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EXTRACTION KINETICS OF TARGET COMPONENTS FROM MINERAL RAW MATERIALS IN COLUMN DEVICES

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Methods for predicting the kinetics of extraction of the target component from mineral raw materials for direct-flow and counter-current column extractors have been proposed. To analyze the operation of various industrial devices, the extraction processes of which are carried out in the layer, technique based on specific productivity has been proposed. The kinetic regularities of Al_2O_3 extraction from bauxite specs and sulfur from sulfur ore have been studied as well as the data of current countercurrent extractors from the field of hydrometallurgical plants of Ukraine have been used.

Key words: layer extraction, inorganic target components, mineral raw materials, extraction kinetics, column type extractors.

Introduction

Solvent extraction, which is also called leaching or solid-liquid extraction, is the process of removal of a solute component from the solid by using a liquid solvent. Extraction processes of target components from porous structures (solid matrixes) are widely used in different industries, especially in hydrometallurgical (copper, Al_2O_3), chemical (ozokerite, sulfur), food (soybean, sunflower, rapeseed), pharmaceutical (amaranth, althaea) and others. Widespread of extraction processes is associated with the ability to achieve the removal of the target component up to 98 % which can be found in porous structures (ore, vegetable and plant raw materials) in solid ore liquid form, under conditions of chemical interaction with the solvent and under conditions of simple dissolution. Therefore, the extraction of target components from various objects by the solvent extraction method requires the development of theoretical foundations for the efficient processes implementation.

In general, the properties of the extraction solvent, the particle size of the raw materials, the solvent-to-solid ration, the extraction temperature and the extraction duration will affect the extraction efficiency. Extraction processes are occur by complex internal and external diffusion mechanisms [1]. Transfer of the target component from the

porous structure to the phase contact surface is the slowest stage (limiting) of the process that determines the rate of the whole extraction process and corresponds to the intra-diffusion transfer. Therefore, mixing processes or application of hydrodynamic effects do not provide the desired effect for the extraction intensification in many cases. Therefore, in some cases, external diffusion transfer can be neglected and for extraction implementation grinding of solid matrixes is an effective.

As for the hardware design of the extraction process, a large number of designs of extractors have been developed for the solid-liquid system of periodic and continuous action. All of them are different from each other in terms of efficiency, energy consumption and applicability in a particular production [2–7]. Increasing the rate of technological processes and the productivity of technological equipment with a simultaneous increase in the quality of the final product are the main goals that developers set themselves when creating new or modernizing existing designs of equipment. Therefore, the research and development of new equipment for efficient processes is an urgent task.

To increase the efficiency of extraction processes, technological schemes are often

complicated and involve the installation of expensive equipment. At the same time, the implementation of the extraction process in a moving or stationary layer can provide more efficient extraction. As it is shown by numerous studies conducted by researchers [8 – 14], the extraction processes in the layer have a number of advantages over others. As it was mentioned, the extraction processes are quite complex and the choice of technological equipment should be made taking into account the kinetic regularities that determine the rate of the process and its economic efficiency.

The aim of the research is to examine the extraction kinetics of target components from porous structures and on the basis of these studies to select a more efficient process as well as to develop an appropriate technique for the analysis of work of industrial equipment.

Materials and Methods

Extraction of target components from porous structures in production conditions is carried out in devices of closed periodic or continuous action. In all cases, the concentration component on the surface of porous structures, which contain different target components in both solid and liquid states, is constantly changing [1, 8–14]. The concentration of the target component in the solution depends on many factors, the main of which is the dissolution rate of the component in the liquid, temperature, structure of the porous solid-matrix, the hydrodynamics of the process, and many others.

Fig. 1 shows schemes of direct-flow and flow-back processes of extraction of target components from porous structures, as well as changes in concentrations of the target component. Each of these schemes corresponds to a certain equation of material balance, which is not the same for different schemes of processes.

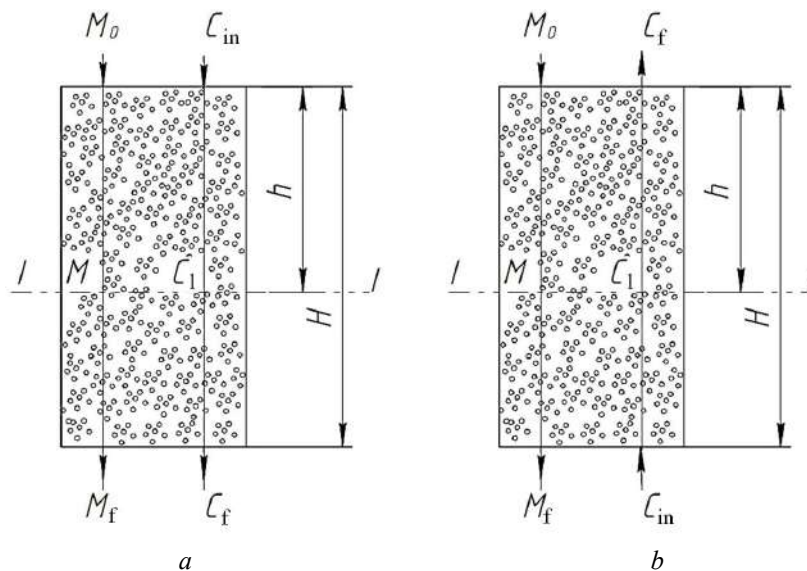


Fig. 1. Schemes of extraction processes:
a – direct-flow processes; b – flow-back processes

According to the scheme shown in Fig. 1, a, the material balance for the arbitrary cross-section of the extraction column and the outlet of the column for the liquid phase for the direct-flow process is determined by the equation:

$$\beta \cdot (1 - \varphi_0^3) = W \cdot (C_1 - C_{in}), \quad (1)$$

where $\beta = \frac{M_0}{W}$ is a content of the target component in the porous structure of mineral raw materials; M_0 is a mass of the target component in porous material,

kg; φ_0 is dimensionless radius, $\varphi_0^3 = \frac{M_f}{M_0} = \frac{r_0}{R}$ is for

spherical particle shape; M_f is a mass of the target component on the outlet of the column; R is the radius of the porous particle; r_0 is the radius, which contains the target component at time τ ; W – is a volume of solvent; C_1 is a concentration of the component in the column of arbitrary cross-section; C_{in} is an initial concentration of component.

Under conditions of a well-organized process for an arbitrary cross-section of the column, the equation may be represented as:

$$1 - \varphi_0^3 = W \cdot \frac{C_1}{C_f}. \quad (2)$$

For conditions of the complete extraction:

$$\varphi_0 = 0, \quad \text{and} \quad t = T,$$

where t is the time of changing (running time), T is the time of complete extraction.

The time of complete extraction may be determined from the equation [13 – 14]:

$$T = \frac{1}{6} \cdot \frac{\eta \cdot R^2}{\Delta C \cdot D}, \quad (3)$$

where η is a mass of the target component in the unit volume of the porous structure, kg/m^3 ; $\Delta C = (C_s - C_{in})$ is the difference of concentrations of the target component (the driving force of the extraction process), kg/m^3 ; C_s is a saturation concentration (solubility), kg/m^3 ; D is the diffusion coefficient, m^2/s .

For conditions of the constant driving force ($C_s \gg C_1$) the equation of kinetics has the form:

$$\frac{t}{T} = 1 - 3 \cdot \varphi_0^2 + 2 \cdot \varphi_0^3. \quad (4)$$

Since, according to the scheme (Fig. 1, *a*) the condition is fulfilled:

$$\frac{t}{T} = \frac{h}{H}, \quad (5)$$

where H is a full height of the material layer, m .

Taking into account equation (5), equation (4) is reduced to:

$$\frac{h}{H} = 1 - 3 \cdot \varphi_0^2 + 2 \cdot \varphi_0^3. \quad (6)$$

The flow-back process (Fig. 1, *b*) has been widely used in industry, despite a number of complications during its organization caused by the flow-back movement of the solid and liquid phases. The advantage of this process is the ability to achieve high concentrations of solution and high degrees of extraction of the target component, which can't be achieved in a direct-flow process. From a hydrodynamic point of view, this process also has advantages, as it provides a more uniform impregnation of the solution.

The flow-back process like the direct-flow is stationary and continuous. At the entrance of the extractant into the apparatus, its concentration is $C_1 = C_{in} = 0$. The mass content of the target component in the porous particles to be extracted is minimal. The equation of material balance according to the scheme for the cross-section I-I (Fig. 1, *b*) has the form:

$$\varphi_0^3 = \frac{C_1}{C_f}. \quad (7)$$

Eq. (7) obtained for conditions $\varphi_0 = 0$; $C_1 = C_m$; $\frac{M_0}{W} = C_f$.

Equations (6) and (7) make it possible to present the kinetic dependence of the extraction for the flow-back process as a function:

$$\frac{C_1}{C_f} = f\left(\frac{h}{H}\right), \quad (8)$$

A series of experimental studies were conducted to study the kinetic patterns of extraction of Al_2O_3 from bauxite specs, sulfur from sulfur ores to confirm the theoretical positions on the basis of which obtained equations (2) – (8). Also, the data of operating flow-back extractors from the field of hydrometallurgical plants of Ukraine were used.

The experiments were performed using the experimental setup represented in Fig. 2.

The experimental setup (Fig. 2) contained column 14, a system for loading material, apparatus for heating the solvent 2, the unloading system of column 5, and the solution storage tank 7. An alkaline solution (NaOH) with a concentration of 2 g/l heated to a temperature of 65 °C was used as a solvent. After the required time to heat the system to the desired temperature at the height of the column was sampling. These samples were analyzed for the content of the target components in the solution. The experiments on the dispersion of particles $d_m = 1,8 \text{ mm}$ and $d_m = 3,8 \text{ mm}$ with a rate of movement $U = 1,66 \cdot 10^{-4} \text{ m/s}$ and $U = 0,7 \cdot 10^{-4} \text{ m/s}$ were carried out. Analysis of samples for Al_2O_3 was performed by the complexometric method.

Results and Discussion

Fig. 3 presents the kinetic dependences $\frac{C_1}{C_f} = f\left(\frac{h}{H}\right)$, which are plotted according to equations (2), (6) and (7) and Tables 1 and 2 for direct-flow and flow-back processes under conditions of constant driving force $\Delta C = \text{const}$. The results of experimental studies are consistent with the corresponding results of the extraction process in the production conditions.

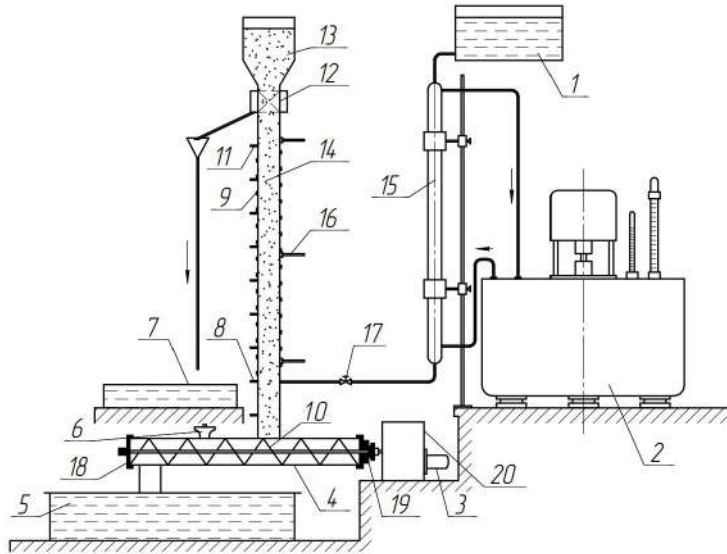


Fig. 2. Scheme of experimental flow-back setup of continuous action: 1 – storage tank; 2 – thermostat; 3 – engine; 4 – unloader; 5 – sludge storage tank; 6 – vibrator; 7 – solution storage tank; 8 – collector; 9 – electric spiral; 10 – auger; 11, 17 – crans; 12 – dispenser; 13 – bunker; 14 – column; 15 – heat exchanger; 16 – thermometer; 18, 19 – hatches; 20 – reducer

Table 1

The values of φ_0 , C_1/C_f , h/H for the construction of kinetic curves of the direct-flow extraction process

φ_0	0	0,1	0,2	0,3	0,4	0,5	0,6	0,7	0,8	0,9	1,0
C_1/C_f	1	0,990	0,993	0,975	0,938	0,874	0,789	0,653	0,493	0,274	0
h/H	1	0,974	0,898	0,786	0,651	0,503	0,354	0,221	0,108	0,031	0

Table 2

The values of φ_0 , C_1/C_f , h/H for the construction of kinetic curves of the flow-back extraction process

φ_0	0	0,1	0,2	0,3	0,4	0,5	0,6	0,7	0,8	0,9	1,0
C_1/C_f	0	0,001	0,007	0,029	0,066	0,127	0,218	0,346	0,515	0,726	1
h/H	1	0,975	0,901	0,786	0,651	0,501	0,355	0,219	0,106	0,031	0

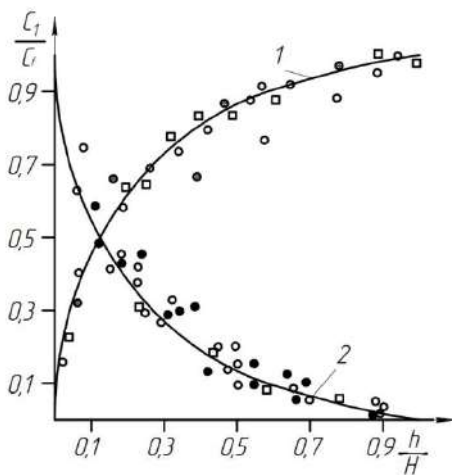


Fig. 3. Kinetics of extraction of Al_2O_3 from bauxite specs in the conditions of a fixed layer for: 1 – direct-flow process; 2 – flow-back process

In some cases, the extraction processes can take place in more complex conditions, when the process is carried out under conditions of variable

driving forces along the height of the layer of the apparatus. This task is more complex and requires a more complex technique.

It should be noted, that the driving force is determined differently depending on that which condition it is – in solid or liquid. If the target component is in the solid state, the driving force is determined by the difference between the saturation concentrations and the working concentration of the solution. If the target component in the porous structure is in a liquid state, the driving force is determined by the difference between the concentration of the component in the porous structure and the working concentration in the solution.

We have developed a number of methods [7] for the conditions of predicting the extraction kinetics of target components from porous structures, taking into account that the driving force has a variable value ($\Delta C = var$). In most cases, the driving force is a constant value, so simpler techniques are used.

The technique based on specific productivity it is possible to use for the analysis of work of various industrial equipment in which extraction processes are carried out in a layer. Specific productivity can be calculated according to the equation:

$$g_s = \frac{M_0}{T} = 3600 \cdot C_s \cdot U \cdot \varepsilon, \quad (9)$$

where g_s is the specific productivity of the extractor, $\text{kg}/(\text{m}^2 \cdot \text{h})$; C_s is a saturation concentration (solubility), kg/m^3 ; U is the filtration rate of the solution, m/s ; ε is the degree of extraction of the target component.

According to equation (9), the dependence between the specific productivity (g_s) and the filtration rate of the solution (U) is plotted (Fig. 4).

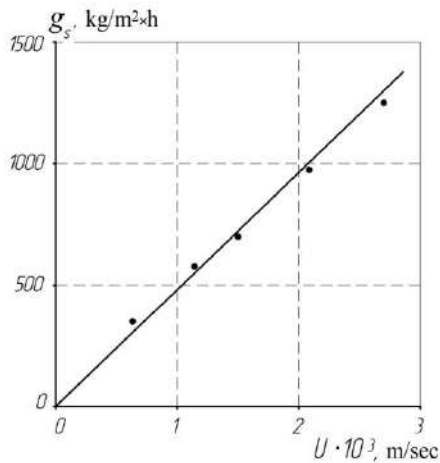


Fig. 4. The dependence of the specific productivity of the extractor on the rate of movement of sulfur ore with a sulfur content of 27 %, $d_m = 5 \text{ mm}$ for a flow-back process

Therefore, the technique based on specific productivity can be used to calculate industrial equipment using an experimental data.

Conclusion

Data of extraction kinetics of target components from porous structures of mineral raw materials in the conditions of constant and variable driving force ($C_s - C_1$) gives the opportunity to develop a technique for the calculation of extractors with a mobile layer.

The advantages of countercurrent extraction in comparison with direct flow in the conditions of variable driving force are established. If the extraction is carried out under a constant driving force ($C_s \gg C_1$), the direct and countercurrent extraction processes are unambiguous.

The technique based on specific productivity (Eq. 9) it is possible to use for the analysis of work of industrial equipment in which extraction processes are carried out in a layer.

References

1. Semenyshyn Y., Atamanyuk V., Rymar T., Ivashchuk O. and Hlukhaniuk A. (2020), Mass transfer in the solid-liquid system: Mechanism and kinetics of the extraction process. *Chemistry and Chemical Technology*, 14(1), 121–128. DOI: <https://doi.org/10.23939/chch14.01.121>.
2. Dyshlyuk L., Babich O., Belova D. and Prosekov A. (2017), Comparative Analysis of Physical and Chemical Properties of Biodegradable Edible Films of Various Compositions. *Journal of Food Process Engineering*, 40 (1), 54–67. DOI: <https://doi.org/10.1111/jfpe.12331>.
3. Gnetko L., Nerovnykh L., Gishveva S., Skhalyakhov A., Siyukhov Kh., Ageyeva N. and Volkova S. (2019), Toxins and Mechanisms of Their Interaction in Fruit Wines. *International Journal of Innovative Technology and Exploring Engineering*, 8 (9), 1978–1981, DOI: <https://doi.org/10.35940/ijitee.i8317.078919>.
4. Kodama S., Shoda T., Machmudah S., Kanda H. and Goto M. (2015), Enhancing pressurized water extraction of β -glucan from barley grain by adding CO_2 under hydrothermal conditions. *Chemical Engineering and Processing: Process Intensification*, 97, 45–54, DOI: <https://doi.org/10.1016/j.cep.2015.08.012>.
5. More N., Gogate P. (2018), Intensification of degumming of crude soybean oil using ultrasound in combination with oxidizing agents, *Chemical Engineering and Processing: Process Intensification*, 128, 132–142, DOI: <https://doi.org/10.1016/j.cep.2018.04.008>.
6. Pradal– D., Vauchel P., Decossin S., Dhulster P. and Dimitrov K. (2018), Integrated extraction-adsorption process for selective recovery of antioxidant phenolics from food industry by-product. *Chemical Engineering and Processing: Process Intensification*, 127, 83–92, DOI: <https://doi.org/10.1016/j.cep.2018.03.016>.
7. Tazova Z., Lunina L., Siyukhov H., Skhalyakhov A. and Marinenko O. (2019), The Efficiency of Extracting Biologically Active Substances from the Extracts Based on Mixtures of Medicinal Plants by the Method of Maceration with the Use of Microwave Treatment and Exposure to Ultrasound *International Journal of Engineering and Advanced Technology (IJEAT)*, 9(1), DOI: <https://doi.org/10.35940/ijeat.A1772.109119>.
8. Korniyenko Y. A. M., Stepanyuk A. R. (2015). *Protse vyluchennya huminovmisnykh materialiv z torfu: Monohrafiya*. [Elektronne vydannya]. 146 s.

9. Poperechnyy A. M., Borovkov S. O. (2007). Do pytannya intensyfikatsiyi protsesu ekstrakuvannya v systemi "tverde tilo – ridyna" / A. M. Poperechnyy, // Obladnannya ta tekhnolohiyi kharchovykh vyrobnytstv: *Temat. zb. nauk pr.* Donetsk: DonNUET. Vyp. 16. S. 104–109.

10. Hayle A. A., Sayfidynov B. M., Koldobskaya L. L., Kolesov V. V. (2010). Ékstraktsyonnaya ochystka vysokosernystoy dyzelnoy fraktsyy ot seraorhanycheskykh soedynenyy y aromatycheskykh uhlevodorodov // *Zhurnal prykladnoy khymyy.* T. 83, № 3. S. 465–474.

11. Hayle A. A., Sayfidynov B. M., Koldobskaya L. L. (2011). Ékstraktsyonnaya ochystka dyzelnoho palyva vid seraorhanichnykh spoluk i aromatychnykh uhlevodorodov // *Neftepererabotka y neftekhymyya.* № 3. S. 11–15.

12. Nho Kuen Kuyi, Safiullin R. V., Hryhorev E. I., Petukhov A. A. (2014). Ochystka vysokonavantazhuvanykh po orhanizovanykh stokovykh vod metodom ekstraktsiyi / *Vestnyk tekhnolohichnoho universytetu.* t. 17, S. 85–88.

13. Semenishyn Yt. M., Rymar T. I. (2014) Metodyka rozrakhunku pryamotechnoho ta protytechnoho ekstraktoriv dlya ekstrakuvannya tsil'ovykh komponentiv iz sharu porystykh struktur. *Visnyk Natsionalnoho universytetu "Lvivska politekhniky".* № 787: *Khimiya, tekhnolohiya rechovyn ta yikh zastosuvannya.* S. 331–336.

14. Semenishyn Ye. M., Rymar T. I. (2017). Intensyfikatsiya protsesu ta kinytika ekstrakuvannya tsilovykh komponentiv z roslynnoyi syrovyny. *Visnyk Natsionalnoho universytetu "Lvivska politekhniky". Seriya: Khimiya, tekhnolohiyi ta yikh zastosuvannya.* – Lviv: Vydavnytstvo Lvivskoyi politekhniky. № 868. S. 298–303.

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КІНЕТИКА ЕКСТРАГУВАННЯ ЦІЛЬОВИХ КОМПОНЕНТІВ З МІНЕРАЛЬНОЇ СИРОВИНИ В КОЛОННИХ АПАРАТАХ

Запропоновано методики для прогнозування кінетики вилучення цільового компоненту з мінеральної сировини різної дисперсності для прямотечійних та протитечійних колонних екстракторів. Для аналізу роботи різних промислових апаратів, процеси екстрагування яких здійснюються в шарі, можна використовувати методику, засновану на питомій продуктивності. Досліджено кінетичні закономірності вилучення Al_2O_3 з бокситових спеків, сірки з сірчистих руд, а також використані дані активних протитечійних екстракторів з області гідрометалургійних заводів України.

Ключові слова: екстрагування в шарі, неорганічні цільові компоненти, мінеральна сировина, кінетика екстрагування, екстрактори колонного типу.