Artificial Increase of Concentration of Useful Components on The Surface of the Massif Before the Start of Mining Works

Mikhailov A. G., Vashlaev I. I.

Institute of Chemistry and Chemical Technology SB RAS,

Akademgorodok str., 50, building 24, 660036, Krasnoyarsk, Russia

***Corresponding Author:** **Mikhailov A. G.,** Institute of Chemistry and Chemical Technology SB RAS,*

Akademgorodok str., 50, building 24, 660036, Krasnoyarsk, Russia

Abstract: *Based on a series of laboratory experiments on a unique installation for ascending filtration lift of solutions of water-soluble salts of non-ferrous metals, the regularities of mass transfer and surface deposition on the evaporation barrier were obtained. It was found that the evaporation intensity has a linear tendency to decrease over time due to changes in the porosity of the massif in the aeration zone. By controlling the evaporation intensity, it is possible to redistribute the vertical zonality of salt immobilization in the surface layer of the massif. The rules for the distribution of precipitated salts in different parts of the massif have been established to model the fluid mass transfer process.*

Key words: *massif, aeration zone, evaporation barrier, aqueous solution of salts, crystallizatio concentration of salts*

1. INTRODUCTION

During the formation of artificial concentration zones in the surface region of the massif with an ascending filtration flow of fluids, a sequential deposition of salts occurs. The regularity of the process of "sliding" mass transfer will allow the use of the mechanism in a number of technological solutions in the development of minerals of both geogenic and technogenic origin, for example, in the storage of enrichment waste or substandard ores of deposits. In rock massifs of the subsoil, the mechanisms of fluid mass transfer processes are the driving force for the transformation and transfer of ore matter [1]. Migration of useful components in massifs of waste from processing mineral raw materials and the occurrence of enrichment processes in situ with the formation of zones of both increased and decreased concentrations of various elements, both in the original geological structures of the massifs and in newly created technogenic mineral formations, is well known [2]. However, the process is not sufficiently formalized for possible application in the artificial formation of highly concentrated zones in situ. Studies of the transformation of substances during mass transfer at technogenic sites and model experiments have also revealed that hypergenic effects lead to changes in the technological properties of both ore and non-metallic minerals [3,4]. For example, enrichment waste, which usually has a finely dispersed composition, poses an ecological hazard to the environment due to its high chemical activity [5], especially in cases where the sulfide content is comparable to the content of non-metallic minerals and when the latter predominate.

Natural geological processes are not aimed at creating highly concentrated zones of useful components in massifs. The presence of deposits in the subsoil, including high-grade ores or large reserves in massifs is associated with the patterns of mechanisms of material transformation in geological processes. Most of those already developed and those being developed are due to fluid mass transfer [6]. Filtration movement of fluids in the subsoil and the presence of geochemical barriers predetermine the immobilization and locational accumulation of useful components. Given the hypothetical direction of the filtration movement of fluids in a particular area of the subsoil, one can assume the natural potential for the creation of deposits and ore occurrences of certain useful minerals. And if the direction of the fluids is controlled or even directed, then the formation of deposits can be localized in the most suitable places for technological development. Knowledge of the mechanism of the directed process of material

and structural transformation of the massif will allow in the future to initiate formation. The essence of initiation determines the creation of a no equilibrium state in the selected area of the subsoil, in which potential energy sets in motion the homeostatic mechanisms of the geological environment [7]. Not all geological processes are suitable for modeling and subsequent scaling. The most productive and technologically acceptable, in our opinion, fluid mass transfer is suitable for research. The results of many researchers are devoted to the study of fluid filtration processes in natural and man-made rocks [8,9,10 and others]. As a rule, concentrations of useful component compounds are confined to zones of geochemical and physical barriers in subsurface massifs. If there are no such barrier conditions in the massif, then concentrated zones of useful components do not arise. One of such barriers is evaporative. It is associated with the surface of the massif. A large number of rich and even unique (in terms of the content of useful components) deposits are known, confined to eversion crusts [11]. From a technological point of view, this type of barrier reprecipitation is especially attractive for several reasons. First of all, the process is controllable, relatively dynamic, scalable. An important advantage is that useful components are concentrated in the near-surface aeration zone of the massif, which is economically attractive during development. Moreover, the direction of fluid movement to the surface is natural and can be easily controlled. Natural conditions for the emergence of an evaporative barrier in nature are low atmospheric humidity and connection with the "mirror" of groundwater occurrence. In such a situation, aqueous solutions are guaranteed to rise from the aquifer to the surface, passing the aeration zone. The rise of fluids in the massif occurs due to the force of surface tension in the capillaries of the massif. In the aeration zone of the massif, the aqueous part of the fluid in the capillaries begins to evaporate, increasing the concentration of dissolved salts, and evaporation from the surface "pulls" new portions of solutions from the aquifer to replace it. And this mechanism operates continuously [12]. Constant evaporation on such barriers is capable of forming concentration zones in the near-surface areas of the massif. Under natural conditions, fluids move in an upward flow to the surface by means of capillary rise. In fact, capillary rise is a powerful natural mechanism that sets solutions in motion through a layer of the massif to the surface. It is capable of passing large volumes of fluids from the rock massif to the daylight surface with evaporation of water into the atmosphere. Ascending movement is a natural mechanism [13]. Evaporation of water in the aeration zone and directly from the surface forms a pressure gradient necessary for the upward movement of solutions. These mechanisms serve as criteria for controlling the velocity of the upward flow [14,15]. The process of evaporation of water from a solution increases the concentration of compounds. When the concentration exceeds the solubility limits of a particular salt in the fluid, these useful compounds precipitate in the capillaries of the massif in the aeration zone. Different mineral compounds have different limits of concentration of aqueous solutions, so the compounds can be fundamentally selectively precipitated at different heights of the massif in the aeration zone, depending on their maximum concentration. The aeration zone is a natural evaporation barrier that should be used in technological solutions in the creation and preparation of mineral deposits. Selective precipitation and accumulation of heterogeneous salt solutions at different levels of the aeration zone of the massif can be achieved due to controlled capillary rise at the sedimentation levels. The evaporation barrier is known in agriculture. The negative impact of the process of salinization of agricultural soils is an important aspect of plant growing, which is being combated. The main patterns of natural capillary rise and its influence on changes in soil properties are studied in the literature [16]. It is reflected that the structure, size of particles and capillaries are the main criteria for the nature of filtration [17,18]. To formalize the process when involving filtration mass transfer in a controlled technological solution in the field of extracting useful components by in situ conversion and sedimentation in the aeration zone on the evaporation barrier, it is important to study a number of parameters, the main ones of which are the speed of the capillary flow, the size of the contact surface area between the solution and the solid material and the parameters of the capillary system. To apply this phenomenon in the technological process, the main parameters should be optimized to ensure complete completion of extraction and control of the process of capillary movement of fluids. Estimates for a number of certain parameters of the ascending filtration flow are based on laboratory experiments. Based on the obtained patterns, the main principles for mathematical modeling of the process can be substantiated.

2. DESCRIPTION OF THE EXPERIMENT AND DISCUSSION OF THE RESULTS

The study was conducted on water-soluble salts of non-ferrous metals. It is well known that copper, nickel and cobalt sulfates are formed during the oxidation of sulfides of the corresponding metals, for example, in the oxidation zones of massifs under hypergenesis conditions. Sulfates are water-soluble salts and, as a rule, are part of the fluids in the subsurface. The study of the process of filtration movement and precipitation of complex salts of non-ferrous metals was carried out on the evaporation barrier. An experimental study of the vertical distribution in the aeration zone and in the massif (by zones) was carried out. Two laboratory mock-up installations were specially created for studying the process (Fig. 1), where the imitation of the massif material was performed by quartz sand with a size of -0.5 + 0.2 mm, which is very typical for the granulometric composition of the material of the weathering crust massif. The column-type installation Fig. 1 was made for the condition of vertical ascending filtration movement of fluids. A solution of sulfates (complex) with a concentration of 20% to 80% was fed into the bottom region (the concentration value was calculated from the values of maximum solubility in water at a temperature of 20°C). A constant fluid feed level was maintained at the base of the column using the Mariotte vessel principle (the fluid mirror level was at the bottom of the column).

Fig1. *Laboratory setup for ascending fluid flow.*

The massif temperature was controlled and recorded with thermometers. Atmospheric temperature and humidity were controlled with a hygrometer and an atmospheric thermometer. The massif temperature was varied by blowing hot air through the column unit. To evaluate the kinetics of fluid filtration in the massif, it is necessary to know the physical and filtration-capacitive properties of the rock. The filtration principles are characterized by known parameters [19], the critical parameters of which include the effective diameter of the particles that make up the porous medium, the height of the capillary rise. According to the conditions of the experiment of the ascending filtration movement of fluids, a water-saturated capillary layer is located above the level of the mirror. The height of the capillary rise of the fluid is specified by the parameters of the capillaries. The calculations of the filtration properties of the experimental massif are compared with the models of the massif in the installation. The calculated filtration-capacitive properties of sand are presented in Table 1

Table1: *Characteristics of the experimental array material*

Indicators	Dimension	Value
Average particle diameter	mm	0,242
Effective particle diameter	mm	0,020
Hydraulic radius	μm	3,210
Permeability	darcy	0,522
Capillary rise height	m	0,645

In accordance with the calculated data on the characteristics of the experimental material, the parameters of the laboratory setup were taken into account, in particular, the minimum diameter and height of the columns. The experiment was long-term, lasting 270 days with control of the main parameters listed above. Upon completion of the experiment, the massif material was extracted from the setup in vertical zones, in each of which a sample was taken for chemical analysis.

3. EXPERIMENTAL RESULTS

Evaporation from the surface usually leads to the formation of crystals at the mouth of the capillaries. The temperature of the massif material and the temperature of the atmosphere determine the kinetics of the evaporation process, which in turn determines the concentration of fluid salts near the meniscus. The concentration in the capillaries in the aeration zone can exceed the maximum concentration, and will lead to the formation of sediment and crystallization on the surface of the capillaries. With regard to solutions with low evaporation rates, the concentration of the solution at the surface of the retreating meniscus should remain constant and equal, according to the theory [20,21], The concentration of salts will increase during evaporation. The composition of the fluid fed to the columns in the experiment is given in Table 2

Table2: *Composition of Fluid Used in the Experiment*

Indicators	$Cu\,SO_4$	$NiSO_4$	$ZnSO_4$
Maximum solubility, g/l	349	220	383
Content at 80% solubility of maximum, g/l	280	176	306
Concentration of maximum solubility, %	26.0	26.0	26.0

During the experiment, the evaporation rate was monitored in order to determine the dependencies for the mathematical model of the mass transfer and sedimentation process in the aeration zone and elsewhere. The obtained dependencies are shown in Fig. 2, 3, 4.
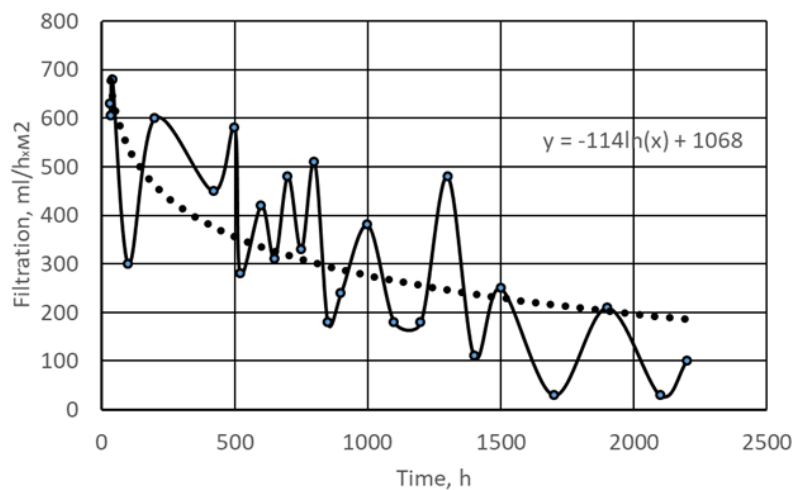

$$y = -114\ln(x) + 1068$$

Fig2. *Change in evaporation rate during the experiment*
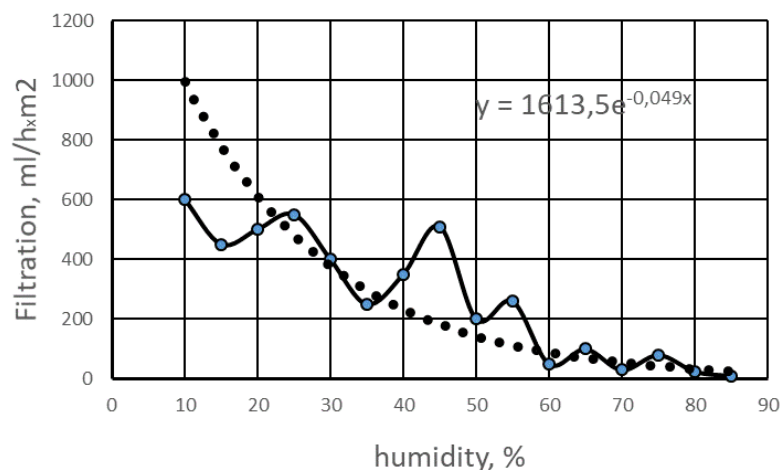

$$y = 1613{,}5e^{-0{,}049x}$$

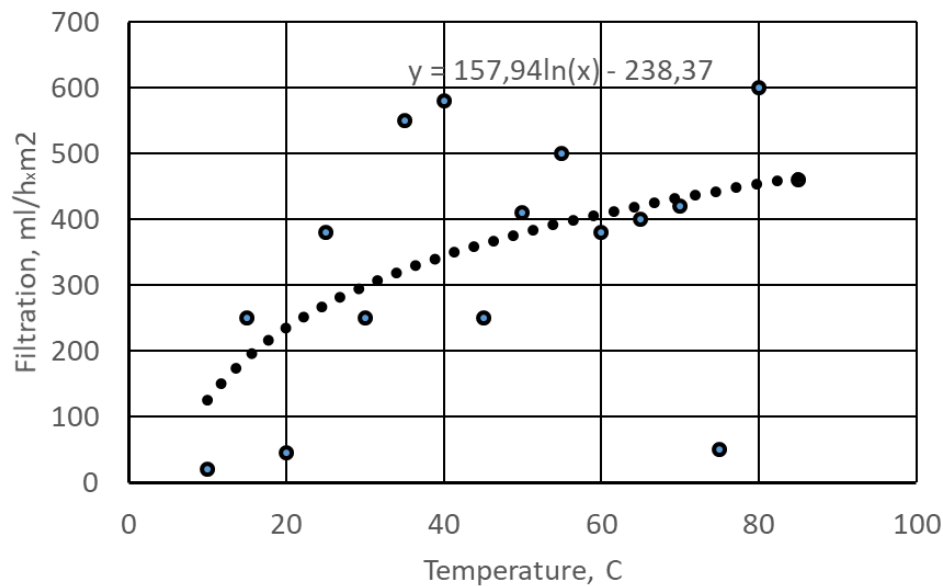**Fig3.** *Dependence of the evaporation rate on atmospheric humidity*

Fig4. *Effect of air temperature on evaporation rate*

The most significant factors were the duration of the process, humidity and air temperature. It is characteristic that over time, copper sulfate is deposited in the sand massif and pores in the aeration zone are calcified. As a result, the cross-sectional area of the capillaries decreases. An increase in air humidity reduces the rate of evaporation from the surface, the range of air humidity is 20 - 49%. The moisture capacity of the atmosphere depends significantly on temperature, so an increase in air temperature by 1 degree Celsius increases moisture absorption by 7-11% in the temperature range from 15 to 24 degrees Celsius [22]. The results of the experiment confirmed the theoretical assumptions [23], according to which, during evaporation, the increase in the concentration of the solution is compensated by the diffusion removal of the crystallization point deep into the capillary and the evaporation rate continuously decreases. Experimental studies conducted with different solutions and materials also indicate a decrease in the intensity of evaporation due to the transfer of salt to the surface layers [24]. For more intensive precipitation with the formation of a crystalline crust on the surface, according to the regularity (5), the evaporation rate and, accordingly, the speed of movement of solutions in the capillaries of the array must be increased. Experimentally, this was achieved by increasing the temperature of the array to 40 °C and additionally using a blower of warm air at a speed of 5-7 m / s on the surface of the array. Such parameters provide an increase in the speed of solution transfer to the surface to values 3 - 5 mm / h, which is 7 - 9 times higher than the speed of movement under normal experimental conditions (20 ° C and without blowing the surface). After the precipitation and its crystallization in the capillaries, the evaporation rate slightly decreases [25]. The appearance of crystals on the surface of the array is observed already in the second week. After 120 days from the beginning of the experiment, the main part (80%) of the salt entering the column is in a crystalline state. At low evaporation rates (t ~ 20 °), crystallization on the surface began to be visually observed in the second month from the beginning of the experiment. It has been experimentally established that the concentration of the solution corresponds to the concentration of the maximally saturated solution and crystal precipitation does not begin, and the evaporation rate decreases by 2 times. After crystallization begins, the evaporation rate begins to decrease linearly (Fig. 5).
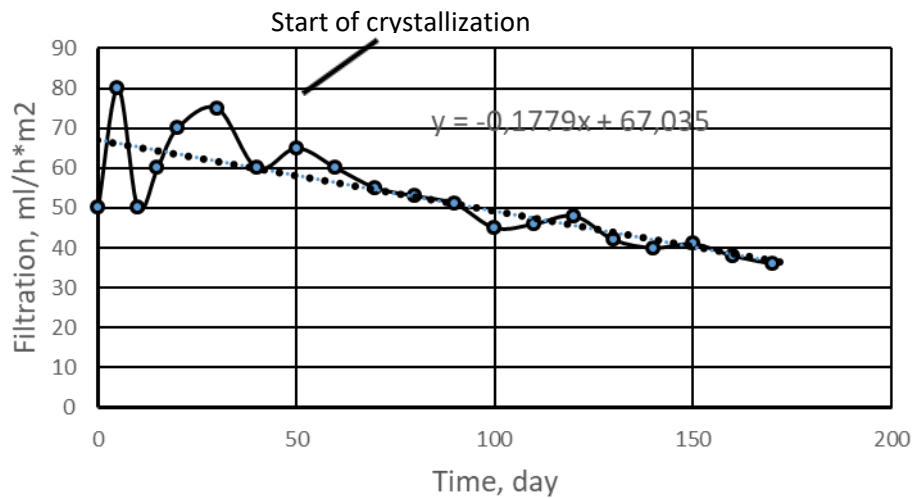
Fig5. *Evaporation rate during surface crystallization of a complex salt of 80% concentration*

The filtration process slows down for a fairly long period (up to 6 months), and the crystal growth is stable, but very slow. This can be explained by the fact that the sediment narrows the cross-section of the capillaries, reduces the real evaporation surface and reduces the evaporation rate. According to theory (5), the concentration of salt at the meniscus should be constant, and this should lead to the dissolution of part of the formed crystals and the transfer of the substance along the capillaries in the sediment to contact with the atmosphere. This, in turn, partially increases the evaporation rate and again promotes an increase in concentration. This promotes crystal growth and then the evaporation surface decreases again. In this mode of change in the volume of crystals, precipitation with the growth of the salt crust occurs for a long time. In the course of our experiment, during the two-year period of the experiments, the speed of movement of the solutions stabilizes, decreasing after 2 months with a stable trend of linear decrease within 7 - 12% per month. It should be noted that during precipitation, the salt crust is not formed uniformly on the surface (Fig. 6). In our opinion, this is primarily due to the heterogeneity of the structure of the salt crust and capillaries between the crystals, which in turn affects the crystallization points. The pores in the salt crust are distributed chaotically. And in the aeration zone, near the surface, as in the massif, there are dead-end pores without an outlet to the surface, which restrains the release of solutions in the surface areas. In areas where there are through pores, a relatively rapid release of solutions to the surface and their crystallization is due. Crystals are formed first in the area of such areas. It has also been experimentally noted that in all cases, including with intense evaporation, salt crystallization gravitates toward the periphery of the massif surface (closer to the column walls). In our opinion, this is due to a higher level of ventilation of the outskirts and, accordingly, the evaporation rate. Under the conditions of the experiments, a threefold excess of contents was recorded in the peripheral areas, along the column walls, compared to the central part of the experimental massif. As for the specific conditions of our experiment, the increased crystallization rate along the perimeter of the columns is due to the higher speed of movement of the solutions along the smooth surfaces of the glass columns. This effect is also consistent with the studies cited in [26]. During evaporation without increasing the temperature, the evaporation flow is much more uniform over the surface and the salt precipitation is comparatively uniform.

4. CONCLUSION

Precipitation on evaporation barriers in the massif aeration zone serves as a combined zone of concentration of complex salts of non-ferrous metals while maintaining the "mirror" of the massif water content level and directed upward movement of solutions to the surface. Water evaporation from the surface causes an increase in the concentration of useful components as a technological solution for preliminary enrichment in the near-surface aeration zone of the massif in situ. The nature of the precipitation of water-soluble copper, nickel and cobalt sulfates depends on the conditions of passage of solutions through the evaporation barrier. The distribution of concentration in the massif aeration

zone is facilitated by the speed of movement of solutions (depending on the evaporation rate). At a low speed of movement, the evaporation zone spreads inside the massif itself, moving towards the central part of the massif (from the surface), due to which the filtration rate of the solution decreases, since the decrease in humidity from the middle part of the massif is compensated by its inflow from the lower, more saturated layer. This leads to an increase in the concentration of the solution in the central part of the massif aeration zone. Low speed of solution movement at low air temperature and high humidity does not provide pronounced zonality of salt crystallization in the massif. In this case, crystallization spreads throughout the aeration zone with a decrease in content from the lower layers to the surface. Such distribution is typical for both the initial highly concentrated solutions and relatively lean ones. With an increase in the speed of solution transfer to the evaporation zone from the surface, a surface crystallization zone is formed. It can be assumed that additional phenomena of thermal and moisture conductivity arise. An increase in the evaporation intensity due to heating of the massif material and blowing of the surface, crystallization begins in the pores of the massif, starting from 7 - 10% (aeration zone) from the surface. With the onset of crystallization on the surface, the speed of filtration rise of the solution and, accordingly, the evaporation rate begins to fall linearly, decreasing to 12% per month. Based on the experiments, it was found that the intensity of solution movement and the formation of a salt crust during crystallization can be controlled by varying the filtration rate to the evaporation barrier and directly inside it.

REFERENCES

[1] Peshkov A. A., Bragin V. I., Mikhailov A. G., Matsko N. A. Geotechnological preparation of mineral deposits. - M.: Nauka, 2007. - 286 p.

[2] Kazdym A. A. Man-made deposits and man-made mineral formation. - M.: VIMS, 2010. - 178 p.

[3] Chanturia V. A., Makarov V. N., Makarov D. V. Ecological and technological problems of processing man-made sulfide-containing raw materials. - Apatity: KSC RAS, 2005. - 218 p.

[4] Chanturia V. A., Makarov V. N., Makarov D. V., Vasilyeva T. N., Pavlov V. V., Trofimenko T. A.Influence of storage conditions on the change in the properties of copper-nickel technogenic products //FTPRPI. — 2002. — No. 6. — P. 96 – 102.

[5] Masloboev V. A., Seleznev S. G., Makarov D. V., Svetlov A. V. Assessment of the environmental hazard of storing waste from mining and processing copper-nickel ores // FTPRPI. — 2014. — No. 3. —P. 138 – 153.

[6] Pospelov G. L. Paradoxes, geological and geophysical essence and mechanisms of metasomatism. — Novosibirsk: Nauka, 1973. — 355 p.

[7] Makarov A. B., Talalay A. G. Technogenesis and ecology. - Ekaterinburg: UGMU, 1999. - P. 4 - 41.

[8] Zosin A. P., Priymak T. I., Koshkina L. B. Ecological aspects of the processes of geochemical transformation of mineral waste from the processing of sulfide copper-nickel ores // Ecol. chemistry. - 2003. - No. 12 (1). - P. 33 - 40.

[9] Chanturia V. A., Makarov D. V., Makarov V. N., Vasilyeva T. N. Oxidation of non-metallic and sulfide minerals in model experiments and in real tailings dumps // Gorn. zhurn. - 2000. - No. 4. - P. 55 - 58.

[10] Maeva S. G. Fundamentals of geochemistry. — Tiraspol, 2016. — 120 p.

[11] Kalinin, Yu. A. Gold-bearing weathering crusts of southern Siberia / – Novosibirsk: Geo, 2006. - 337 p.

[12] Oddie T. A. and Bailey A. W. Subsoil thickness effects on yield and soil water when reclaiming sodic minespoil, J. Environ. Qual., 1988, Vol. 17, No. 4. — P. 623 – 627.

[13] Li X., Chang S. X., and Salifu K. F. Soil texture and layering effects on water and salt dynamics in the presence of a water table: a review, Environ. Rev., 2014, Vol. 22, No. 1. — P. 41 – 50.

[14] Shokri N., Lehmann P., and Or D. Evaporation from layered porous media, J. Geophys. Res., 2010, Vol. 115, B06204.

[15] Ma Y., Feng S., Zhan H., Liu X., Su D., Kang S., and Song X. Water infiltration in layered soils with air entrapment: modified Green-Ampt model and experimental validation, J. Hydrol. Eng., 2011, Vol. 16, No. 8. - P. 628 – 638.

[16] Scanlon B. R., Keese K. E., Flint A. L., Flint L. E., Gaye C. B., Edmunds W. M., and Simmers I. Global synthesis of groundwater recharge in semiarid and arid regions, Hydrol. Process, 2006, Vol. 20, No. 15. - P. 3335 – 3370.

[17] Meiers G. P., Barbour S. L., Qualizza C. V., and Dobchuk B. S. Evolution of the hydraulic conductivity of reclamation covers over sodic/saline mining overburden, J. Geotech. Geoenviron, 2011, Vol. 137, No. 10. - P. 968 – 976.

[18] Shestakov V. M. Hydrogeodynamics. — M.: Moscow State University, 1995. — 368 p.

[19] Umarov N. V., Isamukhamedov Ya. U. Water-salt regime of the aeration zone and groundwater of irrigated areas. — Tashkent, 1991.

[20] Zolotarev P. P. On the evaporation of liquid from a flat surface of a solution // DAN SSSR. — 1966. — V. 168. — No. 1.

[21] Tishkova R. A., Churaev N. V., Ershov A. P. Evaporation rates of concentrated electrolyte solutions from thin capillaries // Ing.-Phys. Zh. - 1979. - T. 37. - No. 5.

[22] Shmeterer S. M. Air humidity // Physical Encyclopedia / Ch. ed. A. M. Prokhorov. - M.: Soviet Encyclopedia, 1988. 704 p.

[23] Gamayunov N. I., Gamayunov S. N., Mironov V. A. Osmotic mass transfer: monograph. — Tver: TSTU, 2007.

[24] Veran-Tissoires S., Marcoux M., and Prat M. Why salt clusters form on basement walls, Physics 5, 15 2012

[25] Mikhailov A. G., Kharitonova M. Yu., Vashlaev I. I. et al. Precipitation of salts from solutions during their capillary rise in the surface aeration zone of the massif // FTPRPI 2019 No. 3, pp. 156-161

[26] Parfenova N. I. Correlation and assessment of the accuracy of rock salinity determination for land reclamation purposes (using the Ushakovsky site of the Sarpinskaya lowland as an example) // Issues of hydrogeological studies for land reclamation. Issue 37. — M.: VSEGINGEO, 1971