INORGANIC SYNTHESIS
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Behavior of Sulfides of Nonferrous Metals
in Hydrochloric-Acid Leaching of Residues Formed
in Synthesis of Carbonyl Nickel

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Abstract—Specific features of hydrochloric-acid leaching of residues formed in synthesis of carbonyl nickel
without removal and with forced removal of the gas phase were studied.

In producing metallic nickel by carbonylation of
a nickel-containing raw material, residues substantially
enriched with cobalt and platinum metals1 are formed.
However, the content of platinum group metals in
these residues is approximately 10 times lower than
that in anodic slimes, and, therefore, their joint pro-
cessing to produce conditioned concentrates of plati-
num metals (PM) seems to be impossible. At present,
residues of carbonyl nickel synthesis (RCS) are re-
cycled, which leads to loss of non-ferrous and plati-
num metals and to the enrichment of the nickel raw
material with copper. Removal of the carbonylation
residues from the pyrometallurgical process to be sub-
jected to a hydrometallurgical processing is a possible
way to raise the recovery of both nonferrous and
noble metals.

It is known [1, 2] that the specificity of synthesis
of nickel tetracarbonyl is primarily associated with
the reactivity of the material subjected to carbonyla-
tion, which is, in turn, proportional to its surface area
accessible to the reaction with carbon oxide. The spe-
cific surface area of the material is most frequently
raised through formation of sulfides at grain bound-
daries in metal phases, which leads to a spongy struc-
ture of the material. After the carbonylation is com-
plete, with the main part of nickel and iron evaporated
as the carbonyls Ni(CO)4 and Fe(CO)5, the impurities,
namely copper, cobalt, noble metals, and sulfur, are
concentrated in a solid residue.

1 Severonikel’ combine of Kola Mining and Smelting Co.

It is known that processing of RCS can be carried
out by either a pyro- or a hydrometallurgical meth-
od, depending on their phase composition. The hy-
drometallurgical method for processing of RCS of
the above-mentioned composition involves two-stage
sulfatization, autoclave sulfuric-acid leaching, and
ammonia-carbonate leaching [1, 3–7]. The low ex-
traction of cobalt and platinum group metals is
a disadvantage of the ammonia method [8], and leach-
ing with sulfuric acid involves autoclave processes,
which requires that expensive and power-consum-
ing equipment should be used. Therefore, we tested
several schemes of hydrochloride processing of these
products [9–12]. These schemes use hydrochloric-
acid solutions of iron(III) and gaseous chlorine and
make it possible to process the material at atmo-
spheric pressure, remove sulfur in the elementary
form, and concentrate platinum metals in the final
product.

As the acidity of the leaching solution strongly
affects the phase transformations in the material un-
der study, the initial stage of development of a hydro-
chloride technology for RCS processing consisted in
a study of the behavior of separate phase components
of the residues in their leaching with hydrochloric
acid. The starting RCS samples, selected as the ob-
jects of study were decarbonylated by keeping them
in a vacuum at the boiling point of nickel carbonyl
(−43°C). They had the following composition (wt %):
Ni 5.1–9.1, Co 12.0–18.0, Cu 29.0–43.2, Fe 3.8–7.9,
S 18.9–21.4, and ΣPM 0.15–0.22.
The redox potentials of solutions in use were measured with a V7-34A voltmeter. Silver chloride and platinum electrodes served as a reference and an indicator electrode, respectively.

Two modes of leaching were used. In the first of these, reaction products were not removed from the reaction space before the process was complete, and in the second, they were forced from the gas-vapor phase (GVP). The effect of leaching parameters on the extraction of RCS components into solution was studied by analyzing samples of solid and liquid phases of the sludge. The concentrations of nickel, cobalt, iron, and copper in solutions and precipitates after their decomposition were determined by the atomic-absorption method, and that of platinum metals in solid products was found by X-ray fluorescence analysis. A comparison of the data for various samples of the starting material did not reveal any significant difference between them.

To study the main RCS phases and to determine their composition, we carried out mineralogical and X-ray phase analyses of the starting samples and products of their leaching. For the mineralogical analysis, we used preparations based on an epoxy resin, which were studied in reflected light under an Opton Ularphot-3 microscope with a resolution of 0.2 μm. The main phases were analyzed by the X-ray fluorescence method on a Cameca MS-46 microprobe analyzer.

The mineralogical and electron-microprobe analyses demonstrated that the structure of characteristic particles of RCS is represented by spongy spherical aggregates with walls formed by a pentlandite-like phase (PP-M₉S₈, where M is Co, Ni, Fe, or Cu) and chalcosine (Cu₅S) in a tight and even accretion in a 50 : 50 (%) proportion. The pentlandite-like phase, in turn, consists of three sulfide components: nickel-rich Ni₃.1₈Fe₃.3₆Cu₂.2₅Co₀.₂₁S₈ (~20%), copper Cu₇.1₃Fe₁.₀₇Ni₀.₄₈Co₀.₃₅S₈ (~40%), and cobalt components Co₄.₇₂Fe₂.₀₆Cu₁.₃₂Ni₀.₈₄S₈ (~40%). A chalcosine mass is situated between sponge walls. The X-ray phase analysis revealed the presence of the main sulfide phases: Cu₁.₉₆S, (Co, Ni, Fe)₉S₈, and Co₈FeS₈ (Fig. 1a).

The behavior of chalcosine and pentlandite in hydrochloric-acid leaching has been adequately described in the literature. For example, the dissolution of chalcosine in hydrochloric acid in the absence of oxidants proceeds in two stages [13-16]: in the first stage, a part of copper is extracted into solution as Cu⁺, and CuS (covellite) is formed; in the second, CuS slowly dissolves as an intermediate phase with evolution of hydrogen sulfide. Presence of an oxidant leads to formation of sulfur in the second stage of decomposition.

It was shown in [17, 18] that the reaction of pentlandite (Fe, Ni)₉S₈, which contains a constant excess of metals over sulfur, with hydrochloric acid (1 M) proceeds mostly as the overall equation

\[
\text{M}_{9}\text{S}_8 + 18\text{HCl} = 9\text{MCl}_2 + 8\text{H}_2\text{S} + \text{H}_2. \quad (1)
\]

It involves reduction of hydrogen ions in the acid medium to the elementary state

\[
2\text{H}^+ + 2e^- = \text{H}_2(g)
\]

and oxidation of pentlandite

\[
(\text{Fe, Ni})_9\text{S}_8(\text{s}) + 16\text{H}_2\text{O}(\text{aq}) = 4.5\text{Fe}^2(\text{aq}) + 4.5\text{Ni}^2(\text{aq}) + 8\text{H}_2\text{S} + 2e. \]

If the potential of pentlandite increases under polarization with an external current or upon introduction of oxidants into the solution (e.g., FeCl₃), it decomposes to give an intermediate phase of violarite (Fe, Ni)_₅S₄.