PURIFICATION METHOD FOR FILTRATE FROM THE TREATMENT OF PROCESS URANIUM-CONTAINING SOLUTIONS

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The article describes the purification method for filtrate generated from the treatment of process uranium-containing solutions that resulted from production activities at JSC "PA ECP". The paper presents the stages of the testing performed at a laboratory stand that enabled to identify an optimal concept flowchart for filtrate treatment.

Keywords: *filtrate, technological uranium-containing solutions, purification of high-salt solutions, radioactive waste.*

PA ECP operation results in process uranium-containing solutions (PUS) generated due to equipment washing and decontamination of working space. To recycle uranium, PUS is subject to processing [1]: deep extraction of uranium resulting in acid solutions with a minimum uranium concentration ranging from 1 to 2 mg/dm^3.

Acidic solution neutralization and separation of the pulp in a centrifuge result in solid sediment and centrifuge centrate. According to its radiation characteristics, centrate is not categorized as liquid radioactive waste (LRW), but the concentration of chemicals in it exceeds the limits established in [2] as regards the composition of water discharged into city sewage treatment plants.

In this regard, a comprehensive solution enabling centrate treatment to remove both the radionuclides and chemical impurities contained in it should be found allowing further treated water discharge into household sewage system. This article summarizes the results achieved in the development of a centrate treatment method and its laboratory testing in VNIINM using genuine centrate from PA ECP.

Properties of the tested object

Fugate is a multicomponent high-salt aqueous solution. Bench tests involved a centrate from different batches with average sediment content of up to 10 % by volume. Total specific activity of uranium and thorium radionuclides in the sediment did not exceed 3,000 Bq/kg. Dissolved components in the clarified part of the centrate had the following chemical composition (averaged by mass. %): NO_3^- —72.4; Ca^{2+} — 22; K^+ — 2.2; Na^+ — 1.2; NH_4^+ — 1.1; SO_4^{2-} — 0.9; other — 0.2.

Components concentrations in the centrate exceeded the standards for chemicals in water [2] considering the following indicators:

- suspended particles — by 45 times (more than 10 g/l);
- NH_4^+ — by 12 times (0.7 g/l);
- NO_3^- — by 955 times (43 g/l);
- SO_4^{2-} — by 12 times (0.6 g/l);
- mineralization — by 47 times (47 g/l).

Laboratory bench for high-salt solution treatment

Centrate treatment method was developed based on a combination of common industrial water treatment methods, which are widely used for LRW treatment purposes [3, 4]. Based on the evaluated centrate treatment options, a flowsheet of the treatment process was developed involving sediment separation, evaporation, membrane and ion-exchange desalting and drying stages. A laboratory bench for high-salt solution treatment (Figure 1) was developed to test the proposed centrate treatment method and tested using model solutions.

Figure 1. Laboratory bench designed to test the proposed centrate treatment method

The developed bench involved modular low-capacity installations (Figure 2) representing the main stages of centrate treatment and providing the following operations:

- adjustment of the chemical composition allowing to change pH, coagulation, flocculation levels;
- separation of mechanical impurities in a flow clarifier;
- additional purification from mechanical impurities by filtration;
- separation of water and concentration of salts by distillation;
- drying of still residue to dry salts;
- additional purification of condensate and concentration of impurities by two-stage reverse osmosis;
- additional condensate treatment by ion exchange method.

The laboratory bench allows to test potential centrate treatment options considering several combinations of salt and water separation stages by distillation, condensate treatment stages by membrane and ion-exchange methods providing the compliance with water standards and providing its discharge into household sewer.

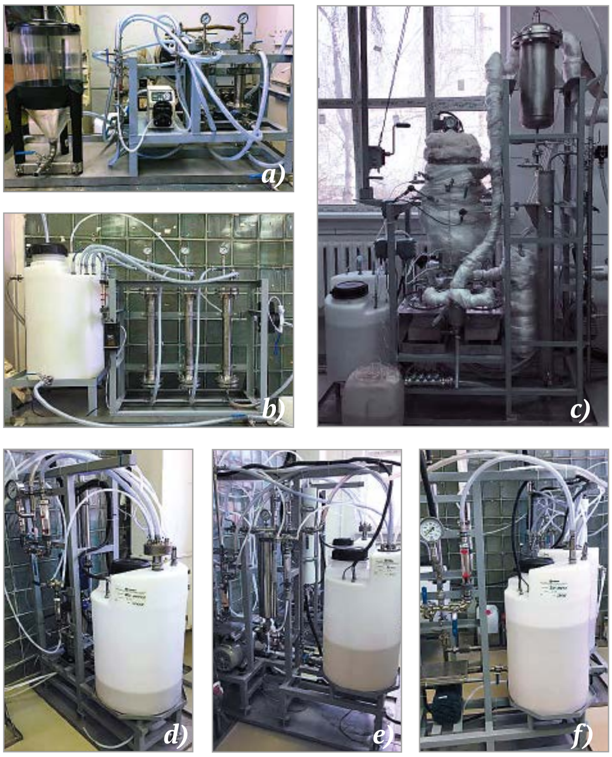

Figure 2. Layout of the laboratory bench for centrate treatment testing: pre-treatment unit (a), ion-exchange post-treatment unit (b), evaporation and drying unit (c), three-stages of condensate purification unit using the reverse osmosis method (d, e, f)

Testing of centrate treatment method

During the tests performed on the laboratory bench, some 1 m^3 of centrate was processed under experimental modes, process parameters of the method and its performance under various conditions were identified at each stage.

At sediment separation stage, the flowrate of Praestol BC 655 flocculant accounted for 5—10 mg per 1 g of dry sediment. During centrate clarification in the settler, the flow of thickened sludge accounted for no less than 25 % of the input flow. Final filtration of the centrate was performed prior to evaporation on two bulk filters with coarse (0.8—2 mm) and fine (0.3—0.8 mm) sand.

Treatment by distillation has proved to be effective when the pH of the solution ranged from 6.5 to 7 with relative pressure above the solution ranging from −0.025 to −0.07 MPa. At pH < 6.5, the content of corrosion products in the condensate increased, whereas at pH > 7.5 the same trend was observed for ammonium being considered as the main condensate contaminant.

The tests showed that during additional condensate treatment at the stage of reverse osmosis desalination, treated water indicators already corresponded to the standards allowing its discharge into domestic sewage system. During reverse osmosis, pH of the condensate was maintained in the range of 5.5—6. At the stage of impurity concentration by high-pressure reverse osmosis, the concentrate volume was reduced up to 1—2 % of the condensate volume. Following the reverse osmosis, the concentrate was returned to the evaporation stage.

At the stage of bottom residue concentration by evaporation, the concentration limit was identified. For this purpose, the bottom residue with the highest density was produced under different temperatures and pressures: 1.6 g/cm^3 — at the solution boiling point of 87 °C and a relative pressure of −0.07 MPa; 1.75 g/cm^3 — at the solution boiling point of 120 °C and a relative pressure of −0.025 MPa.

At the next stage, drying at a temperature of 190—200 °C resulted in a dry salt residue (Figure 3). During drying, the volume of the bottom residue with a density of 1.6—1.7 g/cm^3 decreased by 10—15 %. Centrate treatment to dry salts resulted in 20-fold decrease in the total waste volume.

The cement compound with the salt residue enclosed into it is considered as an ecologically preferable waste form being non-combustible and inert to the environmental effects. Therefore, at the final stage, studied were the opportunities for producing a monolithic inert product by cementing the bottom residue of the centrate with a density of 1.6—1.7 g/cm^3. Cement compound samples were produced (Figure 4) using Portland cement CEM I 42.5 B (PC500D0) with a residue/cement ratio of 1.5. The salt filling of the cement compound accounted for 42 wt %. The samples retained their shape in the air. A 1.4-fold increase in the volume of the cement compound was observed as compared to the one of the bottom residue and a 1.5-fold increase was observed as compared to the dry salt.

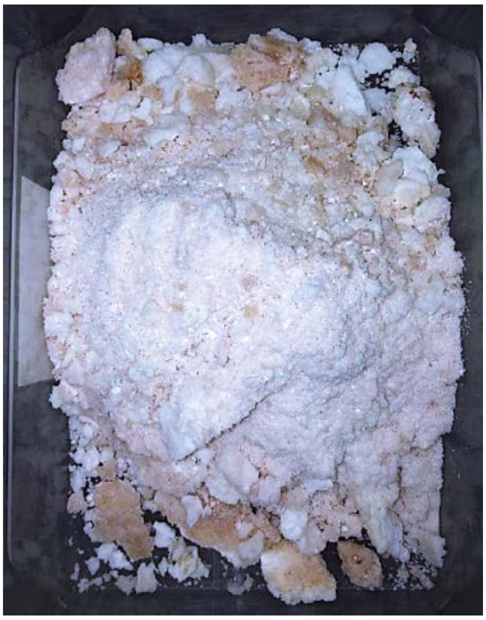

Figure 3. Dry salt residue of the centrate obtained at the stage of bottoms residue immobilization by drying

Figure 4. Cement compound samples manufactured from bottom residues with a residue/cement ratio of 1.5

Flowsheet of centrate treatment process

The number and the sequence of main centrate processing stages was specified based on the tests. The centrate treatment flowsheet (Figure 5) involves the following stages:

- preliminary flocculant-based centrate treatment to remove sediment with the reverse pulp flow to the centrifuge required to be at least 25 % of the incoming flow;
- filtration of the clarified centrate through sandy bulk filters and filtrate pH adjustment to 6.5—7;
- centrate evaporation (at a relative pressure of up to −0.07 MPa) to a bottom residue density of 1.4 g/cm^3;
- additional condensate treatment at one stage of low-pressure reverse osmosis up to water standards allowing its discharge into domestic sewage system, impurity concentration in the concentrate of the high-pressure reverse osmosis stage up to 2 % of the condensate volume and concentrate recycling into evaporation process;
- evaporation of bottom residue to a density of 1.6—1.7 g/cm^3;
- thermal drying of bottom residue to dry salts loaded into sealed metal drums.

In accordance with [5], waste from chemical productions containing calcium nitrate are categorized as waste of the 4th hazard class. Trench-type near-surface storage facility is considered as a facility that can provide the containment of salt residue placed into sealed containers (metal drums).

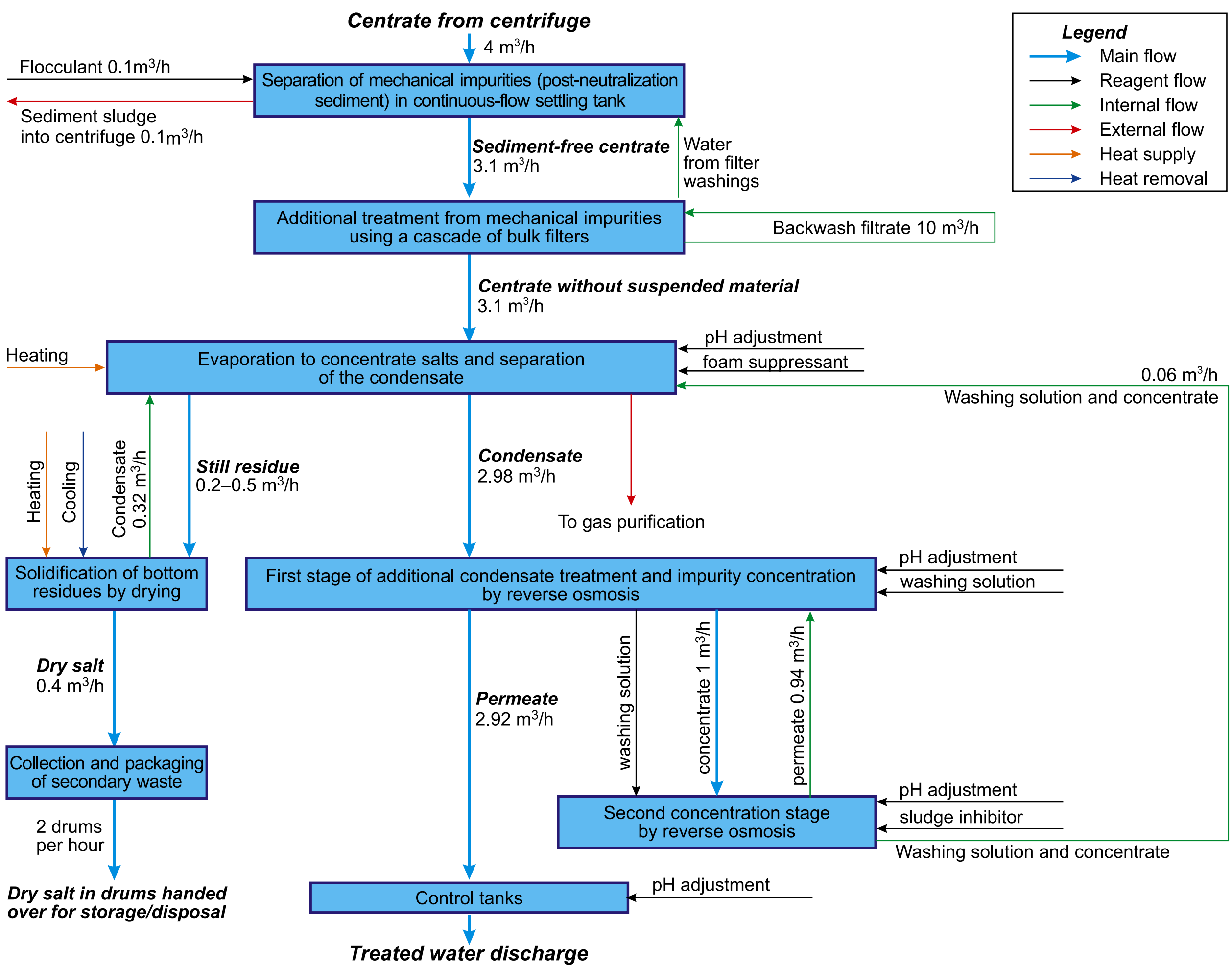

Figure 5. Flowsheet for centrate processing

The sediment separated in the first stage is managed in accordance with [1].

Conclusion

An integrated method enabling centrate treatment from radionuclides and chemical impurities has been developed: it involves the stages providing complete sediment removal, water separation and salt concentration by distillation, bottom residue drying to dry salts, additional condensate treatment following one desalination — reverse osmosis stage. The method developed was tested on a laboratory bench using genuine centrate from PA ECP. It was demonstrated that the treated water indicators corresponded to the standard levels allowing its discharge into the domestic sewage system. Process parameters for centrate treatment stages were specified and served a basis for the development of relevant flowsheets and hardware setup for a pilot industrial installation with centrate treatment capacity of 4 m³/h.

Based on the results obtained, terms of reference for the design development of a pilot industrial treatment installation allowing to process the centrate from PA ECP were developed. The type and parameters of the main equipment have been specified: flow clarifier with a capacity of 10 m³, vacuum evaporation unit (two lines with a capacity of 1,400 kg/h each), condensate purification and contaminant concentration unit based on reverse osmosis method (up to 4 m³/h), cylinder drier for still residue (up to 500 kg/h). The developed centrate treatment method will result in solid industrial waste involving dry salts and spent filtration materials.

References

1. Merkulov S. A., Parshutkin S. V., Svetashev G. O. Pererabotka uransoderzhashchikh tekhnologicheskikh rastvorov i tekhnologii obrashcheniya s ochen' nizkoaktivnymi radioaktivnymi otkhodami, obrazuyushchimisya v AO “PO EKHZ” [Processing of uranium-bearing process solutions and handling technologies for very low-level radioactive waste generated at JSC “PA ECP”]. *Radioaktivnye otkhody — Radioactive Waste,* 2019, no. 4 (9), pp. 101—105. DOI: 10.25283/2587-9707-2019-4-101-105.

2. Postanovlenie Pravitel'stva Rossiyskoy Federatsii ot 29.07.2013 № 644 "Ob utverzhdenii Pravil kholodnogo vodosnabzheniya i vodootvedeniya i o vnesenii izmeneniy v nekotorye akty Pravitel'stva Rossiyskoy Federatsii" [Resolution of the Government of the Russian Federation of July 29, 2013 № 644 "On approval of the rules for cold water supply and sanitation and on amendments to certain acts of the Government of the Russian Federation"].

3. Slyunchev O. M., Bobrov P. A., Akintsev A. S., Zubrilovskij E. N. Opyt ispol'zovaniya baromembrannykh protsessov dlya ochistki zhidkikh radioaktivnykh otkhodov [Experience Gained in Baro-Membrane Process Application for Liquid Radwaste Treatment]. *Radioaktivnye otkhody — Radioactive Waste,* 2018, no. 1 (2), pp. 42—53.

4. Materialy obosnovaniya litsenzii na osushchestvlenie deyatel'nosti v oblasti ispol'zovaniya atomnoy energii "Obrashchenie s radioaktivnymi otkhodami na publichnom aktsionernom obshchestve "Novosibirskiy zavod khimkontsentratov" [Substantiation materials for a license to carry out activities in the field of atomic energy use "Radioactive waste management at the Novosibirsk Chemical Concentrates Plant" public joint-stock company] [Official website of Novosibirsk]. URL:https://novo-sibirsk.ru/upload/iblock/b55/protokol-obshchestv-slush-nzkhk-_-yao.pdf/, April 22, 2020.

5. Ob utverzhdenii federal'nogo klassifikatsionnogo kataloga otkhodov [On approval of the Federal classification catalog of waste]. Order of Rosprirodnadzor, May 22, 2017, no. 242.

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