Adsorber-Settler Structure in the Purification (Deactivation) of Liquid Radioactive Wastes (LRW)

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Abstract. In the conditions of modern progressive pollution by liquid radioactive wastes (LRW), and the ineffective purification of LRW using existing water treatment technologies, it is crucial to investigate and substantiate the application for retaining specific pollutants, particularly heavy metal ions and radionuclides, using sorption materials. One of the parameters affecting the efficiency of sorbents is their sedimentation rate. The sorbent's settling in the settlers occurs during the continuous movement of water at a low speed and uniform distribution throughout the volume of the purification structure from the inlet to the outlet. Experiments aimed at substantiating the constructive and technological parameters of a universal structure capable of working equally effectively with sorbents in different aggregate states. The process of sorbent sedimentation in water is characterized by the kinetics of sedimentation of sorbent flocculant conglomerates. These processes are reflected in the form of sedimentation kinetics graphs. The experiment used powdered bentonite and a solution of copper ferrocyanide, consisting of yellow blood salt and copper sulfate in a given ratio. A virtual full-scale spatial model of the illuminator-adsorber was used as the structure. During the research, the hydraulic size of bentonite powder clay was determined, the efficiency of different designs of the settler with ordinary and modernized thin-layer modules was established, and an increase in the sedimentation area was achieved. The use of virtual models of sedimentation of bentonite and zeolite powder clays and copper cyanoferrate allowed substantiating the optimal design of the illuminator-adsorber for stable and efficient sedimentation of the sorbent.

Keywords: Water purification structures · Water preparation · Bentonite · Illuminator-adsorber · Hydraulic size · Suspended particles · Sorbent · Liquid radioactive wastes

1 Introduction

Ukrainian and global problem of accumulating volumes of LRW:

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- 486 million cubic meters of liquid radioactive wastes accumulated globally, and this number is only increasing;
- 22 thousand cubic meters of liquid radioactive wastes stored in the Chernobyl NPP repositories;
- 70% of Chernobyl NPP repositories are already filled;
- 450 operating reactors and NPPs continue to add thousands of cubic meters of liquid RAW to repositories annually, outpacing the rate of their utilization.

Ways to solve the problem of minimizing the volumes of RAW:

- Extraction of radionuclides from RAW by transforming them from a soluble state to a fixed state in a solid phase, followed by their disposal.
- Returning the deactivated and purified water to its natural cycle on Earth.

Challenges in this pathway:

- A wide variety of organic and inorganic compounds in the composition of RAW.

Besides the need for appropriate sorbents, there is a necessity to develop technological structures capable of ensuring the passage of adsorption and sedimentation processes during the purification of LRW with minimal involvement of additional energy, for example, only due to gravity.

The need for maximum compaction and dehydration of the spent sorbent.

In the context of modern progressive pollution with liquid radioactive wastes (LRW) and the ineffective purification of LRW using existing water treatment technologies, it is relevant to research the application for retaining ions of heavy metals and radionuclides, various sorption materials, and further development of appropriate technological structures where the processes of adsorption and sedimentation will occur.

Research results of the effectiveness of different sorbents are necessary for selecting the most efficient ones; their hydrodynamic characteristics will directly determine the structural solutions for the given structure. In modern conditions, it has become possible to establish the parameters of the technological structure through Computational Fluid Dynamics modeling by the Volume of Fluid – modeling the free flow of fluid by the free surface method. To reduce the model to an acceptable 3–5 million elements, it is necessary to conduct an accurate determination of the hydrodynamic characteristics of sorbent particles. Currently, there is no data on the hydrodynamic characteristics of the vast majority of sorbents in reference literature. This is especially true for colloidal conglomerates formed during the introduction of liquid reagents, the combination of which causes the formation of solid phases with undefined hydrodynamic properties. An example is one of the most effective sorbents - copper ferrocyanide (($Cu2[Fe(CN6)]$), which is formed from a mixture of two solutions: yellow blood salt (($K4(Fe(CN)6)$) and copper sulfate ($CuSO4$) directly in the water being purified. The hydrodynamic characteristics of the promising combination of copper ferrocyanide with powdered bentonite clay are also unknown. The hydrodynamic characteristics of the most promising sorbents were determined for further development of the parameters of a universal adsorber-illuminator, capable of working effectively with both liquid reagents and solid fractions of sorbents, similar to powdered bentonites and zeolites.

Analysis of the Latest Research and Publications. The works [1–7] have investigated the impact of various sorbents on water treatment technologies and water quality in the removal of heavy metal ions. The studies [8–12] considered technologies based on the use of biological factors, and [13–16] focused on sorbents based on bentonite clays. In the research [3, 4], it is asserted that bentonites and zeolites are promising sorbents, primarily due to their availability and technological convenience.

2 Hydraulic Characteristics for the Sedimentation of Sorbents Bentonite, Zeolite, Copper Ferrocyanide, and Their Mixture

The process of sorbent sedimentation in water is characterized by the kinetics of settling of sorbent flake conglomerates. These processes are depicted in sedimentation kinetics graphs. In the study, bentonite clay powder with particle sizes of 0.1–0.072 mm and a solution of copper ferrocyanide ((Cu2[Fe(CN6)]), consisting of yellow blood salt ((K4(Fe(CN)6)) and copper sulfate (CuSO4) in a proportional ratio of 1g yellow blood salt to 1.356g copper sulfate, were used. Mixing occurs in a measuring cup with the addition of distilled water not exceeding 50ml per 10g of dry mixture. The solution of copper ferrocyanide is prepared exclusively before use; otherwise, the effectiveness of the solution decreases.

The obtained data are compiled into tables, based on which the Graph of Dependencies of the Study (Figs. 1 and 2) are constructed, and calculations of hydraulic size [17, 18] are conducted.

As a result of the studies, a model of sorbent sedimentation was built, and their sedimentation speed was established (Figs. 1 and 2, Table 1).

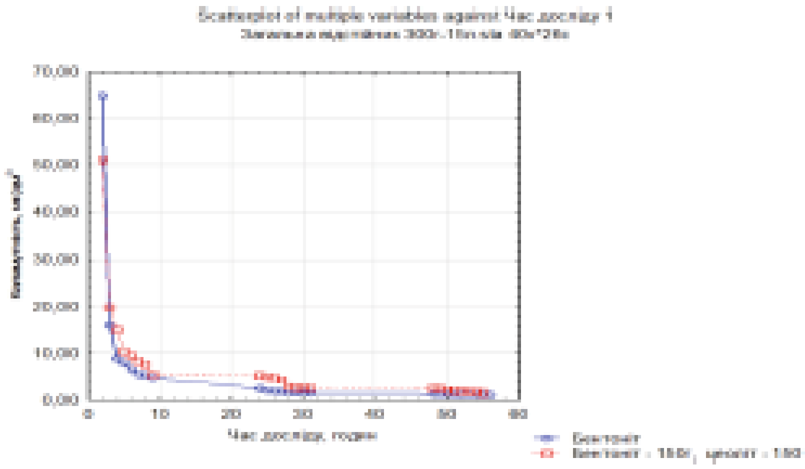

Fig. 1. Graph of dependencies of the hydraulic size of bentonite with an experiment duration of 56 h and a mixture of bentonite and zeolite with a duration of 54 h at a suspension temperature fluctuation of 14–16 °C.

The best result was obtained with a mixture of bentonite powder clay and copper ferrocyanide solution in a ratio of 2/0.5 g/dm^3 of dry matter - 99.8% of suspended particles settled and complete discoloration of the purified water from the remnants of copper ferrocyanide.

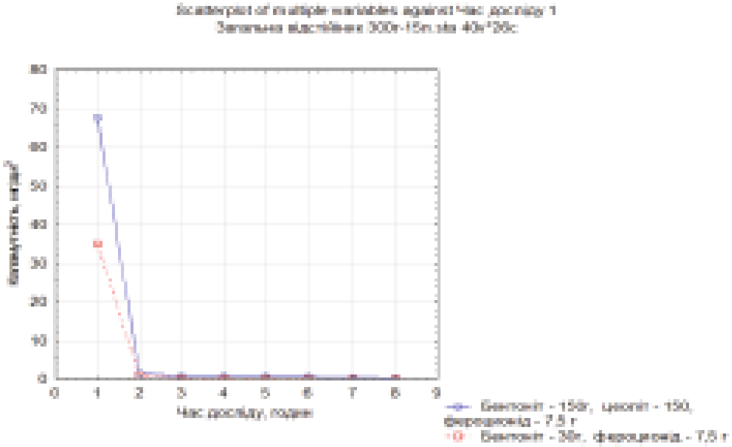

Fig. 2. Graph of dependencies of the hydraulic size of a mixture of bentonite and copper ferrocyanide with an experiment duration of 2 h 20 min and a mixture of bentonite, zeolite, and copper ferrocyanide with a duration of 3 h 30 min at a suspension temperature of 8 °C.

Table 1. Sedimentation speed.

№	Name	Settling Time, t, hours	Hydraulic Size, U_0, mm/s	Proportionality Coefficient, n	Concentration of Suspended Substances, P, %
1	Bentonite	56	0.11	1.39	98.26
2	Bentonite + Zeolite	37	0.44	1.23	96.5
3	Bentonite + Zeolite + Copper Ferrocyanide	3.5	4.99	0.43	98.7
4	Bentonite + Copper Ferrocyanide	2.20	6.185	0.29	99.8

Calculation of Hydraulic Size [17, 18]:

$$U_0 = \frac{1000HK}{t_1(HK/h_1)^n} \tag{1}$$

where H – depth of the working part of the settler, m; K – coefficient of utilization of the settler's volume; t1 – duration of settling in the laboratory cylinder at the height of layer h1, during which the required effect of clarification is achieved; n – coefficient of proportionality, which depends on the agglomeration of suspended particles in the process of settling in different water layers (h1 > h2); it is calculated using the following formula:

$$n = \frac{\lg t_1 - \lg t_2}{\lg h_1 - \lg h_2} \tag{2}$$

where h1 and h2 – heights of settling layers, cm;

t1 and t2 – duration of settling in the respective layers, when the required effect is achieved, s.

The efficiency of suspension settling is calculated as the difference in values of the concentration of suspended substances in water before and after settling, namely:

$$P = \frac{\mu_{вих} - \mu_i}{\mu_{вих}} \cdot 100 \quad (3)$$

where μВих - content of suspended substances in the original water; μi - content of suspended substances in the settled water, g/l, after the end of the settling period.

3 Modeling of Hydrodynamic Processes in Proposed Structures

As a result of simulation experiments conducted using the virtual machine in the Computational Fluid Dynamics Autodesk Simulation (CFD) environment, experiments were conducted to determine the hydrodynamic characteristics of the illuminator-adsorber based on modeling in a virtual environment (Fig. 3).

The presented scheme shows that the total height of the illuminator-adsorber with vertical flow is 6.22 m, the diameter of the illuminator is 3.5 m, and the central tube for suspension supply (hereafter: flocculation chamber) has a diameter of 0.5 m and a height of 3.8 m. The concentration of suspended particles is 7–12 kg/m^3. A structured grid containing 3,868,373 computational cells was used in the three-dimensional model.

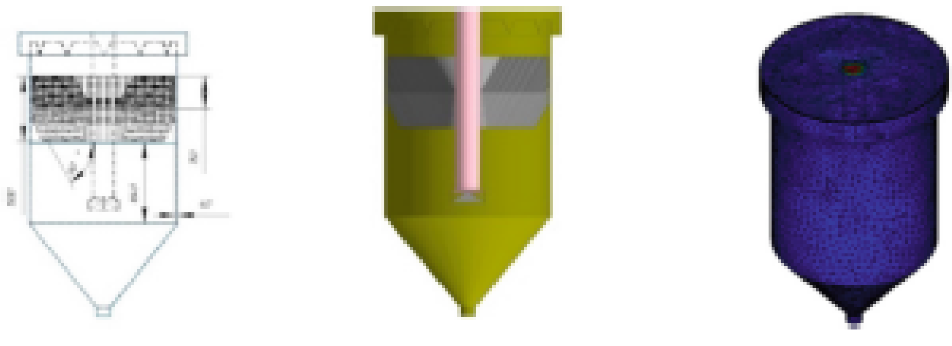

Fig. 3. General view of the illuminator-adsorber with a thin-layer module in cross-section and a sample of the computational virtual model based on the Finite Element Method (FEM).

To substantiate the model of sedimentation of bentonite and zeolite powdery clays and copper cyanoferrate, optimal suspension supply speeds of 0.014 m/s (14 mm/s) were determined. The results of the modeling in the form of flow velocity diagrams are presented in Fig. 4.

The analysis of modeling results showed (Fig. 4a) that in the classic model of the continuous-action illuminator at a fluid flow speed of 0.014 m/s at the entrance to the flocculation chamber with an equipped diffuser-reflector at the exit, there are zones of turbulent flow that hinder the normal formation of sorbent flocculant conglomerates and their sedimentation in the central section of the illuminator. The flow of LRW and sorbent, due to excessive turbulence, is unevenly distributed throughout the volume of

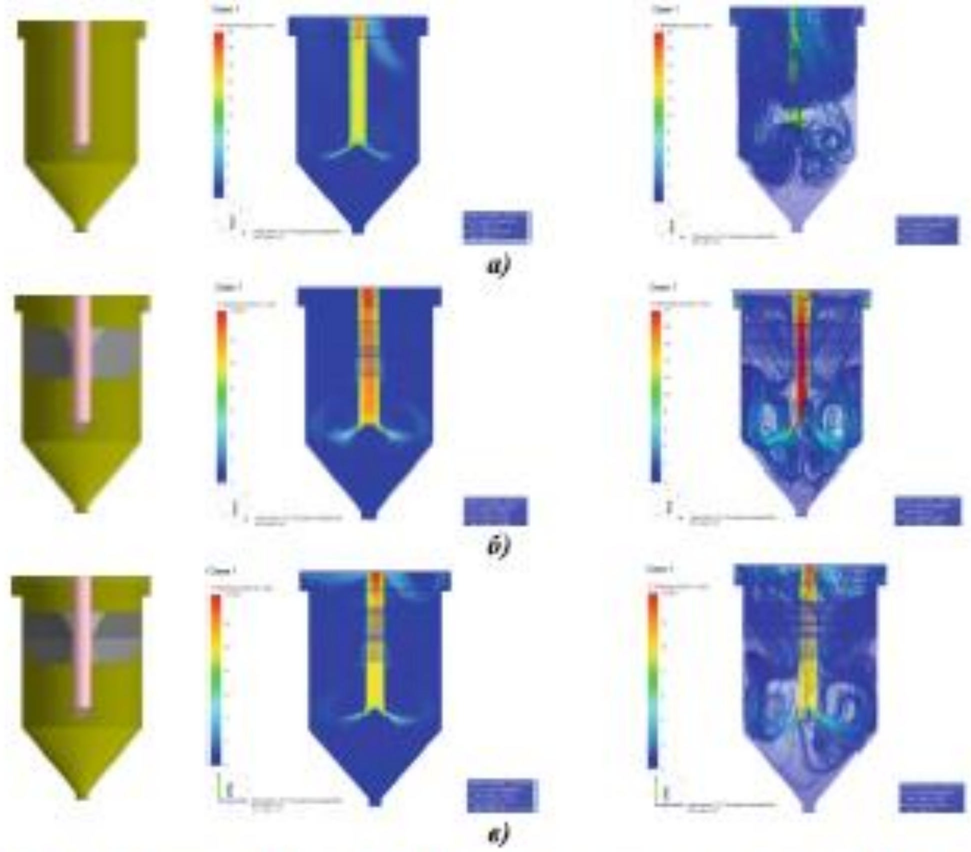

Fig. 4. Tracing of vectors and distribution of flow fields of sorbent solution and liquid radioactive wastes with a fluid supply speed of 0.014 m/s in the continuous-action illuminator-adsorber: a) model of the classic illuminator with a diffuser reflector; 6) model of the illuminator-adsorber with a reflector and a thin-layer module; B) model of the illuminator-adsorber with a reflector and a modernized thin-layer module.

the settler, creating stagnation zones that hinder the sorption process, leading to the suction of spent sorbent into the outlet channel, and preventing the compaction of spent sorbent in the lower part of the structure designated for RAW removal.

In the model of the illuminator-adsorber with a regular and modernized thin-layer module (Fig. 46, B), the sorbent solution is evenly distributed throughout the volume of the illuminator-absorber through the diffuser reflector and the thin-layer module, with a clear distribution into zones: creation of flow turbulence, laminar streamlining of the flow, and discharge of purified water.

Turbulence in the turbulent zone is achieved due to the diffuser reflector: stable, uniform swirls are formed, maintaining constant circulation of flocculant particles, increasing the contact time of the sorbent with polluted water, and accelerating the settling of spent sorbent. In the laminar flow leveling zone, the thin-layer module acts as a final water purification step from suspended sorbent particles by damping turbulent flows and increasing their settling area, preventing the suction of spent sorbent into the outlet channel. The difference between the regular and modernized thin-layer modules is that the modernized thin-layer module has an increased settling area by one and a half times compared to the regular thin-layer module, achieved by introducing additional plates to half the height of the regular thin-layer module.

Thus, the use of virtual models of sedimentation of bentonite and zeolite powdery clays and copper cyanoferrate allowed substantiating the optimal design of the illuminator-adsorber for stable and efficient sedimentation of the sorbent in the illuminator-adsorber with a modernized thin-layer module (Fig. 4B) and an inlet speed for this design of the settler v = 0.014 m/s.

The virtual experiment is described using a mixture model. The mixture model is a simplified model with two liquids that can simulate two-phase flow or particle flow, solve the continuity equation of the mixed phase, momentum energy equation, and volume fraction equation of the second phase, and achieve relative algebraic velocity. Since the mixture model is simple, the calculations are relatively small, and the results are more reliable, it is widely used. Below is the continuity equation of the mixture model:

$$\frac{\partial}{\partial t}(\rho_k) + \nabla \cdot (\rho_m \overline{v}_m) = \dot{m} \tag{4}$$

$$\overline{v}_m = \frac{\sum_{k=1}^{n} \alpha_k \rho_k \overline{v}_k}{\rho_m} \tag{5}$$

$$\rho_m = \sum_{k=1}^{n} \alpha_k \rho_k \tag{6}$$

In Formulas (4)–(6):ρ_m – density of the mixed phase;ρ_k – density of the k-phase;α_k – volume fraction of the final phase k; $\overline{v}_m$ – average mixing speed; $\overline{v}_k$ – average speed of k phase quality; – $\dot{m}$ through quality relative to the user-defined source quality.

The improved RNG (Renormalization Group Model) with two k-ε equations adds two factors: rotation of the average flow and flow turbulence for computation, better addressing situations of high variability and greater bending of flow lines. In this paper, the authors use a turbulence model for modeling the flow scheme in settlers. The turbulent kinetic energy k and the dissipation rate ε of the turbulent kinetic energy transfer equation are:

$$u_i \frac{\partial k}{\partial t_i} = \frac{\partial}{\partial x_i}\left[\left(\mu + \frac{\mu_t}{\sigma_k}\right)\frac{\partial}{\partial x_i}\right] + P_k - \varepsilon \tag{7}$$

$$u_i \frac{\partial k}{\partial t_i} = \frac{\partial}{\partial x_i}\left[\left(\mu + \frac{\mu_t}{\sigma_k}\right)\frac{\partial}{\partial x_i}\right] + C_{\varepsilon 1}\frac{\varepsilon}{k}P_k - C_{\varepsilon 2}\frac{\varepsilon^2}{k} \tag{8}$$

In the formula: μ – viscosity; μt – turbulent viscosity coefficient;
$P_k = \mu_t\left[\frac{\partial u_i}{\partial x_j}\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_i}{\partial x_j}\right)\right]$ is the generated elements of turbulent energy;
$\sigma_k = 0.7179$;$\sigma_\varepsilon = 0.7179$; $C_{\varepsilon 1} = 1.42 - \frac{\eta(1-\eta/\eta_0)}{1+\beta\eta^3}$; $\eta = \frac{Sk}{\varepsilon}$;
$S = (S_{ij}, S_{ij})^{1/2}$; $\eta_0 = 4.38$; $\beta = 0.012 - 0.015$; $C_{\varepsilon 2} = 1.68$.

4 Conclusions

The classic vertical settler provides only primary sedimentation of formed colloidal conglomerates.

The well-known thin-layer module slightly improves the sedimentation process of the sorbent.

The proposed construction, thanks to the specific distribution of hydraulic flow vectors in the water-sorbent suspension, allows one structure to provide the appropriate contact time of the sorbent in the form of a layer of suspended sediment with gradual enlargement of sorbent flake conglomerates forming a sediment that gradually thickens and compacts. Thus, we managed to combine an "adsorber" and a "settler" in one structure.

This allows considering this construction of the structure as universal, combining the processes of adsorption and sedimentation, which, in turn, allows conducting a complete cycle of LRW purification with a reduction in the number of involved technological structures.

References

1. Bulut, G., Yenial, Ü., Emiroğlu, E., Sirkeci, A.A.: Arsenic removal from aqueous solution using pyrite [Text engl]. J. Clean. Prod. **84**, 526–532 (2014)
2. Gao, S., Wang, Q., Nie, J., et al.: Arsenate(v) removal from aqueous system by using modified incinerated sewage sludge ash (ISSA) as a novel adsorbent [Text engl]. Chemosphere **270**, 129–423 (2021)
3. Huo, J., Yu, G., Wang, J.: Magnetic zeolitic imidazolate frameworks composite as an efficient adsorbent for arsenic removal from aqueous solution [Text engl]. J. Hazard. Mater. **412**, 125–298 (2021)
4. Khalil, A., Hashaikeh, R., Hilal, N.: 3D printed zeolite-y for removing heavy metals from water [Text engl]. J. Water Process Eng. **42**, 102–187 (2021)
5. Li, Y., Qi, X., Li, G., Wang, H.: Double-pathway arsenic removal and immobilization from high arsenic-bearing wastewater by using nature pyrite as in situ Fe and S donator [Text engl]. Chem. Eng. J. **410**, 128–303 (2021)
6. Muedi, K.L., Brink, H.G., Masindi, V., Maree, J.P.: Effective removal of arsenate from wastewater using aluminium enriched ferric oxide-hydroxide recovered from authentic acid mine drainage[Text engl]. J. Hazard. Mater. **414**, 125–491 (2021)
7. Rha, S., Waste Jo, H.Y.: Foundry dust (wfd) as a reactive material for removing As(iii) and Cr(vi) from aqueous solutions [Text engl]. J. Hazard. Mater. **412**, 125–290 (2021)
8. Chen, W.-H., Hoang, A.T., Nižetić, S., et al.: Biomass-derived biochar: from production to application in removing heavy metal-contaminated water [Text engl]. Process. Saf. Environ. Prot. **160**, 704–733 (2022)
9. Rilstone, V., Vignale, L., Craddock, J., et al.: The role of antibiotics and heavy metals on the development, promotion, and dissemination of antimicrobial resistance in drinking water biofilms [Text engl]. Chemosphere **282**, 13–1048 (2021)
10. Shamim, M.A., et al.: Metal organic frameworks (MOFs) as a cutting-edge tool for the selective detection and rapid removal of heavy metal ions from water: recent progress [Text engl]. J. Environ. Chem. Eng. **10**, 106–991 (2022)
11. Shen, C., Wu, S., Meng, Q.: Construction of portable drinking water device using an agricultural biomass-derived material of polyethylenimine-grafted-corncob [Text engl]. Food Control **130**, 108–375 (2021)
12. Zhang, Y., Zheng, H., Zhang, P., et al.: Facile method to achieve dopamine polymerization in MOFs pore structure for efficient and selective removal of trace lead (II) ions from drinking water [Text engl]. J. Hazard. Mater. **408**, 124–917 (2021)