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Chapter

Upward Capillary Mass Transfer as a Process for Growing Concentration Zones

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Abstract

The natural process of circulation of ground and atmospheric water through evaporation from the surface and precipitation from the atmosphere to the surface leads to colonization of the surface soil layer. The main source of salts in the soil is groundwater. Groundwater reaches the surface soil layer and evaporates, and its constituent salts accumulate in the soil. The concentration of salts on the surface can reach to 100% (crust). This process is widespread. Vast areas of solonchaks are located in deserts and semideserts of Asia, Australia, South America, northern Africa, and the western United States. This natural process can be applied in the field of extraction of natural resources from the bowels. The process of salting the soil surface is low and gradual and is subject to study for possible use in technological solutions for the extraction of minerals. In this chapter, the authors intend to show the beneficial advantages of the phenomenon of surface salinization of the soil layer. Water-soluble salts due to their high mobility allow directional mass transfer along the capillary system of the soil and deposition in the aeration zone. However, the utility does not belong to plant biota. This phenomenon can be effective and safely used in the creation of near-surface concentration zones. The natural process of the filtration upward of salt solutions from the depths of the massif to the surface will purposefully carry out the transfer of valuable components with deposition in the area of the evaporation barrier. The speed of the process of ascending capillary mass transfer is technologically low but rather suitable as a preparatory operation at the place of storage of industrial wastes and burials and in the formation of zones of high concentration of small substandard natural mineral deposits. The chapter presents the results of experimental studies of ascending mass transfer of useful components from the waste material of the concentrating production of nonferrous metals.

Keywords: upward mass transfer, geochemical barrier, soil capillaries, aeration zone, upward fluid, sedimentation, vapor barrier, leaching

1. Introduction

Many natural minerals that form mineral deposits during oxidation become water-soluble like the conversion of metal sulfides to oxides. Mineral deposits

located near the surface are exposed to oxygen from the atmosphere, and minerals oxidized (hypergenesis) become water-soluble and can be subjected to water leaching by filtration mass transfer. Hypergenesis is a strong geological process of chemical and physical transformation of minerals and rocks in the upper parts of the Earth's crust and on its surface under the influence of the atmosphere, hydrosphere, and living organisms at temperatures characteristic of the Earth's surface. Among them, hypergene transformation refers to the number of common and most productive geological processes. Hypergene transformations are very dynamic in the geological sense, but very slow in the technological sense. The process of geological formation of such deposits consists in the mass transfer and deposition of useful components on physical and geochemical barriers. The study of these processes and their application may be appropriate as a preparatory process before the extraction of minerals by common technological technologies. The directed application of geological processes in the technological foundations of the structural and material transformation of the array will lead to the achievement of standards to the existing capabilities of technology.

The water-based mass transfer occurs by dissolving salts with water from the capillary surface, moving as a salt solution and precipitating salt from the solution under the influence of physicochemical factors. Water-soluble forms of mineral compounds (salts) are involved in such mass transfer. The shape, content of non-ferrous oxides, the location, and size of ore concentration zones depend on the conditions of the source and the potential of the subsoil (water content of the subsurface massif, pressure gradient, mass structure porosity, etc.), which causes the fluid to move. Natural geological ore concentration zones do not always correspond to the technological conditions of mining. Sometimes it is required to look for the presence of driving factors or, if it is possible, to create them.

The principle of filtration formation of concentrated zones is a kinetically dynamic geological process [1]. It involves three operations: transfer of water-soluble mineral compounds to the fluid, movement of the fluid in the capillary medium of the massif, and deposition on the physical or geochemical barrier. Due to the high kinetics (in geological sense) of this process, it can be applied in the field of mining as a preparatory stage—bringing the parameters of the subsoil section to effective technological conditions. The process due to the inconsistency of the speed by the technological processes should be brought to a separate—preparatory—stage. The whole complex of leaching operations must be assessed in studies of the potential formation of artificial concentration zones.

The presence of water-soluble compounds, the minimum and maximum concentrations of the studied solutions, and the kinetics of the capillary motion of fluids are very important in the complex for the leaching process. If there are no such mineral compounds, they must be created.

The most suitable object for using such an approach is enrichment waste zones. The waste flotation enrichment of Norilsk mining was taken as the object of study in such objects in which there is always a useful component in a dispersed form. The whole object of tailing dump is located on the surface and is isolated from the natural environment by an engineering dam. The waste mass is flooded and finely dispersed; as a rule it has water-soluble metal oxides, and with the access of oxygen from the atmosphere, oxidation of sulfides is possible with the formation of water-soluble minerals. These conditions completely provide guaranteed controllability of mass transfer. In order to assess the feasibility of the filtration formation of oxidized ores of nonferrous metal concentration zones, expert studies were conducted on directional upward mass transfer for the conditions of the tailing dump of waste flotation enrichment of the Norilsk mining and smelting hub.

According to the laws of communication of groundwater with the atmosphere, the solutions of groundwater can move upward through the evaporation zone to the surface by capillary action mechanism. Along with this, a very powerful natural mechanism for solution flow through a massif enables upward vertical movement due to the pressure gradient between the surface and the fluid level in the water table. The reason for the formation of a pressure gradient consists in evaporation of water from the surface of the array. The upward fluid flow rate is controlled by all the forces in the capillary system and the humidity [1–3]. Water evaporation from the solution increases the concentrations of the useful mineral compounds along the direction of flow in the surface aeration zone. When these concentrations exceed the solubility limits, the useful compounds are deposited in the column. Different mineral compounds have different concentration limits in the solution; therefore, the compounds can be selectively precipitated at different heights in the aeration zone. Essentially, the aeration zone acts as a natural evaporation barrier. Selective enrichment can be achieved due to the physical nature of the capillary action in the upward direction and the deposition surface. Partial laws for the upward capillary rise of solutions were formulated in studies of agricultural soils [4–9]. The soil particle size and stratification structure were shown to influence the capillary action considerably [9–14]. To leach valuable compounds in a column, their velocity and the large contact surface area between the solution and solid material in the capillary system are important [15]. These parameters must be optimized to ensure that the extraction is complete and the upward capillary leaching process can be controlled. Upward capillary leaching was studied by investigating the upward capillary flow of solutions with access to the column surface and of the solutions that deposit salts in the near-surface aeration zone. The concentration of precipitated salts was estimated by samples at different levels of the evaporation barrier in the columns.

The leaching process is one of the main technological solutions for recovering useful components from poor ore [16, 17]. Leaching can sometimes be the only and therefore the most important method for recovering components from poor-quality ores. Now, underground leaching and heap leaching are well-known technological solutions that are widely used for metal ores [18–21] and nonmetallic minerals [20] (such as Chilean saltpeter). Very often the leaching is one of the only effective extraction technologies for removing valuable components from ores given that their contents have been decreasing recently. In fact, the United States and Australia are world leaders in the gold mining industry through the use of leaching technologies. Heap leaching technology is the most widely used. In heap leaching, gravity-driven fluid flow through the column is exploited. For each type of ore, the leaching technological process must be optimized. For example, Padilla et al. [20] analyzed two parameters of heap leaching, the leaching time and heap height, to determine the best performance indicators. Ghorbani [23] examined the effects of the surface characteristics and mineralogy of particles in the heap leaching process. The mineralogical composition of the ore and the leaching reagent properties control the transfer kinetics of useful species between the solid and liquid phases, demonstrating the applicability and efficacy of leaching under specific conditions. In addition to the dissolution of the column material in the fluid and precipitation of valuable compounds in the column, the fluid flow kinetics and direction are also important parameters in heap leaching technology. Depending on the initial concentration of solutions and the size of a subsurface aeration zone, the precipitation distribution can be varied, and these very parameters can play a key role in monitoring of component concentrations.

As for technogenic formations, the evaporation barriers can be helpful for purposeful concentration of components in tailing dumps to mitigate the environmental load. The presence of salts with different solubility in solutions at evaporation barriers makes it possible their selective extraction. The filtration type of natural deposits plays an important role as a mineral source of minerals. Geological processes of filtration mass transfer formed quite a few deposits with a rich content of useful components [24].

In geological filtration processes, the main solvent and main carrier is water and aqueous solutions of salts. The possibilities of water mass transfer of useful components for low concentrations in the field of mining and hydrometallurgy in the process of upward capillary movement were carried out in the conditions of an array of separate wastes from the enrichment of nonferrous and noble metal ores. Low content of nonferrous and noble metals in tailings can identify the diffuse distribution of components in the bowels of the Earth. In addition, the mining industry has created a huge amount of waste enrichment. All of them are located on the surface of the Earth and have an area many times larger than the area of the deposits themselves. The overwhelming part of the man-made mining waste has a high degree of danger. The total reserves of useful components in industrial waste are several times higher than the proven reserves in the bowels of the Earth. Carrying out extraction is currently unprofitable due to its low content. There is a great temptation to find and launch the natural process of structural and material transformation of the array, which forms the concentration zones of useful components from the diffuse state that will be profitable for the existing technological level. This approach will make a profit and eliminate toxic environmental pollution. With the application of this solution, experimental studies of the ascending capillary movement of aqueous solutions of the soil layer near the surface were carried out. Nature uses this process extensively and suggests a variety of technological solutions.

The mineralogical composition of the ore and the leaching reagent properties control the transfer kinetics of useful species between the solid and liquid phases, demonstrating the applicability and efficacy of leaching under specific conditions. In addition to the dissolution of mineral materials and its movement in the column and precipitation of valuable compounds in the column, the kinetics and mass transfer direction are also important parameters in leaching technology. To assess the applicability of the natural mechanism, only water and aqueous solutions of salts were used in technological solutions. The upward velocity of the fluid flow depends on the pressure gradient, which is the driving force of in situ leaching.

2. Materials and methods

2.1 Capillary rise with fluid release of the column surface

Drinking mineralization water was used in mass exchange experimental studies. The results of studies have been obtained on the directional upward mass transfer of water-soluble salts of nonferrous and noble metals in the conditions of the tailing dump of mineral processing. The speed and variability over time of the directed capillary ascending rise of aqueous solutions were obtained for dispersed materials of enrichment waste. The kinetics of formation of water-soluble salts of nonferrous and noble metals was evaluated for the tailing dump. This process is basic of the water leaching for enrichment waste. The experiments were performed using the setup shown in **Figure 1**. The core polycarbonate column had a height of 1.5 m and a diameter of 110 mm. The bottom of the column was connected to a solution tank by

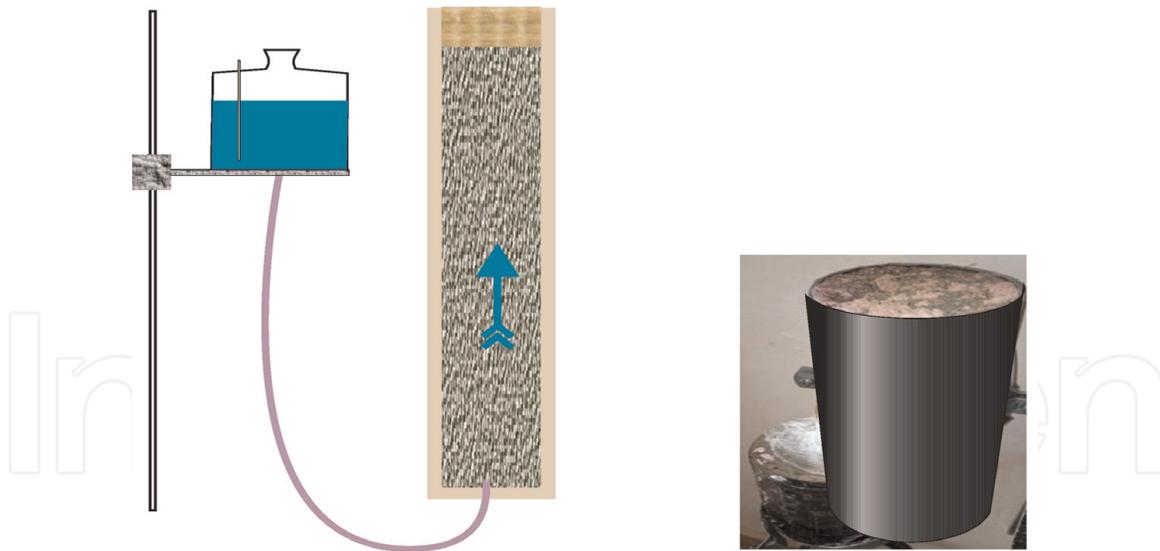


Figure 1.
Installation of the upward movement of water-soluble solutions.

a flexible pipe. The solution tank, which was a Mariotte bottle, was mounted on a platform that could be moved along the entire column height. The material to be tested was charged in the column. The solution was fed to the column at a constant feed rate through a bottom opening. The feed rate was controlled by the solution level in the Mariotte bottle, which was set to the height of the material surface in the column. In the first pilot version of the continuous upward flow system, the column was loaded with flotation tailings from the Norilsk industrial hub. These flotation tailings consisted of finely crushed ore with a predominant fraction particle size of 0.05–1.2 mm. The main minerals in the ore were rock-forming minerals, i.e., aluminum silicates (muscovite, illite, serpentine) and quartz. The ore also contained pyrrhotite, chromite, and minor amounts of chalcopyrite, calcite, brucite, and pentlandite. The sulfide mineral content was as high as 10%. The flotation tailings looked like a gray sand. The nonferrous and platinum group metal contents of the tailings were 0, 34% Cu, 0.39% Ni, 0.019% Co, 1.3 g/t Pt, 3.1 g/m Pd, and 0.23 g/t Au (atomic absorption spectroscopy). The content of useful components in the materials of the experiment was obtained by chemical analysis of its own chemical laboratory and was compared with the values of the chemical laboratory of the Norilsk mining and smelting hub. The initial working solution had a mineral content similar to that of mineralized drinking water at $\text{pH} \sim 7.0$ and flowed through the capillaries in the material to the surface. The solution that reached the surface was removed for extraction. The useful component content of the flotation tailings in the column was monitored by serial geochemical analysis during the experiment by the method [14], which showed that the exchangeable fraction consisted of readily water-soluble compounds and accounted for the largest percent of the noble metal species (31–46%). Crystalline Fe and Mn oxides constituted the second largest fraction of the tailings (20–30%). The copper, nickel, and cobalt sulfide mineral contents were in the range of 13–27% and, together with the oxide phases, accounted for 43–61% of their total contents. The nonferrous metal content of the exchangeable fraction ranged from 4 to 10% (**Figure 2**). During the entire experiment, which was conducted for 15 months, the level of water was at the same level using a Mariotte vessel to evaluate fluid kinetics over time. The water solution at the surface was periodically analyzed for Cu, Ni, Co, Pt, Pd, and Au. In addition to these experiments, experiments in which an absorbent layer was placed on the surface were performed. This layer was designed to collect the product solution. A

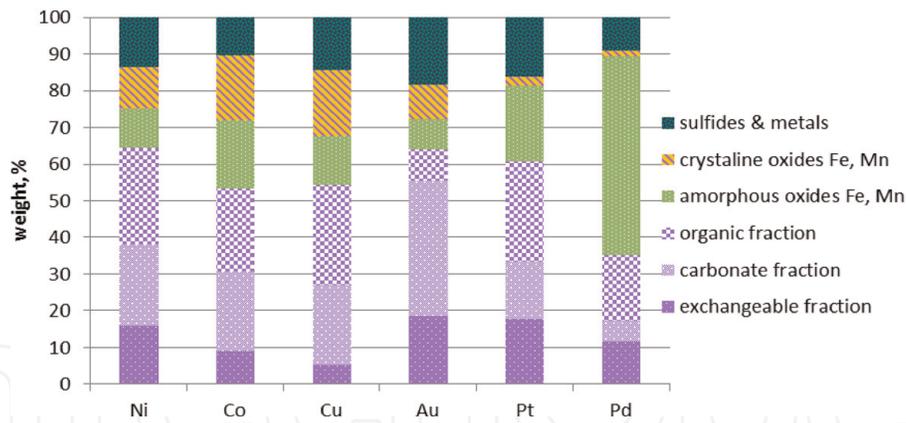


Figure 2.
Geochemical phase analysis of the metal distribution in the feedstock.

series of experiments (**Figure 1**) in which the starting feed solution level was decreased relative to the material surface height in the column were performed with the hygroscopic layer.

2.2 Capillary selective precipitation in the vapor barrier

To assess the distribution of sediment in the aeration zone in the quartz sand massif, nickel and cobalt nitrates of different concentrations were used. Experimental studies in which the feed solution level was either variable (level varied from bottom to surface) or fixed based on the calculated capillary rise height were performed in a pilot plant (**Figure 1**). The experiments were carried out with the supply of aqueous solutions of cobalt and nickel nitrates of different initial concentrations. The Co and Ni nitrate concentrations of the feed solution were varied to assess the distribution of salts on a surface of the aeration zone. The column was filled with quartz sand with a narrow particle size range, and the capillary radius of the material, which was chemically neutral for the Ni and Co nitrate solution, was calculated. The experiment was conducted over a 15-month period. During the entire experiment, the solution filtration speed and nitrate concentration distribution along the column height were estimated. The concentration distribution in the column material was determined by periodic testing. The effect of the column surface (atmospheric pressure, temperature, and humidity) on the upward fluid flow rate was also evaluated, which correlates with [13].

3. Kinetic of filtration capillary moving

A series of experiments to study the kinetics of the ascending capillary rise of the solutions were studied on a laboratory bench. The zone of the capillary hoist of solution works as an aeration zone with variable humidity in height. The upward capillary mechanism of fluid and pressure gradient forces stimulates the solution hoist through pores to subsurface areas of the massif. When the solution passing through the aeration zone, the salt concentration grows due to water evaporation with follow-up. Precipitation solid phase in the porous mass medium [8]. The mass humidity varies from complete inside to atmospheric levels in the aeration zone. For this experiment the aqueous solutions nickel nitrate and cobalt have been used. Nitrates have different initial concentrations: from 0.34 Mol/l (unconcentrated) to 2.75 Mol/l, (close to extremely saturated concentration). Evaporation proceeded at different capillary hoist velocities. The rate of evaporation was controlled by the temperature of

the array, the temperature of the atmosphere, and humidity, taking into account the atmospheric pressure. The correlation between speed and temperature (from 18 to 30°C) and atmospheric humidity is proportional, and the coefficient is 0.70–0.85 (linear with varying atmospheric pressure). Experiment imitates condition migration and evaporation in summer in moderate climate regions of Russia. In other test conditions, the capillary motion of the solutions was intensified by heating of massif material up to 50°C in the upper zone and by subsurface blowing with a directed warm air jet at 5–7 m/sec to imitate speedy evaporation in hot climate conditions. The massif structure and variations of mineral content of material in experimental columns were comprehensively analyzed in terms of structure to evaluate salt precipitate distribution in the porous aeration zone. The theory of the salt precipitation phenomenon with crystallization from the capillary mouth is developed in [12]. Condition for salting out can be approximately written as:

$$a \leq \frac{D}{L} \ln \left(\frac{C_{\text{sat}}}{C_0} \right) \quad (1)$$

where a is evaporation rate, cm/s; D is coefficient of salt diffusion in a solution, cm^2/s ; L is capillary length, cm; C_{sat} is concentration of saturated solution, g/cm^3 ; and C_0 is initial solution concentration, g/cm^3 .

Formula (1) determines the evaporation rate, which excess of concentration can cause crystallization in the capillary mouth. At the high evaporation rate, the solution concentration on the capillary surface due to size changes can exceed C_{sat} limit and result in the formation of precipitate and salt crystals. As for solutions and low evaporation rates, the solution concentration nearby retreating meniscus C_m should remain constant and equal by theory [15]:

$$\frac{C_m}{C_0} = 1 + \left(\frac{\pi\beta}{D} \right)^{1/2} \quad (2)$$

where β is an evaporation factor, cm^2/s . The direct experimental verification confirmed the correctness in terms of the theory [11].

In the course of long-term experiments on rising capillary filtration, the kinetic regularities of lifting solutions in the aeration zone were obtained (**Figure 2**). In the initial period of long-term experiments of ascending filtration of solutions, periods with a high rate of rise were recorded. The real velocity of the solution in the array repeatedly (up to 7 times) exceeded the calculated value (Darcy's law) [21, 22]. It is difficult to unambiguously explain this effect; most likely this may be due to the unsteady capillary flow of solutions due to a change in viscosity when external factors are superimposed.

The experiment showed us that at low evaporation rates ($t \leq 22^\circ$), the salt crystallization at surface was visually observed since 43 days from the start of the experiment. **Figure 3a** shows a dependence obtained for a solution motion rate at capillary hoist of concentrated nickel nitrate solution at the initial stage of the test. It is obvious that when the solution concentration does not exceed the saturated solution concentration and no crystallization is observed, the evaporation rate varies rather intensively, and evaporation mode can be estimated as unstable. Since the crystallization starts, the evaporation rate reduces in regular linear fashion. It is a long-lasting process at rather slow crystal growth, perhaps, due to the fact that a precipitate narrows capillary section, reduces actual evaporation surface, and diminishes the evaporation rate. Under the theory (2) the salt concentration nearby meniscus should be constant with probable partial dissolving of fresh-formed crystals. This, in its turn, increases evaporation rate and growth of concentration.

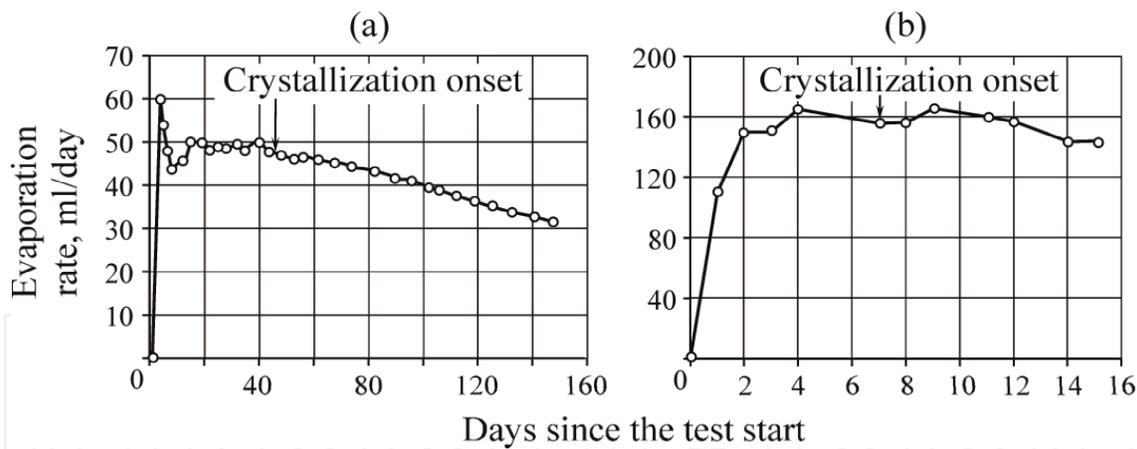


Figure 3.

The evaporation rate for aqueous $\text{Ni}(\text{NO}_3)_2$ solutions from porous material under different evaporation conditions: (a) $t = 22^\circ$; (b) $t = 52^\circ$, blowing velocity 5–7 m/s.

Crystals increase in volume and the evaporation surface reduces again. This mode of variability in crystal volume lasts for a long term. For 2 years of the experimental work, the solution motion rate stabilizes at 0.4–0.7 mm/h level with possible linear reduction within 3–5% per year. The test results confirmed theoretical conclusions made in [14], viz., in the course of evaporation, the growth of solution concentration is compensated with diffusive diversion of electrolyte in the depth of a capillary, where the evaporation rate tends to lower on the regular basis. The reduction in evaporation intensity due to transfer of salt to surface layers is proven by experimental data on different solutions and materials [15]. To intensify subsurface crystallization requires increasing evaporation rate, therefore, the velocity of solution motion in capillaries of the mass according to Formula (1). In the tests this effect was gained by raising the temperature of a mass material up to 50–52°C with blowing of a warm air jet toward the mass surface. These parameters contribute to the growth up to 3–4 mm/h of the solution transition velocity to the surface; this is 5–10 times higher than the solution motion velocity under conventional test conditions. After a precipitate is formed and crystallized in the capillaries, the evaporation rate used to lower negligibly (**Figure 3b**). The crystals appear at the mass surface in 7 days, and their further growth remains intensive even after the feeding of the solution is canceled. In 10 days from the test launch, the most portion (80%) of salt fed to the column is found in a crystallized state.

It is apparent in **Figure 3a** that salt, crystallized from unconcentrated solution with no heating, distributes practically uniformly throughout the height of sand column. The effect of local concentrated salt cluster on subsurface aeration zone is not really detected. The growth of initial solution concentration conditions the precipitation of most portion of salt in the middle section of mass height. This effect may relate to the diffusion of solution in rock pores. Under the present experimental conditions at incomplete moisture saturation in pores in the middle section of column height, the diffusion of the solution declines, thus resulting in the growth of solution concentration in this section of the test mass. In tests with intensified evaporation distribution of precipitated nickel nitrate, salt appreciably differs by the zoning of precipitation. The highest concentration with high content of nickel and cobalt nitrates is detected at the surface of the test mass. **Figure 3b** presents the plot of zoning of nickel nitrate (2.75 Mol/l) distribution. The identical relationship is established for other solutions. It is established experimentally that the covering formed at the surface of the test mass is not regular, but with discrete crystal clusters (**Figure 4**). We suppose that it is mainly due to irregularities in the structure of a porous material. Pores distribute in a random manner, intercrossed; there

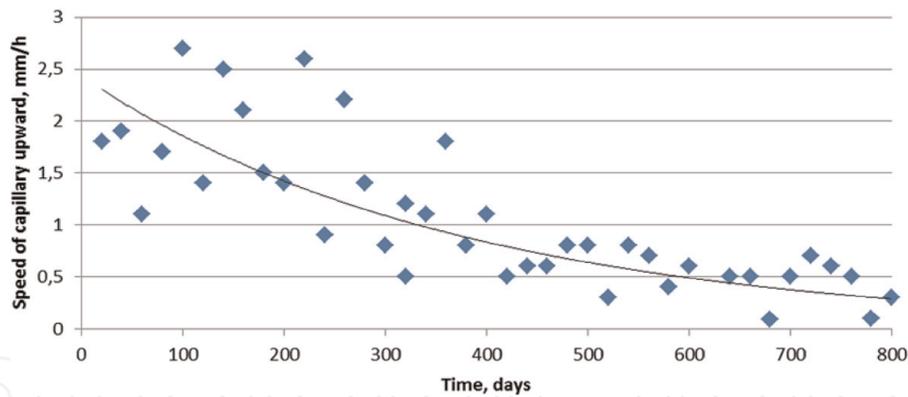


Figure 4.
The rate of the filtration upward flow of the aqueous solution.

are blind pores with no outcrop to the surface. There are also through pores, providing prompt passage for the solution to the surface. Crystallization proceeds primarily nearby such pores. It is also found that in all the cases, including the intensified evaporation tests, salt used to crystallize in the mass periphery closer to the column walls (**Figure 3b**). Under the present test conditions, a threefold higher salt content is recorded in the periphery along the column walls as compared to the central experimental mass section. One of the reasons for this effect can be higher evaporation rate nearby column walls than that in the central section, thanks to higher solution motion velocity along the smooth column surface, confining the test mass. The established effect is in compliance with experimental data reported in [16]. A series of tests on measurement of intensity of the evaporation stream at the porous body surface revealed that at a rather small distance (about 2.5 mm) between porous material surface and an outlet of a hollow cylinder (that is correct for our tests), the evaporation stream is much higher in the periphery. In the tests with no heating, the evaporation stream is more homogenous at the surface with relatively uniform salt deposits (**Figure 3a**). The evaporation barrier in the aeration zone of mineral processing tailings serves as an integrated zone of valuable component accumulation under sustaining of “water mirror” at tailing mass and a directed ascending motion of solutions to the surface. The water evaporation from the surface contributes to the preliminary concentration of valuable components in the subsurface aeration zone of the tailing mass. The precipitation nature of water-soluble nickel and cobalt nitrates depends on how solutions pass the evaporation barrier. Distribution of nitrate concentration in the aeration zone depends on a solution motion velocity (evaporation rate). At low motion velocity, the evaporation zone develops in the depth of the mass displacing to the central section of the mass thanks to the decreasing diffusion of solution because the reduced humidity in the middle section of the mass height is compensated with inflow from more water-saturated lower section. This process results in the growth of solution concentration in lower and central sections of the mass aeration zone. The low solution motion velocity at indoor temperature and average humidity level does not provide the sharp zoning of salt crystallization. The salt crystallizes throughout the aeration zone with reduction in content from lower layers to the surface. This distribution is specific for both initial high- and low-concentrated solutions. As the moisture-transition rate increases, the evaporation area forms closer to the surface of the mass aeration zone, perhaps, due to the appearance of extra thermo-moisture-conductivity phenomena. With the increase in evaporation intensity by heating or surface blowing, 61% of salt fed to the column tend to crystallize inside the mass pores starting from 7 to 10% from the surface, thus indicating the local higher nitrate concentration zone. It is established experimentally that it is possible to

control the processes of precipitation and crystallization of salts and to localize delivery of soluble salts to the mass surface with their respective lower concentration in the inner mass layers by regulating the intensity of solution motion in porous masses.

The capillary structure of massif has areas of “high-speed” pathways that allowed more rapid fluid flow and thus developed crystals more rapidly at their exit points on the surface. But instead of blocking evaporation at the pore, these crystals would boost the rate of evaporation by providing more surface area from which the fluid could evaporate. The increased evaporation would draw up fluid even faster along these high-speed pathways. In response, the flow through neighboring pathways would become slow, and the corresponding pores would be starved of salt. The salt crystallization in the salt mass on the surface forms capillaries commensurate with the capillaries of the soil. The height of the “salt mass” layer corresponds to the maximum height of the capillary rise of salt solutions with its own viscosity.

We have conducted experiments on the study of moisture transfer using media with different filtration characteristics: a layer of quartz sand and a layer of sand with a surface layer of hygroscopic material (microfiber). Investigated the suction effect of the material of the array above the boundary of the groundwater level. We studied the parameter of water capacity of a gyroscopic material with the aim of its possible use in calculations for production geotechnology. The influence of the hygroscopic layer on the surface of the changes in the kinetics of filtration and the groundwater level is established. The surface layer of a hygroscopic microfiber material increases the suction pressure by 100–250 mm and raises the water table by 40–45 mm.

Experimental evaluation is given for mineral preconcentration in a bed of a sorption collector in aeration zones from aqueous solutions of salts of low concentration useful components. Sorption collectors represented by interior layers of lignite, peat, marble, and vermiculite are included in an evaporation barrier installed in the subsurface zone of rock mass aeration in medium distance aeration zone in column (**Figure 1**). Migrating solution was aqueous solutions of salts of cobaltous and nickelous nitrates. The character of cobalt nitrate and nickel nitrate distribution is identical in all the tests. In view of this, the regularities of solely cobalt nitrate distribution are reported. Under conditions of bottom-up ascending of the test solution and its filtration through a marble sand layer, the distribution of cobalt nitrate content over the aeration zone height is close to linear and uniformly fading toward the surface (**Figure 3a**, curve 1).

Selective estimates of the influence of geochemical and sorption barriers on the kinetics and nature of the deposition of useful components in the indicated concentration zones were carried out experimentally. Layers of marble, vermiculite, brown coal, and peat were used in the aeration zone. The geochemical barrier made of a marble interlayer does not actually exhibit sorption properties and does not influence the character of cobalt nitrate distribution over the aeration zone height. In tests with bottom-up ascending of the solution through the aeration zone with the geochemical barrier made of lignite, the distribution of cobalt nitrate and nickel nitrate content is characterized with the increasing concentration of nitrates before the interlayer and nearby the upper boundary of lignite layer (**Figure 5a**, curve 2). The nitrate content linearly diminishes on the zone from the interlayer up to the surface. Cobalt nitrate content was not high at the surface of the column through the entire test. Lignite layer contributes to a partial reduction in cobalt content thanks to cobalt transition upward with ascending solution from lower layers. More than twofold rise of cobalt nitrate content was detected when the cobalt nitrate solution ascended through geochemical barrier made of Seibinsky peat (**Figure 5b**, curve 3). The higher cobalt nitrate content was recorded practically through the

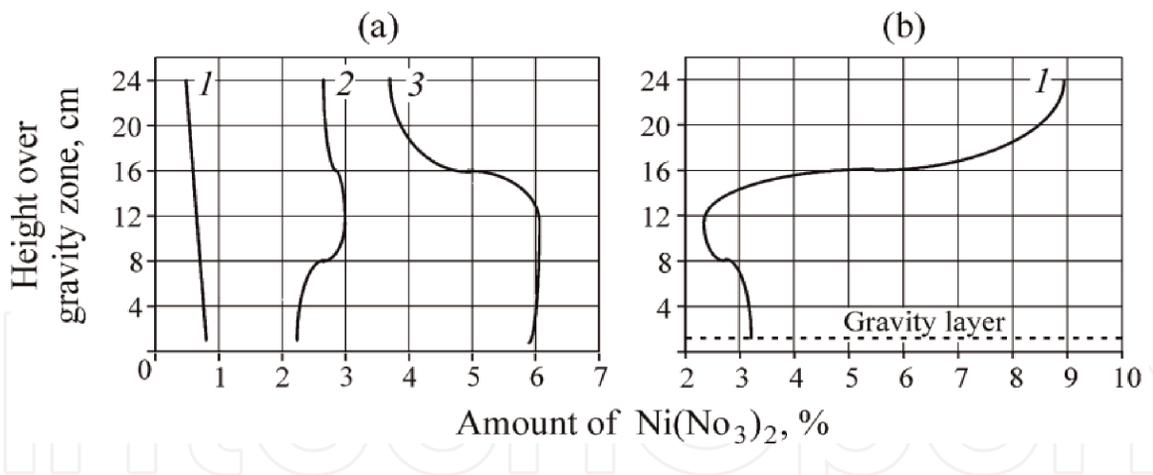


Figure 5. Distribution of salt throughout the column height under different evaporation conditions: (a) $t = 22^\circ$; (1) 0.34 Mol/l; (2) 1.7 Mol/l; (3) 2.75 Mol/l; (b) $t = 52^\circ$, blowing rate 5–7 m/s.

whole peat layer. Humic acids are supposed to perform chemisorption concentration and provoke immobilization of cobalt nitrates in the form of complex compounds. Close-in-character cobalt nitrate distributions were obtained in the test with a geochemical barrier made of foamed vermiculite originated from Severny site of Low Angara area (**Figure 5b**, curve 4). A threefold increase in cobalt nitrate content was recorded in the sorption layer. In the background of neutral properties of vermiculite, the well-developed micro-, meso-, and macro-porosity of the interlayer material promotes concentration of cobalt nitrate in the layer. Velocities of solution motion in the aeration zone are closely related to atmosphere humidity (pair correlation factor $r \approx 0.8\text{--}0.9$). The tendency to lower solution velocity 1 month later in a long-term test is traced. Variation in velocity of capillary ascending of the solution in the test with lignite interlayer is shown in **Figure 6**.

Investigation into the filtration of solutions through sorption collector being a component of the evaporating barrier in the aeration zone of the massif enabled to establish that in the course of ascending capillary lifting of the solution, the components redistributed with 1.5–3-fold concentration of cobalt nitrates in the neutral sorbent layer. The concentration in the sorption barrier does not depend on the sorption layer location in the aeration zone in the massif. In the tests with peat, the interlayers revealed feasibility to accumulate cobalt nitrate (nickel nitrate) from a solution with presumptive formation of a partially complex compound (approximately 10–12%). The sorption barrier made of marble with permeability, identical to permeability of the massif layer, does not actually generate the concentrating zone. Regularities of distribution in this case are similar to general regularities, specific for the evaporating barrier in the aeration zone. Sorption of cobalt and nickel nitrates in sorption barriers made of lignite and foamed vermiculite is not the

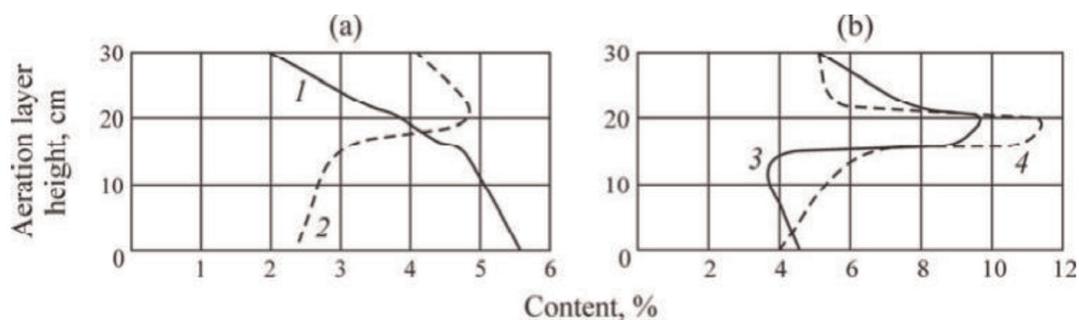


Figure 6. Distribution of $\text{Co}(\text{NO}_3)_2$ content in aeration zone in the column with an interlayer: (a) (1) marble; (2) coal; (b) (3) peat; (4) vermiculite.

same. Nevertheless, their content in sorption layers exceeds two to three times nitrate content in the aeration zone free from sorption interlayers. The technological potential of sorption interlayers being a component of evaporating barriers of the aeration zone proves the reasonability to apply them as a preconcentration stage. Artificial sorption and evaporating barriers mounted in the way of solution motion make it possible to enrich the material of the sorption barrier with a valuable component with its feasible recovery in follow-up processing circuits. Application of sorption and geochemical barriers for the rising flow of fluids warranted performance deposition and accumulation of salts in the barriers.

4. Upward capillary leaching

The evaporation from the surface forms a capillary ascending rise of groundwater from the bowels. The groundwater contains water-soluble salts and passes by capillary flow through the aeration zone of the massif. When water evaporates into the atmosphere, all mineralization is retained and accumulates in the aeration zone and on the surface. This very powerful natural mechanism for solution flow through a column enables upward vertical movement due to the pressure gradient between the surface and the fluid level in the column. We see this mechanism as the main one for the formation of concentration zones on the surface of such man-made objects as tailing dumps. The water that evaporates from the solid surface into the atmosphere leads to the formation of this pressure gradient. The upward fluid flow rate is controlled by all the forces in the capillary system and the humidity. Water evaporation from the solution increases the concentrations of the useful mineral compounds along the direction of flow in the surface aeration zone. Here is a powerful natural method for the upward movement of solutions from the groundwater horizon to the surface. This very powerful natural mechanism for solution flow through a massif enables upward vertical movement due to the pressure gradient between the surface and the fluid level in this distance. Water evaporates from the solid surface into the atmosphere leads to the formation of this pressure gradient. The upward fluid flow rate is controlled by all the forces in the capillary system and the humidity. In agricultural areas, this phenomenon leads to harmful soil salinization. The lifting of salts in the solution to the surface and their deposition can be used in technological leaching solutions. This phenomenon has not yet been used in the leaching process and is just getting ready to become one. Solutions with a low concentration of salts are very mobile, have high fluidity, and are able to quickly move a useful component to the surface. They can move upward through the evaporation zone to the surface by capillary action. Water evaporation from the solution increases the concentrations of the useful mineral compounds along the direction of flow in the surface aeration zone. When these concentrations exceed the solubility limits, the useful compounds are deposited in the column. Different mineral compounds have different concentration limits in the solution; therefore, the compounds can be selectively precipitated at different heights in the aeration zone. Essentially, the aeration zone acts as a natural evaporation barrier. Selective enrichment can be achieved due to the physical nature of the capillary action in the upward direction and the deposition surface. Partial laws for the upward capillary rise of solutions were formulated in studies of agricultural soils. The soil particle size and stratification structure were shown to influence the capillary action considerably. To leach valuable compounds in situ, their velocity and the large contact surface area between the solution and solid material in the capillary system are important. These parameters must be optimized to ensure that the extraction is complete and the

upward capillary leaching process can be controlled. For estimation of some main parameters, the laboratory experiments were made.

The tailing sample 5500 cm³ was placed in the cylindrical process column. The process solution was fed from below of the column; the solution was drinking water with pH ~ 7.0 and acid water with pH ~ 3.0. The column was equipped with branch tubes to sample the solution after filtration through different layers of solid phase (17, 40, 63 cm). The experiment was ran in two stages: water washing for 2.5 months and weak acid solution washing for same months. Daily, the contact solution was sampled, and chemical composition of the samples was analyzed using mass-spectrometer Agilent 7500 IGPMS. The content of Cu, Ni, Co, Fe, Mg, Pt, Pd, and Au was under control. Phase compositions of mineral forms were determined by geochemical analysis [10] of samples from the top, middle, and bottom layers of the process column. The initial geochemical analysis is presented in **Figure 2**. Mineralogical analysis of original material showed that the water-soluble forms made up the major part of the precious metals (31–46%), and the next largest was the part of crystal iron and manganese oxides (20–30%). Copper, nickel, and cobalt were in the form of sulfide minerals (43–61%); oxide phases were 13–27%. Exchange phases contained 4–10% of precious metals.

The test with drinking water for 2.5 months revealed that nonferrous and precious metals are prone to transit to a water-soluble exchangeable phase from the old tailing material. The transition of precious metals to the exchangeable phase runs no more intensively as compared to copper, nickel, and cobalt. Very weak partial dissolution of precious metals and their transition to the solution were established: gold and platinum up to 0.0006 mg/l and palladium up to 0.018 mg/l. The maximum content in the production solution was recorded for Au on the 5–7th days of activation, for Pt and Pd on the 2nd–3rd days with the further concentration decrease of the said components in the production solution. Redeposited mineral forms of precious metals contained water-soluble forms (9–17% gold and platinum, 5–8% palladium), iron oxide forms (26–53% platinum and 16–55% palladium), and organic matter forms (to 50% gold, to 17% platinum and palladium) as shown in **Figure 1**. Transfer of precious metals in the exchange form causes secondary geochemical processes when precious metals can go to amorphous oxides. That was observed experimentally: to 39% palladium and to 16% gold and platinum passed into amorphous oxides. Distribution of precious metals in the phase forms is different at different check levels heightwise the column of the tailings. For Pt in the top and middle layers, 50% are oxide forms, and the bottom layer is mainly carbonated. Pd oxide forms prevail in any layer. Gold from 31 to 50% is bound to organic matter forms and from 14 to 32%—to oxides. The water-washed nonferrous metal distribution in mineral forms is nearly identical in the tailings' column layers. There are almost no soluble forms, except for a few in the top layer (to 3%). In the middle and bottom layers, 54–71% nonferrous metals occur in sulfide and metal forms; in the top layer, there are few sulfides and more carbonates and sulfates (29–36%) and oxide phases (20–30%). There is low transfer of nonferrous metals to the exchange phase because these metals occur in the original material in weak-soluble forms of sulfide and oxides, which prevents from the redistribution. A low content of copper, cobalt, and nickel ions in the solution, mg/l: Cu up to 1.8, Co up to 0.11, and Ni up to 4.1, is explained by the fact that they are present in the initial material in the hardly soluble form as sulfides and oxides, thus hampering their redistribution. Migration capabilities of copper, nickel, and cobalt species are extremely low in an actually neutral aqueous medium. It is found that with the increase in time of percolation through a tailing layer, the content of copper, cobalt, and nickel tends to grow in the solution with the respective correlation versus iron content in the solution. This fact justifies the statement that nonferrous metals (copper and cobalt

in a greater degree and nickel in a less degree) are prone to adsorb onto iron compounds, for example, on its hydroxides (III), and to transit to the solution with decomposition of iron-containing minerals: pyrrhotite and chalcopyrite with the release of iron species into the solution. The acidity of the solution in the middle part of the column increased to $\text{pH} \sim 3.0$ after 2.5 weeks of filtration. At the top of the column, the acidity was close to normal ($\text{pH} \sim 6.0$) until the end of the third week. Geochemical phase analysis shows significant changes in the massif structure (Figure 7). This effect is due to water filtration. Phase transformations of mineral compounds in the bowels of the Earth are due to the occurrence of geological processes of hypergenesis. The geological natural process of hypergenesis in the presence of filtration does not stop, and even more than that, it proceeds more intensively than when there is no access of oxygen to the massif.

With an increase in the acidity of the medium, a more intense transition of nonferrous metals into the solution should be associated. Due to the effect of changing the acidity of the fluids during the supply of neutral water, experimental studies were carried out with the supply of initially weakly acidic water.

Pretreatment of the sampled material by acid solution to $\text{pH} = 3$ also changes the composition of nonferrous and precious metals subject to the thickness of the filtering layer. In this case, the correlation is direct unlike the first stage of the experiments. For thicker filtering layers, it is typical that the solutions have higher average values of the commercial mineral contents. The solutions sampled from layer 85.5 cm thick have nickel and cobalt contents 1.5 times higher than the solutions sampled from layer 40.5 cm in thickness. The platinum and gold contents change three times, while the copper and palladium contents are scarcely changed. The metal recovery in solution results obtained on the samples after the water washing and acid solution washing for 90 days is significantly different. The major portion (75%) of the soluble ion exchange forms of precious metals has gone to solution or redeposited in the epigenetic mineral forms. This share for nonferrous metals is 50–75%. Thus, water-soluble forms of nonferrous and precious metals are mobile, and their water leaching is quite feasible. The higher recovery is observed for gold (24%) and platinum (3.9%) in the filtering layer of tailings 85.5 cm thick, with the acid water pretreatment. Dissolution of the components with the weak acid solution is more intensive than with the water drink solution. The weak acid solution pretreatment improves copper, nickel, cobalt, and palladium recovery 4–9 times and platinum and gold recovery 500–4000 times. The analysis of redistribution of nonferrous and platinum group metals and gold in different mineral phases has confirmed the assumption on soluble forms of nonferrous and precious metals to appear in weathered aged tailings; some of the water-soluble forms go to solution and some redeposit as epigenetic minerals. Passing into solution intensifies in a weak acid solution with $\text{pH} = 3$. A weak acid solution forms independently in massif

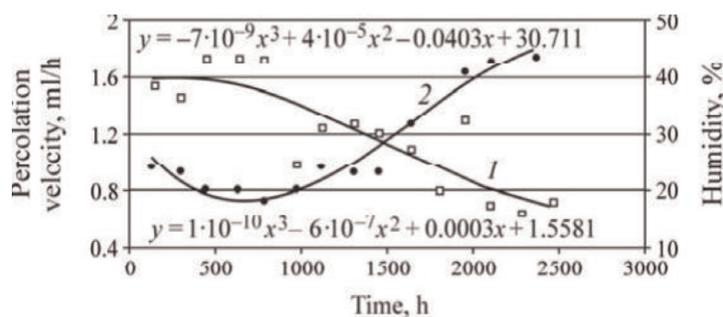


Figure 7.

Variations in velocity of $\text{Co}(\text{NO}_3)_2$ solution filtration with geochemical lignite barrier in terms of variations in atmosphere humidity during the test: (1) percolation velocity; (2) humidity.

in the presence of crystalline and sulfide phase states in the original massif. Redistribution intensity of metal in mineral phases is different with different thickness of filtering layers and with different treatment solutions. After the water washing, epigenetic minerals contain precious metals in the form of organic compounds and iron oxide phases and a few soluble and ion exchange forms (9–17% gold and platinum, 5–8% palladium). After filtration of the weak acid solution, the amount of soluble forms remains the same, but metal passing into solution is higher. Passing of metals into solution correlates with the thickness of the filtering layer: under the water treatment, the thicker is the filtering layer, the less is the metal passing into the solution; under the weak acid solution treatment, the metal passing into solution is higher in the thicker filtering layer. The occurrence of soluble forms of precious metals inspires further research toward the creation of brand-new methods of commercial mineral recovery from processing waste. One of the methods may be the method of leaching by ecological nonaggressive solutions. The test experiments have shown recoverability of 28.4% gold and 3.9% platinum using the weak acid treatment solution. The water leaching approach requires smaller investment and is ecologically friendly. This research direction seems advisable.

Experimental studies with the upward movement of solutions in the array, at the water base, are aimed at carrying out a fundamental assessment of the technological applicability of direct concentration formation in the near-surface place of the massifs. The development option for the natural part of the field can be formed along the directions of concentration of mineralization on the surface of the massif, in the near-surface zone of the evaporation barrier, hygroscopic accumulation, and collection of the production solution from the surface area of the massif. In addition, there may be new approaches with geochemical and physical barriers to the upward capillary movement of solutions. The basis of such technological options for the extraction of useful components lies in the use of the hydrogeological natural resource of the Earth's interior.

Figure 8 shows the scheme of surface collection of the production solution with rising capillary filtration for an enrichment waste massif as a probable technological variant of the upward capillary lifting of the solution.

The content of useful components in the places of storage of the wastes is very low, and it is unprofitable to extract them by existing technology. The natural effect of the ascending capillary movement of fluids in the near-surface layer of the Earth's subsoil array allows preliminary selective concentration of useful and harmful components. When the zones of accumulated concentration of the useful component are created, the technology allows extracting profitably (**Figure 9**).

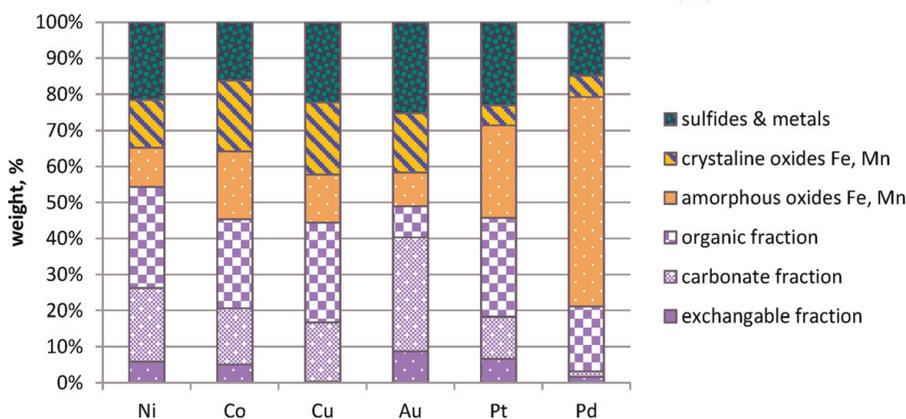


Figure 8.
Geochemical phase analysis of the metals at the end of the experiment.

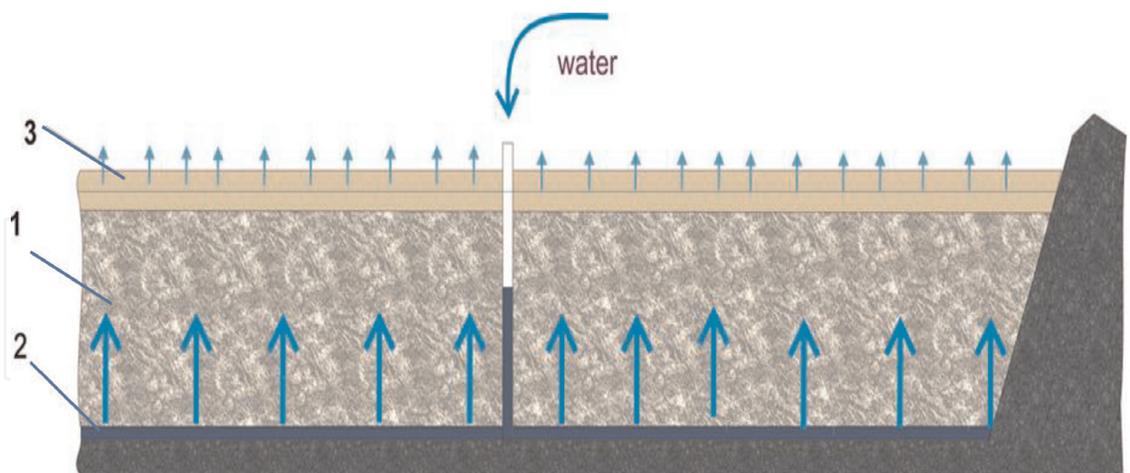
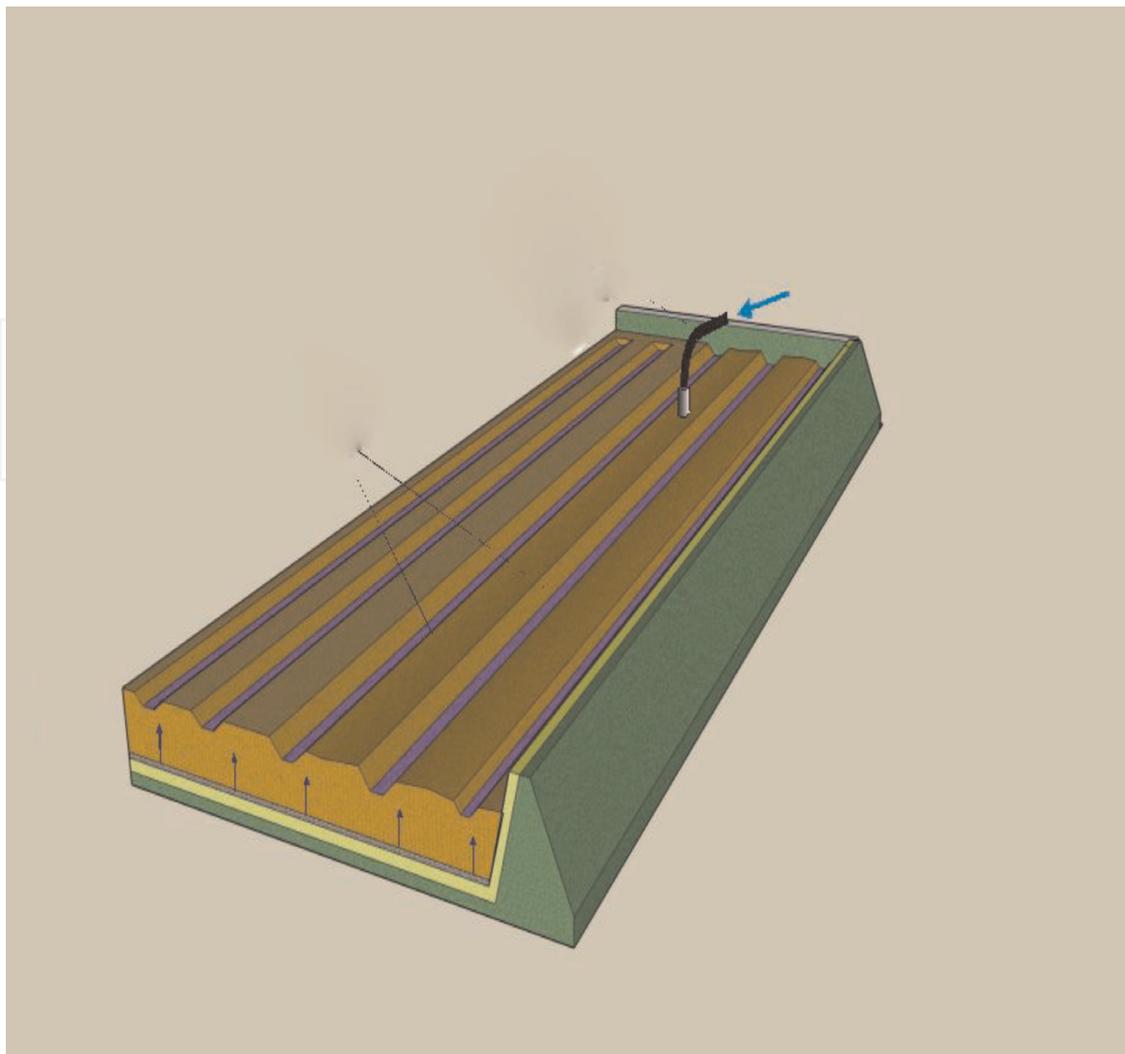


Figure 9. Technological scheme for extracting useful components by water leaching and filtration lifting with surface collection of the production solution. (1) waste massif; (2) aquifer; (3) catchment surface channels (hygroscopic material).

5. Conclusion

The capillary leaching method is considered to be subsequently intensive and nontoxic to biota extraction of useful components. This way allows the subsequent intensive extraction of useful components. The mass exchange process in the capillary rise of hypergenesis carries out a gradual redeposition of the salts of nonferrous

metals from the bottom up to the direction of movement of aqueous solutions. In such a way, the carried out experiment with water as a leaching agent for moving water-soluble compounds of nonferrous metals in the massif of flotation tailings shows that the geological processes of hypergenesis allow the leaching by water to conduct a directed preliminary concentration of nonferrous metals near the surface. The conducted simple experiments with enrichment waste materials for the entire test period allowed more than 70% of water-soluble nonferrous metal salts to rise to the surface. The concentration of nonferrous metals in the surface layer rose and exceeded the values of the existing conditions. So the content of Ni, Co, and Cu in the aeration layer amounted to 0.11, 0.09, and 0.07%, respectively. This way allows the subsequent intensive extraction of useful components. To accumulate useful components in close proximity to the surface of the array, both physical barriers (evaporation) and geochemical (sorption) barriers can be used.

The nonferrous metals are constantly present in the aqueous solution throughout the entire experiment. The concentration of the salts of nonferrous metals in the solution is not the same at different levels of the massif. In the initial period of the experiment, the trend of decreases of all elements of nonferrous metals in the solution from the bottom-up takes place. In the final period of the experimental cycle, the concentration of nonferrous metals in the upper zone exceeds the concentration of the lower zone by a factor of 2–4. The mass exchange process of hypergenesis carries out a gradual redeposition of the salts of nonferrous metals from the bottom-up in the direction of movement of aqueous solutions. The concentration of the zone of nonferrous metals shifts in the direction of movement of aqueous solutions in the array. After 1.5 years of experiment, the concentration of water-soluble compounds of nonferrous metals moved to the surface. Such results allow us to propose technological schemes for preparing the deposit for development. This approach to the development of deposits is suitable for natural deposits with a low subgrade content of useful components in the massif. Also, this approach is applicable to technogenic objects, such as wastes of enrichment and warehouses of substandard ores. The basic schemes are given in the materials of this article.

The such experiment with water as a leaching agent for moving water-soluble compounds of nonferrous metals in the massif of flotation tailings shows that the geological processes of hypergenesis allow the leaching by water to conduct a directed preliminary concentration of nonferrous metals near the surface. This way allows the subsequent intensive extraction of useful components. To accumulate useful components in close proximity to the surface of the array, both physical barriers (evaporation) and geochemical (sorption) barriers can be used.

The geochemical analysis of the material composition showed that the capillary water flow intensifies the process of hypergenesis and changes the ratio of the phase composition of nonferrous and noble metals. To the end of the experiment, the content of the sulfide phase is reduced by 80%, the carbonate phase is increased by 24%, and the oxide phase is increased by 41%. Such hypergene transformations increase the proportion of water-soluble salts and increase recovery by capillary leaching.

A more complete extraction of useful components from enrichment wastes will significantly reduce pollution of the groundwater and increase the natural attractiveness of the development territory.

The presented studies, which are quite simple, made the first step toward the development of a new technology for the cultivation of mineral deposits with the maximum use of natural processes for the transformation of the material composition in situ.

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