nickel reserves. However, choice of a cost-effective nickel ore processing technology is difficult due to the dispersed distribution of nickel compounds in refractory minerals, low nickel content, presence of a large amount of consuming host rocks, and impossibility of beneficiation by conventional physicochemical methods. The paper presents studies on the ONO processing technology by means of chloride sublimation roasting. Sodium and calcium chlorides were used as chlorinating agents both individually and in various ratios. It has been shown that roasting allows for nickel and cobalt conversion into chloride form followed by selective distillation of the resulting compounds into the gas phase by 89–90% at a roasting temperature of 1100 °C.

1. Introduction

Ural ONO deposits are characterized by a high content of magnesium and silicate components, as well as high content of iron oxides. Pyrometallurgical technologies traditionally being used at Ural plants – matte and ferronickel smelting – are currently unprofitable due to high cost of energy carriers, which led to a halt in production. At the same time, the reserves of oxidized nickel ores in the region are large, which makes it reasonable to search for new technologies that would significantly reduce the cost of ore processing. The most low-cost technologies are geotechnological heap and in-situ leaching, but the problem in this case is that oxidized nickel ores contain significant amounts of slimy particles and clay minerals, which complicate the process of solution percolation through the rock layer, a large solvent consumption, a long leaching time, low nickel recovery due to the impossibility of minerals digestion, etc. [1–12]. Therefore, the application of the technologies mentioned has not been industrially implemented in the region. The traditional hydrometallurgical technologies used for oxidized nickel ores processing abroad, such as autoclave sulfuric acid leaching and the Caron process [13–20] are not applicable for the Ural ores due to the high content of magnesium oxide in the ores and high cost of the processes.

A combined technology, including in the first stage, chloride sublimation roasting of the ore, and in the second, leaching of the obtained fumes might be one of the promising options for the processing of ONO. The essence of chloride sublimation roasting is the formation and distillation into gas phase of volatile chlorides of recoverable metals during the interaction of their initial compounds with a chlorinating agent. In this case, all compounds of the extracted metals are transformed into one class of chlorides having a high vapor pressure at temperatures of 900–1100 °C, which allows the process to be carried out without melting the entire mass of processed raw materials. As applied to the processing of oxidized nickel ores, the process is based on selective chlorination of nickel and cobalt compounds, host rocks remain in their original state,
and selective distillation of nickel and cobalt chlorides into gas phase. The parameters that determine the course of the process are properties of metal chlorides, composition of gas phase, temperature and duration of roasting. Recovery of metals from chlorides after their condensation is carried out by water leaching under standard conditions.

The temperature of the material during chloride sublimation roasting of oxidized nickel or cobalt ores should not exceed 900–1100 °C in order to exclude the formation of low melting eutectics. The source material must maintain the porosity necessary for the access of chlorine to nickel and cobalt compounds, which are included in the minerals of iron and silicates.

For relatively poor raw materials such as oxidized nickel ores, solid compounds CaCl₂ and NaCl can be used as a chlorinator. In this case, chlorination can occur additionally due to the formation of gaseous chlorine:

\[2\text{NaCl} + \text{SiO}_2 + 0.5\text{O}_2 = \text{Cl}_2 (\text{gas}) + \text{Na}_2\text{SiO}_3.\]  

The choice of such compounds stems from their availability and low price. The cost of an alternative reagent, hydrochloric acid, is significantly higher, which negatively affects the expenditures for the process and can be a decisive factor in the choice of processing technology.

2. Research methods

As the object of research, we selected oxidized nickel ore from the Serovskoye deposit, one of the largest in the Urals. The ore composition is shown in Table 1. The ore is typical of the Ural deposits – low nickel and cobalt content with a high content of silica and iron oxides.

| Material          | Ni  | Co  | MgO | SiO₂ | CaO | Al₂O₃ | FeO | Others |
|-------------------|-----|-----|-----|------|-----|-------|-----|--------|
| Oxidized nickel ore| 1.15| 0.08| 6.25| 32.57| 1.64| 7.13  | 43.56| 11.62  |

When conducting experiments on chloride sublimation roasting, the residual metal content in the cinder was chosen as the main criterion for the process. Preliminary preparation of raw materials (pelletizing, tableting, etc.) before chloride sublimation roasting was not carried out. Limestone was used as a fluxing agent that prevents sintering and melting of ore. The limestone consumption was established at the stage of preliminary studies, the optimal limestone consumption prevented melting at a calcination temperature of 1100 °C was 28% of the mass of the initial ore. A portion of the ore was thoroughly mixed with a chlorinating agent and limestone and loaded into a crucible with a thin layer.

The initial ore moisture was 12%; no additional wetting of the sample was carried out. Roasting was carried out in a tube furnace with the capture of sublimates. The crucibles were not sealed, oxygen was not supplied during roasting. The consumption of chlorinators (CaCl₂ and NaCl) was varied – 10–60% by weight of dry ore, roasting temperature – 900–1100 °C, roasting duration 10–90 min. We studied both the effect of each chlorinating agent separately, and their mixtures in various ratios on the distillation of nickel and cobalt chlorides into the gas phase.

3. Results and discussion

The experiments showed that the transition of nickel and cobalt chlorides to the gas phase begins 10–15 minutes yet after experiment starts, and completely stops after 50 minutes at a process temperature of 1100 °C. The cinder yield is 57.5–62.7% of the mass of the loaded charge and increases with increasing content of the mixture CaCl₂. The main cinder compounds according to phase analysis are calcium compounds 3CaO * SiO₂; 3CaO * Al₂O₃; 2CaO * Fe₂O₃; Ca₃Mg(SiO₄)₂; CaO, which are formed due to the introduction of limestone into the mixture.

The addition of calcium chloride allows for deeper extraction of both nickel and cobalt into gas phase at a lower consumption of chlorinator and the same roasting conditions - temperature 1100 °C, duration – 40 min. Tests results are presented on Figure 1, 2.
Figure 1. Dependence of the transition of metals into gas phase on the consumption of the chlorinating agent.

Figure 2. Dependence of the transition of metals into gas phase on the consumption of the chlorinating agent.

The most interesting results were obtained in experiments with a mixture of chlorinating agents NaCl and CaCl₂ at a roasting temperature of 1100 °C and a duration of 40 minutes (table 2, figure 3).

Table 2. Consumption of chlorinating agents when using NaCl and CaCl₂ together.

| Test | CaCl₂ % | NaCl % | Total additive % |
|------|---------|--------|------------------|
| 1    | 5       | 30     | 35               |
| 2    | 10      | 25     | 35               |
| 3    | 15      | 20     | 35               |
| 4    | 17.5    | 17.5   | 35               |
| 5    | 20      | 15     | 35               |
| 6    | 25      | 10     | 35               |
| 7    | 30      | 5      | 35               |
4. Conclusion
The addition of reagents in the ratio of 10% NaCl and 25% CaCl₂ by weight of dry ore allowed for about 90% nickel and 95% cobalt transfer into sublimates. The transition to sublimates of iron was about 7%. Despite the low extraction of iron into sublimates, which is a positive factor, since it allows one of the main problems of oxidized nickel ores processing to be solved - the selective separation of nickel and cobalt, iron chlorides make up the bulk of the sublimates. The average composition of sublimates in a series of experiments with a mixture of chlorinators, %: 37–40 NiCl₂; 2.7–3 CoCl₂; 57.7–58 FeCl₂. The percentage of cobalt was very low in the cinder, which suggests an almost complete transition of cobalt to the gas phase. Nevertheless, for a sufficiently complete transition of nickel and cobalt to the gas phase, a temperature of 1100 °C and a duration of at least 40 minutes are required.

References
[1] Kalashnikova M I, Tsymbulov L B, Naboychenko S S and Kolmachikhina O B 2019 Innovative processing applicable to the oxidized nickel ores found in the urals region J. Non-ferrous metals 8 4–12
[2] Khalezov B D, Gavrilov A S, Petrova S A and Mel'chakov S Yu 2019 Investigation of Solid Residues Obtained After Oxidized Nickel Ore Leaching J. Metallurgist 63 860–866
[3] McDonald R G and Whittington B I 2008 Atmospheric acid leaching of nickel laterites review. Part I. Sulphuric acid technologies J. Hydrometallurgy 91 pp 35–55
[4] McDonald R G and Whittington B I 2008 Atmospheric acid leaching of nickel laterites review. Part II. Sulphuric acid technologies J. Hydrometallurgy 91 56–69
[5] Watling H R, Elliot A D, Perrot F A and Shiers D W 2009 Impacts of mineralogy on the chemistry and microbiology of heap bioleaching Conf. 18th International Biohydrometallurgy Symposium (Bariloche) 71–73 369–372
[6] MacCarthy J, Nosrati A, Skinner W and Addai-Mensah J 2016 Atmospheric acid leaching mechanisms and kinetics and rheological studies of a low grade saprolitic nickel laterite ore J. Hydrometallurgy 160 26–37
[7] Elfimova L G Korol Yu A and Naboychenko S S 2016 Possibilities of hydrometallurgical processing of oxidized cobalt-nickel ores of Belinskoe deposit J. Non-ferrous metals 3 23–30
[8] Khalezov B D, Gavrilov A S, Petrova S A and Ovchinnikova L. A. 2019 Nickel extraction from solutions using sodium hydrosulfide J. Non-ferrous metals 3 33–38
[9] Oxley A, Smith M E and Caceres O 2016 Why heap leach nickel laterites? J. Minerals Engineering 88 53–60

Figure 3. Dependence of the transition of metals into gas phase on the consumption of the chlorinating agent.
[10] Zablotskaya Yu V, Sadykhov G B, Khasanov M Sh and Smirnova V B 2018 Kinetics of sulphuric acid leaching of nickel from reduced limonite ore of the buruktal deposit J. Non-ferrous metals 12 27–31

[11] Ayanda O S, Adekola A F, Baba A A, Fatoki O S and Ximba B J 2011 Comparative Study of the Kinetics of Dissolution of Laterite in some Acidic Media. J. Journal of Minerals & Materials Characterization & Engineering 10 1457–1472

[12] Sosnovskiy M G, Gulyaev S V and Zarkov A. V.2019 Possible processing of nickel-cobalt ores of the buruktal deposit at Southern Urals nickel plant J. Non-ferrous metals 3 21–27

[13] Loveday B K 2007 The use of oxygen in high pressure acid leaching of nickel laterites J. Minerals engineering 21 531–538

[14] Thompson G and Senanayake G 2018 Effect of iron(II) and manganese(II) on oxidation and coprecipitation of cobalt(II) in ammonia/ammonium carbonate solutions during aeration - An update and insight to cobalt losses in the Caron process for laterite ores J Hydrometallurgy 181 53–63

[15] Senaputra A and Nicol M J 2010 Effect of thiosulfate, sulfide, copper(II), cobalt(II)/(III) and iron oxides on the ammoniacal carbonate leaching of nickel and ferronickel in the Caron process J. Hydrometallurgy 105 60–68

[16] Saykova S V, Pantaleeva M V and Saykova D I 2019 Cation exchange processing of buruktal oxidized nickel ore autoclave solutions J. Non-ferrous metals 9 16–21

[17] Ilyas S., Srivastava R R, Kim H, Ilyas N and Sattar R 2020 Extraction of nickel and cobalt from a laterite ore using the carbothermic reduction roasting-ammoniacal leaching process J. Separation and Purification Technology 232 115971

[18] Mano E S, Caner L, Petit S, Chaves A P and Mexias A S 2019 Ni-smectite ore behaviour during the Caron process J. Hydrometallurgy 186 200–206

[19] Whittington B I and Muir D 2000 Pressure acid leaching of nickel laterites: a review J Mineral Processing and Extractive Metallurgy Review 21 527–599

[20] Chen J, Jak E and Hayes P C 2019 Investigation of the reduction roasting of saprolite ores in the Caron process: microstructure evolution and phase transformations J. Mineral Processing and Extractive Metallurgy: Transactions of the Institute of Mining and Metallurgy