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**Mathematical prediction of the scale of migration of heavy metals in the soil profile**

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**SUMMARY**

During the field development, metal mining and ore-dressing treatment, as a rule, waste are generated that pollutes the environment, in particular, soils and groundwater.

The article presents the results of the study of the mechanism of diffusion of minerals in the soil environment, as well as the determination of the diffusion coefficient of the component in the dispersed solid-liquid system in the steady state. The results of the study of the migration of copper ions, which are contained in the wastewater of galvanic industries, etc. are presented. To mathematically describe the distribution of contamination in the soil, a mathematical model for the diffusion of the component in a semi-confined space was used. Model of physical and mathematical description of the movement of pollution from phosphogypsum dumps, which allows to improve the ecological situation around the dumps and takes into account the parameters of the density of the substance and the parameters of convective-diffusion transfer of pollution. According to experimental data and a mathematical model of the process, the diffusion coefficient in the soil environment under the conditions of a stationary process and at a constant concentration of pollutants on the soil surface was calculated. The distribution of the pollutant concentration on the soil profile from time to time according to experimental and data is given. As a result, according to the established dependence, according to experimental data, the concentration distribution in the area of action of phosphogypsum heaps along the soil profile was constructed.



## Introduction

A large number of minerals that are by-products of mining and chemical production are stored in the form of dumps and stored in the form of brine in dumps and tailings. In the production of phosphoric acid by sulfuric acid method as a by-product is formed phosphogypsum - calcium sulfate with impurities of phosphates. Per 1 t of P<sub>2</sub>O<sub>5</sub> in phosphoric acid, depending on the raw material used, from 3.6 to 6.2 t of phosphogypsum in terms of dry matter (7.5-8.4 tons in terms of dihydrate) are obtained. Depending on the conditions of phosphoric acid production, CaSO<sub>4</sub> • 2H<sub>2</sub>O dihydrate, CaSO<sub>4</sub> • 0.5H<sub>2</sub>O hemihydrate or anhydrous calcium sulfate are formed in the precipitate, which determines the corresponding product names - phosphogypsum, phospho hemihydrate and phosphate hydrite. These wastes are gray fine-crystalline powder with a moisture content of up to 25-40% (depending on the conditions of phosphoric acid production). In terms of dry matter, they contain up to 94% CaSO<sub>4</sub>. The main impurities in them are unreacted phosphates, one-and-a-half oxides, fluorine and strontium compounds, unwashed phosphoric acid, organic substances. They contain compounds of strontium, fluorine, manganese, molybdenum, cobalt, zinc, copper, rare earth and some other elements (*Trus et al., 2020*). The purpose of the work is to study the mechanism of diffusion of minerals in the soil environment, as well as to determine the diffusion coefficient of the component in the dispersed solid-liquid system in the steady state.

## Method and Theory

The processes of diffusion distribution of heavy metals in the environment undoubtedly create a potential danger to the environment, namely: soil pollution, hydrosphere by heavy metals, etc (*Wang and Liu, 2020*).

To assess the migration of heavy metals, an important point is the mathematical interpretation of the process, which allows you to realistically calculate the rate of penetration of heavy metals into the environment. We described the process of diffusion of heavy metals by a system of equations:

$$\begin{cases} \frac{\partial C}{\partial \tau} = D \cdot \frac{\partial^2 C}{\partial z^2} \\ C(0,0) = C_{n0} \\ C(\infty, \tau) = 0 \\ \left( \frac{\partial C}{\partial z} \right)_{z=\infty} = 0 \end{cases} \quad (1)$$

Applying the method of separation of variables to solve this system, taking, we obtain the value of the concentration at time  $\tau$  at a distance  $Z$  from the soil surface.

$$C(Z, \tau) = \int_0^{\infty} e^{-a^2 \lambda^2 \tau} [C_1 \cos \lambda Z + C_2 \sin \lambda Z] d\lambda \quad (2)$$

where  $\lambda$  – constant, which must be found for this differential equation.

By integrating the equation on  $\lambda$  in the range from 0 to  $\infty$  and substituting in the equation the values of the constants of integration  $C_1$  and  $C_2$  we obtain:

$$C(Z, \tau) = \frac{1}{\pi} \int_0^{\infty} e^{-a^2 \lambda^2 \tau} \int_{-\infty}^{\infty} [\phi(\alpha) \cos \lambda(\alpha - Z)] d\alpha d\lambda \quad (3)$$



By making a substitution  $a\lambda\sqrt{\tau} = x$   $\frac{a-Z}{a\sqrt{\tau}} = \beta$  we can calculate

$$K(\beta) = \int_0^{\infty} e^{-a^2\lambda^2\tau} \cos \lambda(\alpha - Z) d\lambda$$

$$K(\beta) = \frac{\sqrt{\pi}}{2} e^{-\frac{\beta^2}{4}} \quad (4)$$

Substitute (4) into (3) and obtain:

$$\int_0^{\infty} e^{-a^2\lambda^2\tau} \cos \lambda(\alpha - Z) d\lambda = \frac{1}{2a} \sqrt{\frac{\pi}{\tau}} e^{-\frac{(\alpha-Z)^2}{4a^2\tau}} \quad (5)$$

Substituting (5) in (2) we obtain:

$$C(Z, \tau) = \frac{1}{2a\sqrt{\pi\tau}} \int_0^{\infty} f(\phi) e^{-\frac{(Z-\phi)^2}{4a^2\tau}} - e^{-\frac{(Z-\phi)^2}{4a^2\tau}} d\phi \quad (6)$$

where  $\phi$ ,  $\alpha$  – constants that must be found for this differential equation.

After integrating equation (6), substituting the initial conditions, we obtain the expression for determining the concentration of the released component at a distance  $Z$  from the soil surface at time  $\tau$ :

$\frac{C_n - C}{C_n} = \text{erf}\left(\frac{Z}{2a\sqrt{\tau}}\right)$  (Symak, et al., 2021). Substituting in the equation:  $a^2 = D$  we obtain:

$\frac{C_n - C}{C_n} = \text{erf}\left(\frac{Z}{2\sqrt{D\tau}}\right)$ . Then we get:

$$C = C_{II} \left( 1 - \text{erf}\left(\frac{Z}{2\sqrt{D\tau}}\right) \right) \quad (7)$$

At the initial moment of time  $\tau_0$  mass of dissolved heavy metal salt  $M_0 = FdZ \cdot C_{II0}$ , where  $F$  – the surface area of the heavy metal salt particle.

At the moment of time  $\tau$   $M = FdZ \cdot C_{II}$

$$M = jF\tau$$

$$M_0 - M = M_0 - jF\tau$$

Given that the mass flow rate:

$$J_F = -D \cdot \left( \frac{\partial C}{\partial z} \right)_{z=0} \cdot \varepsilon \cdot F \quad (8)$$

where  $\varepsilon$  – soil porosity.

$$M_0 - M = \int_0^{\tau} -D \cdot \left( \frac{\partial C}{\partial z} \right)_{z=0} \cdot d\tau$$

$$1 - \frac{M}{M_0} = \frac{1}{M_0} \int_0^{\tau} -D \cdot \left( \frac{\partial C}{\partial z} \right)_{z=0} \cdot d\tau$$

$$\frac{C_{II}}{C_{II0}} = 1 - \frac{1}{M_0} \int_0^{\tau} -D \cdot \left( \frac{\partial C}{\partial z} \right)_{z=0} \cdot d\tau$$

The solution will be as follows:



$$C_{II} = C_{II0} - \frac{2 \cdot \varepsilon}{M_0} \cdot \sqrt{\frac{D}{\pi}} \cdot \sqrt{\tau} \quad (9)$$

$$C^* = \frac{M_0}{\varepsilon}$$

The average concentration of metal ion in the soil solution

$$C_n = C_{n0} - \frac{2}{C^*} \cdot \sqrt{\frac{D}{\pi}} \cdot \sqrt{\tau} \quad (10)$$

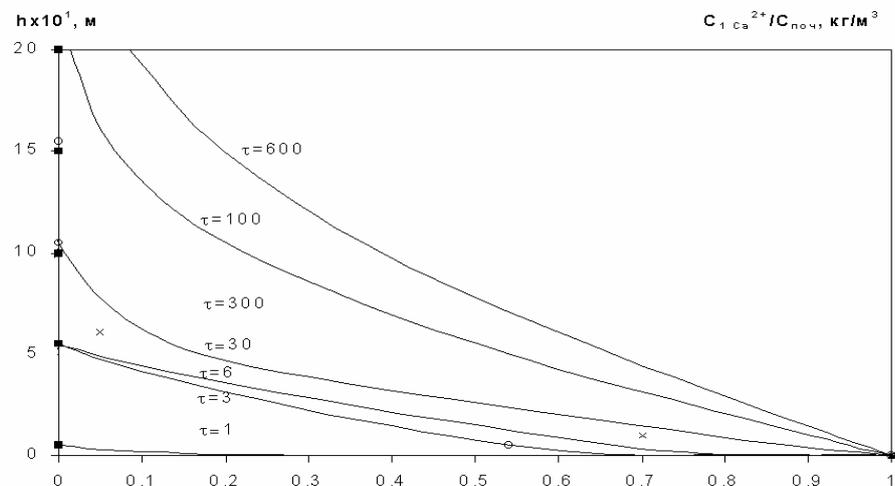
Substituting expression (10) in (7) we obtain the equation for calculating the concentration of heavy metals at a depth of Z from the soil surface:

$$C = \left( C_{n0} - \frac{2}{C^*} \cdot \sqrt{\frac{D}{\pi}} \cdot \sqrt{\tau} \right) \cdot \left( 1 - \operatorname{erf} \cdot \frac{z}{2 \cdot \sqrt{D \cdot \tau}} \right) \quad (11)$$

To study the mechanism of migration of heavy metals in the soil environment, consider a zone with a concentration of  $C_1 = \text{const}$  on the soil surface. The distribution of the substance occurs in a fixed layer of soil with a porosity of  $\varepsilon = 0.4$ . The pores of the medium are filled with water. Copper sulfate was used to study the migration of heavy metals in the soil environment (Sabadash et al., 2017). To ensure a constant concentration of  $\text{Cu}^{2+}$  on the soil surface, 50 g of salt was added to the measuring cells. Determination of ion concentration was performed by X-ray fluorescence analyzer and spectrophotometric method.

### Examples

The study of the mechanism of migration of heavy metals in the soil environment with a concentration of  $C_1 = \text{const}$  on the soil surface was performed according to the above procedure. The distribution of the substance occurs in a fixed layer of soil with a porosity  $\varepsilon = 0.4$  from the bottom of the cell to the surface, ie in the positive direction of the Z axis.



**Figure 1** The distribution of the concentration of  $\text{Cu}^{2+}$  on the soil profile from the bottom of the cell to the surface in the positive direction of the Z axis at  $t = \text{const}$ , days, where ■ -  $\tau = 1$ , ○ -  $\tau = 3$ , x -  $\tau = 30$ ,  $D = 2.27 \cdot 10^{-11}$ .

Analyzing the data of experimental studies using the solution of the mathematical model, the value of the diffusion coefficient  $\text{Cu}^{2+}$  in the soil medium on the vertical profile in the direction of the coordinate axis Z -  $D = 2 \cdot 10^{-6}$  Fig. 1. This indicates the migration of the component in the soil environment by the mechanism of turbulent mass transfer (Sabadash et al., 2018).



Diffusion coefficient  $\text{Cu}^{2+}$  in the soil medium along the vertical profile in the positive direction of the coordinate axis  $Z$  -  $D = 2.27 \cdot 10^{-11}$ . The correspondence of the developed mathematical model to the experimental data indicates the validity of the introduced simplifications and allows to predict with sufficient accuracy for practical purposes the time and speed of migration of contaminants in the soil. (Sabadash et al., 2020). The process of mass transfer of the released component takes place smoothly, in the form of the so-called diffusion front, in the zone of length  $l = Z$ , which in the experimental conditions is limited by the overall dimensions of the measuring cell. At the initial time in all areas of the measuring cell, the concentration of the target component will be zero. The change in the diffusion front in time is a curve of the distribution of the concentration of the released component in the solution placed in the pores of the inert medium along the length  $l$  of the fixed layer of wet granular material, and  $\tau_1 < \tau_2 < \tau_3 \dots < \tau_n$ , where  $\tau_i$  into the release medium. Despite the fact that according to experimental data the component penetrates rather slowly into the underground soil layers in real conditions in addition to molecular diffusion there is a convective mass transfer of pollutants and the process of filtration of groundwater through the mineral rock to underground aquifers.

Comparing the experimental and theoretical data and taking into account the value of the standard deviation  $\delta = 0\%$ , we can indicate a satisfactory convergence of the results.

### Conclusions

The processes of diffusion distribution of heavy metals in the environment undoubtedly create a potential danger to the environment, namely: soil pollution, hydrosphere by heavy metals, etc. The nature and degree of resistance of soils to pollutants is determined by the nature of the chemical bonds that are formed between the pollutants in the soil solution and in the equilibrium of mobile compounds in the solid phase of the soil. Here some chemical reactions are possible: precipitation - dissolution of pollutants in the form of sparingly soluble sediments (hydroxides, salts, complex compounds), exchange and non-exchange sorption-desorption on the active surface of solid soil phases.

### References

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