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To cite this article: M V Boshnyak *et al* 2020 *IOP Conf. Ser.: Mater. Sci. Eng.* **969** 012053

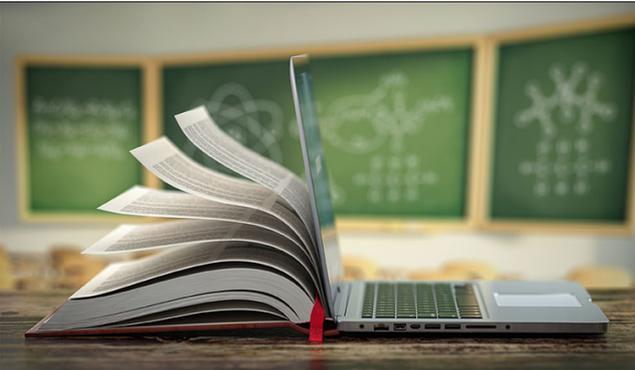
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# Oxidized Nickel Ore and Galvanic Sludge Combined Treatment Investigation

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**Abstract.** Galvanic sludges have been accumulated in large quantities in Ural region. These materials contain low concentration of non-ferrous metals (nickel, zinc, chromium) and iron, and are not being processed. Another difficult for treatment nickel containing materials are oxidized nickel ores, deposits of which are located in Ural. However, the nickel ores aren't processed due to low economic efficiency. In this article simultaneous treatment of oxidized nickel ore and galvanic sludge was investigated. The proposed technology includes nickel ore sulfatization at high temperature in presence of sulfuric acid and further water leaching. Therefore, maximum nickel extraction in solution at leaching of oxidized nickel ore after sulfatization was 82 %. Solutions after leaching are neutralized by nickel containing galvanic sludge. Due to partial nickel chromite dissolution in sulfuric acid a total nickel concentration has been substantially increased. Selective nickel extraction from such solutions is possible by sorption methods, and further metal nickel obtaining – by electrowinning.

## 1. Introduction

Significant quantity of technogenic wastes (electrodeposition sludges in particular) have been accumulated in Ural region. The reason is that machine-building industry enterprises overcoat metallic details by electrodeposited coating from aqua solutions or molten metals salts for increasing corrosive resistance and visual improvement. For example, nickel plating in sulfuric acid electrolytes, which contain various brightening additions, including chlorine and sulfated salts of cobalt and cadmium, is being used widely [1]. Covering by this technology leads to formation of toxic waste waters in large quantities with acids and heavy metals salts containment [2, 3].

Widely applied method of such wastes detoxification is neutralization by lime. This method is cheap and accessible because it doesn't require sophisticated equipment, expensive reagents and allows to achieve high neutralization and purification levels for one stage. Produced sludges contain metals hydroxides (nickel, zinc, iron, etc.) and being industrial wastes. Treatment of galvanic sludges is complicated due to complex composition and low concentration of non-ferrous metals (nickel content in different sludges is estimated at the level of 2–6 %) [4, 5]. At the present time these wastes are disposed on special waste landfill deposits. This compromised solution damages the environment and demands significant investments for construction and operation of toxic wastes landfill [6–12].

At the same time, Ural holds large oxidized nickel ore deposits, which were a raw material during long time for Ural plants (JSC Ufaleynickel, JFC Rezhnickel). Nickel in such ores presents as complex oxidized compound, nickel content in which is about 1 % [13, 14]. Pyrometallurgical methods of oxidized nickel ores treatment used by Ural plants were unprofitable. This is connected, primarily, with



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oxidized nickel ore beneficiation impossibility and melting necessity of poor material in large quantities. Using of such technologies have led to stoppage of all Ural nickel plants in period 2012–2018. Nevertheless, presence of ore materials, large quantity of nickel containing wastes and industrial facilities make finding of new technologies relevant objective from ecological and economical points of view [15–19].

## 2. Research methods

There is a strong need for a technology which allows to include oxidized nickel ores in treatment, along with nickel-containing galvanic sludges. Investigation of oxidized nickel ore and galvanic sludge simultaneous treatment were carried out on ore of the Buruktal deposit and galvanic sludges which were collected from abandoned sludge landfill.

The Buruktal deposit, placed in Orenburg area, is one of the biggest deposits of oxidized nickel ore in Russia. The Buruktal deposit consists of 7 sections and nickel total reserves are 1.5 million tons. At the present time, this deposit isn't developed due to shutdown of nickel metallurgical plants at Urals.

The main aim of this investigation was opportunities estimation for combined hydrometallurgical treatment of these materials. Chemical analysis of sludge and ore were carried out using atomic absorption spectrophotometer Vario 6 "Analytik Jena AG" (Table 1).

**Table 1.** Raw materials composition, %.

Material	Fe	Si	Ni	Cr	Ca	Mn	Cu
Galvanic sludge	2.46	16.49	2.7	6.76	5.79	0.15	2.39
Oxidized nickel ore	37.69	21.48	1.35	1.43	0.85	0.61	-

Effectiveness of a hydrometallurgical technology depends on chemical composition of raw materials. The oxidized nickel ore and the galvanic sludge contain iron, chromium, copper, silicon and other elements that makes their hydrometallurgical treatment difficult, in particular, due to high consumption of leaching reagents which are spent not to transfer valuable metals into solution but to neutralize the gangue and other components. Cost of leaching agents at oxidized nickel ores treatment is a significant economic factor. At the moment, sulfuric acid is the most available and cheap reagent for leaching in Russia. Furthermore, sulfuric acid is produced abundantly at Urals copper smelting plants as a minor and an inevitable product.

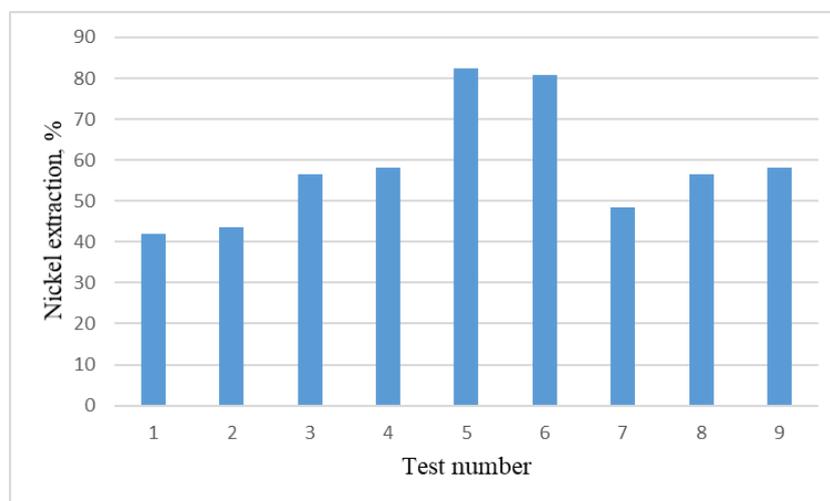
## 3. Results and discussion

On the first stage of the study, we carried out investigation of oxidized nickel ore acid consumption. Results have showed that specific sulfuric acid consumption leveled at 0.67–0.78 g of acid/g of ore, it is high order, especially with account of low nickel extraction in solution – maximum value was about 76 %. Such efficiency is characteristic of oxidized nickel ores from Ural deposits.

For the purpose of nickel extraction enhancing preliminary ore sulfatization were carried out by sintering with sulfuric acid in muffle furnace at 270–420 °C. Sulfuric acid consumption was varied in a range of 0.37–1.1 g/g of ore. Physical-chemical basis of this process is formation of water-soluble sulfates of non-ferrous metals and iron during ore heat treatment in presence of sulfuric acid. High temperature level of oxidized ores and acids mixture sulfatization is close to 700 °C. At the further temperature increasing nickel and cobalt sulfates decomposition occurs with oxide formation, wherefore extraction efficiency of these metals in solution is decreased at following leaching [20]. In our opinion, preliminary sulfatization allows to transfer valuable metals into solution in shorter period and at more mild conditions, without application of high temperature conditions and concentrated solutions.

After sintering obtained byproduct has been repulped by water with liquid and solid ratio on a level of 6:1 and has been leached by water for several hours at 50 °C. Obtained suspensions were filtered, cakes were washed. Filtrates and washing waters were analyzed on nickel concentration. At calculation of nickel extraction, we took into account total nickel extraction to filtrates and washing solutions. Such

accounting is necessary for possibility estimation of washing solutions including in a technological scheme for the ore treatment. Tests results are presented on Figure 1.



**Figure 1.** Nickel extraction in solution.

Therefore, maximum nickel extraction in solution at leaching of oxidized nickel ore after sulfatization was 82 %. Conditions of sulfatization were sulfuric acid consumption 0.73 g/g of ore, sintering temperature – 420 °C, sintering duration – 60 minutes. Nickel concentration in such solution was 5,5 g·l<sup>-1</sup>. Also, it has been noted that at sulfuric acid consumption increasing a nickel extraction on solution was dramatically decreased. Obtained solutions pH level was in a rage 3–4. For nickel precipitation from such solution, it is necessary to neutralize solutions. We recommend nickel galvanized sludges to be used as neutralizer due to it consist of calcite which reacts with sulfuric acid according to the equation (1):

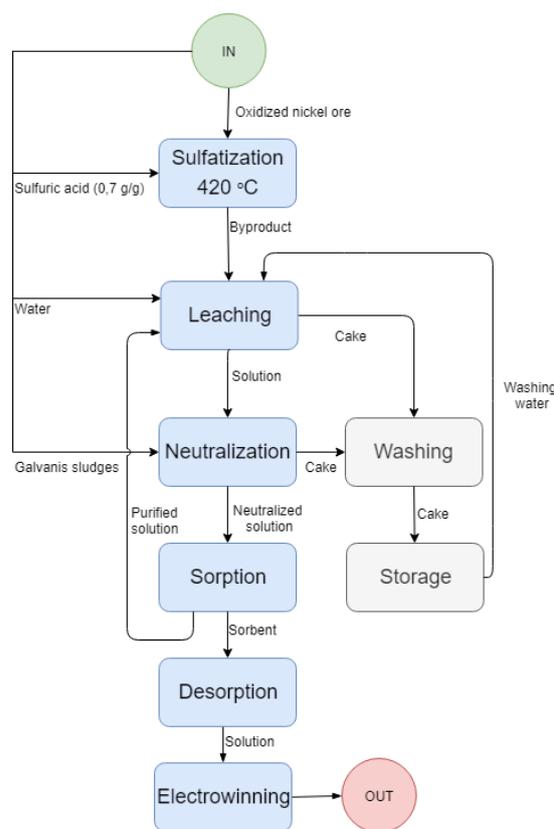


Value of solutions pH after neutralization must be in range of 6–7. At lower values a nickel hydroxide starts their precipitation from solution. Neutralization was carried out by small dosing of galvanic sludge in solution at continuous agitation and pH monitoring. Obtained data is presented in Table 2.

**Table 2.** Test results of solution neutralization.

Test	Initial solution			Galvanic sludge weighed portion (g)	Final solution		
	Volume (l <sup>-1</sup> )	pH	Nickel concentration (g·l <sup>-1</sup> )		Volume (l <sup>-1</sup> )	pH	Nickel concentration (g·l <sup>-1</sup> )
1	0.302	4.2	4.5	35	0.295	5.8	8.9
2	0.302	4.2	4.5	45	0.295	6.1	11.4
3	0.302	4.2	4.5	50	0.295	6.4	12.7
4	0.302	4.2	4.5	60	0.295	6.9	15.2

Galvanic sludge addition has allowed to neutralize initial solution. Therewith, due to partial nickel chromite dissolution in sulfuric acid total nickel concentration has been substantially increased from 5.5 g·l<sup>-1</sup> to 15.2 g·l<sup>-1</sup>. Such low nickel concentrations in solutions don't allow to process it by electrowinning. Selective nickel extraction from such solutions is possible by sorption methods, and further metal nickel obtaining – by electrowinning. It is way forward for this work. In accordance with the findings scheme of oxidized nickel ore and galvanic sludge hydrometallurgical treatment has been proposed (Figure 2).



**Figure 2.** Proposed scheme of oxidized nickel ore and galvanic sludge combined treatment.

Industrial implementation of this technology will lead to release of galvanic sludges landfill deposits, liquidation of emissions which are formed at conventional pyrometallurgical processing of nickel oxidized ores, extracted nickel quality improvement, organization of non-waste processing.

#### 4. Conclusion

The part of proposed technology of simultaneous treatment of oxidized nickel ore and galvanic sludge was tested in this work. Preliminary sulfatization allowed to increase nickel extraction at leaching up to 82 %. Neutralization of solutions after leaching led to increasing of nickel concentration up to 9–15 g·l<sup>-1</sup>. These solutions could be processed by sorption using nickel selective ion exchange resins and further nickel electrowinning.

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