Geocological validation of mechanisms and parameters of physical-chemical processes facilitating the in-depth processing of complex sulphide ores and mining wastes

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Abstract. The advisability of processing copper-nickel ore dressing tailings of current production has been substantiated. The optimal parameters of metal leaching with sulphuric acid have been determined. In laboratory experiments the geotechnological extraction of non-ferrous metals from a leaching layer representing a tailing material of fraction +0.063 mm has been studied. When investigating the geotechnological processes of non-ferrous metal extraction on the basis of two copper-zinc ore deposits located in the Urals, the authors have come to the conclusion that heap leaching is of little use for the ores of the Letneye deposit. Leaching results for the Yaman-Kasy ore have shown more promise.

Key words: complex sulphide ores, sulphide mining wastes, hydrometallurgical technologies, heap leaching

1. Introduction

Nowadays, sulphide off-grade ores from both depleted and currently developed deposits, overburden rock, and reject material of concentration plants are regarded both as a source of valuable materials and a hazard for the environment (Chanturiya, 2001). They occupy huge areas, disturb the hydrological and hydrogeological regimes, pollute the air and open water bodies with dust, and contain minerals and flotation reagents decomposing to form toxic soluble compounds. Waste storage is accompanied by vigorous oxidation of sulphide minerals creating sulphuric acid and iron and non-ferrous metal sulphates. Therefore developing of technologies for sulphide ores and mining wastes is a challenge for both ecology and economy with both material and environmental gains.

2. Possibility of extracting non-ferrous metals from copper-nickel benefication wastes

The purpose of the study was enhancing the processes of leaching out valuable components from technogenic deposits by using sulphuric acid and various oxidizers, searching for optimal conditions for geotechnological processes whereby metals are extracted from products prepared from copper-nickel ore dressing tailings.

The composition and properties of minerals and solutions were investigated by using microscopic, XRD, and chemical analyses. Microscopic examination of current and stored copper-nickel ore dressing wastes was performed at a Versamet-2 microscope. The XRD analysis was carried out at a DRON-2 diffractometer (Cu Kα radiation). The chemical analysis involved flame atom-absorption spectrometry at a Kvant-2 AFA device. The experiment results were treated using the method of experiment planning.
In the course of microscopic examination of current copper-nickel ore dressing tailings of the Pechenganikel Combine JSC (Kola MMC) the following grains types and sulphide aggregates were identified:

- open grains and rich non-ferrous metal sulphides aggregates with pyrrhotite, magnetite and silicates (Fig. 1a);
- open grains and rich agggregates of pyrrhotite with non-ferrous metal sulphides (Fig. 1b);
- small aggregates of pentlandite (more rarely, chalcopyrite) with magnetite;
- small and dust-like aggregates of pentlandite (more rarely, chalcopyrite and pyrrhotite) with silicates (Fig. 1c).

The data of microscopic investigations of sulphides from stored dressing tailings (Concentration Plant in Afrikanda), presented in Fig. 2, have revealed that the processes of leaching and phase alteration in open sulphide grains are quite intensive. This becomes evident in open pyrrhotite grains and in open grains and rich sulphide aggregates of non-ferrous metals with pyrrhotite, magnetite and silicate. In pyrrhotite grains, pyrrhotite is sometimes entirely displaced by iron hydroxides, goethite in the first place (Fig. 2a,b). The role of iron hydroxide aggregates is also prominent in polymineral grains, although in this case slightly altered grains of non-ferrous metal sulphides are also observed. The rarely occurring open pentlandite or violarite grains do not contain any secondary iron hydroxides, demonstrating instead clear signs of dissolution, their surface being covered by cracks and pores (Fig. 2b).

Microscopic investigations have disclosed a relationship between the sulphide oxidation intensity and composition of the nonmetallic matrix, including the size and shape of impregnations. The larger the ore aggregates, the more obvious the sulphide oxidation. Moreover, we have recorded oxidation on the contact area of monoclinic and hexagonal pyrrhotites (Fig. 2c).

As it has been previously shown, sulphide oxidation in stored wastes may proceed differently, including the electrochemical mechanism (Chanturiya et al., 2000; Kalinnikov et al., 2001). Iron, nickel and copper sulphides are known to be good conductors, with pentlandite and pyrrhotite displaying nearly metal properties (Chanturiya, Vigdergauz, 2008). Contact in solution affects the oxidation rates of two sulphide minerals by
slowing down the rate of the electropositive mineral and accelerating the rate of the electronegative one (Chanturiya et al., 2000).

As revealed by our microscopic studies, the surfaces of contacting pyrrhotite and pentlandite grains of pentlandite are less oxidized than in the absence of aggregates. The pyrrhotite potential in alkaline solutions was found to be by 0.07-0.10 V more negative than that of pentlandite (Makarov, 2006). The process occurring on the pyrrhotite surface is anodic, whereas on the pentlandite surface it is that of oxidizer reduction (Bokzart et al., 1998). This oxidation pattern is also controlled by the hydrodynamic conditions prevailing at the mineral surface, namely, the oxidizer concentration and the depth of diffusion layer, the rate of dissolved oxygen reduction on various sulphides, and the surface ratio of mineral grains (Chanturiya et al., 2000).

On the basis of our investigations the sulphide minerals oxidation can be arranged in the following sequence: pyrrhotite – pentlandite – chalcopyrite. Most of the ore minerals are dumped into tailings as part of lean aggregates with nonmetallic minerals, magnetite, and iron sulphides. Some of it is lost as open grains and rich aggregates. Due to the selective character of supergenic processes in old tailings, the grains will yield more readily to grinding. However, it will be problematic to decompose the sulphide grains because the process will be mainly occurring on areas containing loose hydroxides (Chanturiya et al., 2000). This negative factor will have to be considered when developing processes incorporating both concentration and hydrometallurgical methods.

In (Chanturiya et al., 2004), the ratio of nickel silicate and sulphide forms in copper-nickel ore dressing tailings after 30 years of storing was reported. While in current tailings the content of silicate nickel was 10 %, in stored tailings it was found to be 40 %. The probability of nickel passing to silicate form was proportionate to the material grain size and the chemical activity of serpentines and hydrochlorites. The fact of nickel migration as sulphates and its precipitation by chemically active silicates changes its distribution among the large and small classes typically found in current tailings. As the result of nickel altering its form, the value of stored tailings as a prospective deposit goes down (Chanturiya et al., 2004). If we also remember that the hazard for the environment, posed by stored wastes, persists for decades, it becomes evident that both economical and environmental considerations it is current, not stored, tailings that should be processed (Chanturiya, 2001).

It is known that technologies for technogenic materials incorporate both flotation and hydrometallurgical methods (Chanturiya, 2007). Working in cooperation with the Institute of Problems of Complex Development of Mineral Resources of RAS, we have studied the repeat flotation of non-ferrous metals from tailings of the +0.063 mm fraction. Pre-grinding was employed to facilitate the grain opening. The first stage consisted of varying the consumption of collectors representing a mixture of xanthate and aerofloat. The pH value was controlled through lime addition. Although the metal concentrations in resulting flotation products were high enough for subsequent hydrometallurgical processing, the experiments revealed a necessity of developing new reagent and process regimes taking into account the specificity of sulphide minerals under study (Chanturiya, 2007).

Non-ferrous metals are conventionally processed by hydrometallurgical methods, with sulphuric acid as a solvent (Snurnikov, 1986; Khalezov, 2009). Thus, the author of the work (Fedoseev, 2006) reported the kinetics of sulphuric acid leaching of nickel, copper and iron from copper-nickel ore dressing tailings of Concentration Plant No 1 in Norilsk under atmospheric pressure depending on temperature and ferric ions concentration. It appeared that using concentrated Fe$_2$(SO$_4$)$_3$ (≥200 g/l Fe$^{3+}$) solutions provided an almost total extraction of copper, increased the level of nickel oxidation, oxidizing sulphide sulphur to the sulphate form. Evidence is cited in favour of iron (III) salt solutions as reagents in comprehensive processing of tailings yielding marketable copper, nickel, iron, and platinum metal products.

On the basis of this knowledge, we experimented to establish the regularities of leaching nickel, copper, cobalt and iron by sulphuric acid of different concentrations, which included varying of the S/L ratio, temperature, leaching time, mixing rate, and admixing of oxidizers (Fe$_2$(SO$_4$)$_3$, NaN$_2$O, air oxygen) and priming powders. Taking into account the metal distribution in large and small classes of current copper-nickel ore dressing tailings, we examined the sand fraction (+0.063 mm). The chemical composition of the tailings was, %: SiO$_2$ 37.4; MgO 28.3; CaO 2.71; Al$_2$O$_3$ 3.74; TiO$_2$ 0.95; Fe 13.3; Ni 0.18; Cu 0.08; S 0.71. The H$_2$SO$_4$ concentration varied between 0.5 and 15 %.

The highest extraction level was achieved in a 15 % acid solution, with trivalent iron as an oxidizer. The process temperature was varied in the interval of 20-80 °C. Decomposition was the most complete at 80 °C. At these parameters, the levels of nickel, copper, and cobalt extraction were 79, 89, and 60 %, respectively. Interestingly, within the leaching period of 0.5–4 hours, the metal extraction tended to increase and then decline steadily. Both the incomplete metal leaching, observed in the experiments, and diminishing yield on increasing the process time from 4 to 5-6 hours may be caused by amorphous silica emerging on dissolution. As it has been reported, the non-ferrous metal sulphate solutions tend to react with active silica, forming layered hydrosilicates (Makarov et al., 2009). Moreover, the resulting amorphous silica gel hinders filtration.
To prevent these undesirable processes, the pulp was admixed with an amorphous silicium oxide coming as a product of the sulphuric acid process of vermiculite concentrate. This primer operated as a silica coagulator, preventing the synthesis of hydrosilicates containing non-ferrous metals, as the result of which the minerals were almost totally decomposed and the filtration characteristics of the solid residue were improved. The experiments lasted for 5.5 hours, dissolving about 99 % nickel, cobalt and copper. The amorphous silica can then be used for building artificial geochemical barriers and in construction.

The process parameters were optimized by employing the method of experiment planning. The independent variables were the temperature $t$ and time $\tau$. The lower and upper $t$ levels were equal to 20 and 80 °С, and $\tau$ was equal to 1 and 6 hours, respectively. The range of independent variables was: $\Delta t = 20$ °C, $\Delta \tau = 1$ hour.

The following dependences for non-ferrous metal extraction have been obtained:

$$\varepsilon_{\text{Ni}} = 28.015 - 0.605 t + 2.375 \tau + 0.008 \tau^2 - 0.557 \tau^2 + 0.111 \tau \tau; \quad (1)$$

$$\varepsilon_{\text{Co}} = 18.483 - 0.154 t + 2.426 \tau + 0.003 \tau^2 - 0.304 \tau^2 + 0.054 \tau \tau; \quad (2)$$

$$\varepsilon_{\text{Cu}} = 52.865 + 0.138 t + 3.362 \tau + 0.0001 \tau^2 - 0.464 \tau^2 + 0.057 \tau \tau; \quad (3)$$

where $\varepsilon_{\text{Ni}}$, $\varepsilon_{\text{Co}}$, $\varepsilon_{\text{Cu}}$ are the extraction of nickel, cobalt and copper to solution, respectively, %; $t$ – temperature, °С; $\tau$ – time, hours. Fig. 3 is a graphic representation of the dependence of nickel extraction to solution.

It can be seen that the optimal parameters for metal leaching include: acid concentration of 15 %, leaching time of 5.5 hours, temperature 80 °C, the S:L ratio = 1:5, and the mixing rate of 900 min⁻¹.

![Fig. 3. A plot of nickel extraction to solution vs process temperature and time](image)

However, operation in high acid concentrations and process temperatures requires special corrosion protection for the equipment. Alternative approaches propose achieving the metal gain in relatively mild conditions by using complexing agents. Thus, B.D. Khalezov examined the effect of humic additives on copper and zinc sulphide oxidation kinetics (Khalezov, 2009).

Our other goal was studying the possibility of geotechnological leaching of non-ferrous metals from products prepared from copper-nickel ore dressing tailings. In laboratory experiments, the closest to real physical-chemical conditions of heap leaching is percolation leaching. Portions of tailing products were loaded into separating funnels with a diameter of 40 mm. To facilitate the sulphide grain opening, the fractions +0.063 mm were ground to −0.05 mm. By adding 3 % of Portland cement as a binding agent, we prepared granules with a diameter of 10 um and compression strength of 1.0-1.4 MPa.

The initial stage included varying of the sulphuric acid concentration (1 and 3 %) and the spraying interval (2 to 4 days). In some of the experiments, an oxidizer (Fe₃⁺) was added. The ore was not preliminarily saturated with water. This stage did not include experiments on solution circulation. The process temperature was 20±2 °C. In 50 days, six experiment sets were performed. The highest performance was noted for 3 % sulphuric acid, an oxidizer and an wetting interval of 2 days.

The following dependences of non-ferrous metal extraction have been obtained:

$$\varepsilon_{\text{Ni}} = 1.074 \tau - 2.792; \quad (4)$$

$$\varepsilon_{\text{Co}} = 0.584 \tau - 0.951; \quad (5)$$
\[
\alpha_{\text{Cu}} = 0.688 \cdot \tau - 1.091,
\]

where \( \alpha_{\text{Ni}}, \alpha_{\text{Co}}, \alpha_{\text{Cu}} \) – are the nickel, cobalt and copper extraction, %; \( \tau \) – time, days. The calculated values of metal extraction for 90 days either without or with an oxidizer, were, respectively: Ni – 54 and 94 %, Co – 36 and 52 %, Cu – 30 and 61 %. Clearly, the metal is better extracted in the presence of an oxidizer. The best results were achieved for nickel. They were worse for copper due to its incorporation in the hardly soluble chalcopyrite. As to cobalt, its inferior extraction indices, including the lowest extraction increment in the presence of oxidizer, can probably be explained by its partial incorporation in magnetite as an isomorphic impurity. The acid consumption was 380 cm\(^3\) per 1 kg of tailing products.

3. Investigating the geotechnological processes of metal extraction from copper-zinc ores

Nowadays attention is focused on utilizing dumps and ores from incompletely developed mines (Snurnikov, 1986; Khalezov, 2009; Rylnikova et al., 2010). Moreover, there is a multitude of relatively lean deposits containing either highly oxidized ore minerals or low contents of valuable components, or hardly yielding to benefication (Snurnikov, 1986; Khalezov, 2009).

Minerals of this kind are conventionally processed by employing underground, heap and vat leaching. In recent decades, these processes have been intensified by involving microbiological oxidation of sulphide minerals.

The theory of hydrometallurgical extraction of copper from oxidized and sulphide ores has been thoroughly discussed in works (Snurnikov, 1986; Khalezov, 2009; etc). The leaching solutions contain sulphuric acid (in the case of oxidized and mixed low-sulphur ores) or without it (for massive sulphide ores). In the latter case, the acid producers are mainly iron sulphides. A.B. Pitsyn has developed geochemical foundations for geotechnology of non-ferrous metal processing, operating at negative temperatures and in permafrost (Pitsyn, 2011; etc.). The factor limiting its commercial introduction is insufficient rate of phase transitions caused by filtration properties of the ore massif and low intensity of chemical reactions. The new technologies for sulphide mineral decomposition are environment-friendly and energy-saving, being based on electrochemical, electric-pulse and mechanical-chemical treatment (Chanturiya, 2007).

The ores of the Letneye and Yaman-Kasy deposits, although having a similar mineral and chemical composition (Table), differ essentially in the rate of sulphide minerals oxidation. The ores are different in structure, Fig. 4.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Copper, %</th>
<th>Zinc, %</th>
<th>Lead, %</th>
<th>Cadmium, g/t</th>
<th>Cobalt, g/t</th>
</tr>
</thead>
<tbody>
<tr>
<td>Letnee</td>
<td>6.84</td>
<td>1.54</td>
<td>0.187</td>
<td>70</td>
<td>2310</td>
</tr>
<tr>
<td>Yaman-Kasy</td>
<td>7.50</td>
<td>6.00</td>
<td>0.045</td>
<td>198</td>
<td>161</td>
</tr>
</tbody>
</table>

Table. Chemical composition of ores

Fig. 4. Structure of massive sulphide ores from: banded primary ores of Letnee (a), collomorphic ores of Yaman-Kasy (b).

Mt – magnetite, Py – pyrite, Cpy – chalcopyrite, Sph – sphalerite

Banded ores from Letnee consist of major pyrite and chalcopyrite with minor sphalerite, magnetite, and rare galena. Actinolite, quartz, epidote, albite, chlorite and calcite are gangue minerals. Banded structure of ores reflected of uneven distribution of sulphide enriched layers in gangue matrix and resulted of clastogineneous origin of ore. Grain size of sulphides varies from 1 mm to 0.01 mm excluding smaller sphalerite or chalcopyrite inclusions within pyrite. All minerals from ore form euhedral, subhedral or xenomorphic grains. Some chalcopyrite-pyrite small zonal aggregates can be identified as recrystallization products after primary reniform pyrite (Belogub et al., 2005).
Breccia-like ores from Yaman-Kasy consist of major pyrite, sphalerite and chalcopyrite with minor marcasite and very rare tellurides and fahlo ore. Gangue minerals are presented by quartz, some barite, sericite and, probably, albite. All minerals are fine grained. Their size is about limit of flotation. Clasts are composed of different textural types of sulphide aggregates. Some of them include collomorphic pyrite and pyrite-marcasite products of their recrystallization. Some clasts are relics of the palaeothermal tubes with concentric-zoned structure and collomorphic rims (Makarov et al., 2007). Fine-grained polysulphide aggregate with gangue minerals is cement of clasts.

We have looked into the dynamics of non-ferrous metal leaching under conditions modeling physical-chemical geotechnologies. These ores are hardly suited for heap leaching because copper here is incorporated in chalcopyrite (Khalezov, 2009). At the same time, the ores contain sizable quantities of zinc, cadmium, cobalt, and others, extractable by geotechnological methods, which will improve the process economic performance on the whole.

When modeling the sulphuric acid leaching of ores as part of physical-chemical geotechnologies, we varied the filtration coefficient (percolation rate), the acid consumption and spraying regime. Separating funnels with the diameter of 40 mm were used. The ores of the Letneye and Yaman-Kasy deposits were ground to the sizes of −5+2.5 and −2.5+0.5 mm. The filtration coefficients were 23.1 and 16.1, respectively, m/day for the ore of the Letneye deposit and 22.2 and 15.5 m/day for the ore of the Yaman-Kasy deposit. The ore had not been preliminarily saturated with water. No experiments on solution circulation were performed in this case. The process temperature was 20±2 °C. All in all, there were four experiment sets based on 2 % sulphuric acid.

Experiment No 1. The ore weight was 100 g. The volumes of leaching solution for ore sizes of −5+2.5 mm and −2.5+0.5 mm were, respectively, 25 and 20 ml per day. The solution was poured into an ore-containing column, exposed for 8 hours, after which the column was emptied. The ore remained dry for 36 hours whereupon the process was repeated.

Experiment No 2. The ore weight was 89 g. The volume of leaching solution was 16 ml per day, with 4 ml added every 2.5 hours, following which the solution was filtered. After 36 hours in dry condition, the process was repeated.

Experiment No 3. The ore weight was 70 g. 14 ml of solution were added every day for the ore fraction of −5+2.5 mm and 10 ml for the −2.5+0.5 mm fraction. The solution was poured into an ore-containing column, exposed for 8 hours and then filtered. The sample was not wetted for 36 hours. After that it was washed with acid solutions in the same volumes. The process was then repeated.

Experiment No 4. The conditions were the same as in experiment No 3 with one exception of a 2 % Fe₂(SO₄)₃ addition to the acid.

The filtrates were analyzed for the contents of non-ferrous metals and iron once in 5-9 days. The experiments lasted for 45-55 days.

Judging by the dynamics of metal leaching in experiments Nos 1-4, the leaching is the most effective in fraction −2.5+0.5 mm. The highest leaching intensity was observed for the Yaman-Kasy ore, in all process variants. Copper transition to solution was inhibited due to chalcopyrite slow dissolution. The exceptions were experiments No 1 and 4 for the Yaman-Kasy ore.

Figs 5 and 6 demonstrate the kinetics of metal leaching in experiments Nos 1-4 for ore samples of the size −2.5+0.5 mm.

For the ore of the Letneye deposit, the copper extraction indices were unsatisfactory. The same refers to cobalt. The best results for zinc and cadmium incorporated in sphalerite were obtained in Experiment No 4.

More encouraging were the leaching results for the Yaman-Kast ore. As it had been expected, sphalerite was the easiest to leach. The cobalt extraction indices were high in all experiments due to incongruent dissolution of collomorphous cobalt-containing pyrites creating conditions more favourable for cobalt, rather than iron, dissolution. The best results were obtained in Experiment No 4, involving an oxidizer, where 9.4 % copper was extracted in 55 days.

By way of example, let us consider the equations of metal extraction (ΔMt, %) versus leaching time (τ) in days for Experiment No 4 (the ore of the Yaman-Kasy deposit, size −2.5+0.5 mm): \( \Delta_{Cu} = 0.2705 \tau - 0.1544; \) \( \Delta_{Zn} = 0.5979 \tau - 0.8723; \) \( \Delta_{Cd} = 0.6854 \tau - 0.7716; \) \( \Delta_{Co} = 0.3606 \tau - 0.4876. \)

The leaching intensity was, per day: copper − 0.169 %; zinc − 0.603 %; cadmium − 0.687 %; cobalt − 0.37 %. It is evident that per day extractions were high for all the components. According to B.D. Khalezov, the intensity of copper leaching depends on the material composition of other components and varies between 0.02-0.17 % (Khalezov, 2009). In our case, the results were high due to both the rich composition of the Yaman-Kasy ore and peculiarities of its structure and mineral composition.
Fig. 5. Leaching kinetics for the Letneye ore deposit sample. By numbers the following metals are designated: 1 – zinc; 2 – cobalt; 3 – copper; 4 – cadmium; 5 – iron.
The leaching regimes: No 1 (a), No 2 (b), No 3 (c), No 4 (d)

Fig. 6. Leaching kinetics for the Yaman-Kasy ore deposit sample. By numbers the following metals are designated: 1 – zinc; 2 – cobalt; 3 – copper; 4 – cadmium; 5 – iron.
The leaching regimes: No 1 (a), No 2 (b), No 3 (c), No 4 (d)

4. Conclusions
Using microscopic investigations of different-age copper-nickel ore dressing tailings, we have determined the peculiarities of supergene alterations occurring in sulphides of stored wastes and their effect on the material processibility. The advisability of processing tailings of current production has been substantiated.
The optimal parameters of metal leaching with sulphuric acid have been determined: acid concentration 15 %, leaching time 5-6 hours, temperature 80 °C, the S:L ratio of 1:5, the stirring rate of 900 min⁻¹, adding ferric ions as an oxidizer and amorphous silica as a primer. In laboratory experiments the geotechnological extraction of non-ferrous metals from a leaching layer representing a tailing material of fraction +0.063 mm has been investigated. The best results were obtained in experiments involving an oxidizer (Fe³⁺ ions), 3 % sulphuric acid, and an inter-spraying interval of 2 days. The calculated indices for metal instruction for 90 days were: Ni – 94 %, Co – 52 %, Cu – 61 %.

When investigating the geotechnological processes of non-ferrous metal extraction on the basis of two copper-zinc ore deposits located in the Urals, we have come to the conclusion that heap leaching is of little use for the ores of the Letneye deposit. Leaching results for the Yaman-Kasy ore have shown more promise because it yields not only zinc and cadmium but copper and cobalt as well, being particularly responsive to the addition of ferric ions as an oxidizer.

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