Denitration of radioactive waste with formaldehyde during evaporation in the natural-circulation evaporator

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Abstract. The paper presents a scheme of an experimental full-scale evaporation rig and a description of the tests carried out on it for the evaporation of nitric acid solutions with simultaneous denitration with formaldehyde. The results of work on a full-scale evaporator rig confirmed the possibility of using evaporation method with simultaneous denitration by formaldehyde in a natural-circulation evaporator with external heating chamber. The dependence of concentration of nitric acid to the molar ratio of formaldehyde to nitric acid was obtained.

1. Introduction
Concentration of high-level radioactive waste (HLW) by evaporation is a stage of processing and disposal of this type of waste. HLW are diverse in composition and usually contain nitric acid and sediment-forming elements (Ba, Sr, Mo, etc.). An increase in nitric acid concentration during evaporation of HLW leads to crystallization of barium nitrate [1]. Heavy precipitation of barium nitrates can accumulate in the bottom solution of the evaporator, clog the pipes, and, ultimately, lead to the stoppage of the HLW concentration process.

One of the ways to reduce the concentration of nitric acid during the evaporation of HLW is denitration of HLW by introducing formaldehyde [2]. The operating experience of the HLW concentration unit at a radiochemical plant in France [3] has demonstrated the reliability and efficiency of HLW denitration with formaldehyde during the concentration process. Despite the positive operating experience, the installation has the following disadvantages:
- the evaporators of the type used (kettle type evaporator) have a small heating surface and low productivity;
- the unit operates in a semi-continuous mode with the need to stop the evaporation cycle;
- during denitration, nitrous oxide is formed, which leads to the loss of nitric acid and the need to install complex gas cleaning systems.

The modern technical solution is the method of HLW concentration, eliminating the above disadvantages, in which evaporation with simultaneous denitration by formaldehyde is carried out in a continuous mode in a natural-circulation evaporator [4].

The purpose of this work is experimental development of denitration modes (discharge coefficients) in the process of evaporation on a full-scale steam stand.
2. Methods

Studies were carried out at the experimental (full-scale) evaporator rig. The scheme of the rig is shown in Figure 1. The rig consists of: evaporator EV2, condenser C1, absorption column AC1, steam generator SG2, tank for feed solution T1, feed tank solution T3, receiving tanks T5 and T7, distillate tank T6, reagent tanks TR1 and TR2, and pumps P1 – P3.

![Evaporator stand scheme.](image)

The used EV2 is a natural-circulation evaporator with external heating chamber. The heat exchange surface of the evaporator is 0.9 m², the flow rate feed solution (calculated) is up to 35 l/h.

Nitric acid solutions were used as working solutions (solutions of HLW simulators).

Before starting the evaporator stand, the following operations were performed:
- the evaporator EV2 was filled with a pre-prepared bottom solution, the concentration of nitric acid in the solution was 4.0 mol/l;
- the feed solution tank T3 was filled with a feed solution, the concentration of nitric acid in the solution was 2.6 mol/l. The feed solution for filling the tank T3 was prepared in the tank for preparing feed solution T1;
- the reagent tank TR1 was filled with a reagent solution with a formaldehyde concentration of 6.5 mol/l;
- the reagent tank TR2 was filled with a hydrogen peroxide solution.
The order of operations is as follows. At the start of the operation, heating steam was supplied from the steam generator SG2 to the evaporator EV2. The heating steam condensate was continuously discharged. After the feed solution began to boil, reagent supply started from the reagent tank TR1. The reagent was fed continuously during evaporation of the solution. When the level of the bottom solution in the evaporator EV2 decreased, the feed solution was automatically fed into it from the initial solution tank T3. The evaporator EV2 was kept at a constant level of the bottom solution. To maintain the required degree of evaporation, the bottom solution was periodically (in predetermined portions) removed from the EV2 evaporator. Secondary steam from the evaporator EV2 was fed to the condenser C1. Cooling water was supplied to the condenser C1 for condensing the secondary vapour and cooling the distillate. The distillate from the condenser C1 is directed to the distillate tank T6. Distillate from condenser C1 was discharged into distillate tank T6. The air (blow-off) from the distillate tank T6 was directed through the absorption column AC1 to the exhaust ventilation. Hydrogen peroxide from the reagent tank TR2 was fed to the AC absorption column to capture nitrogen oxides.

During the tests, the flow rate of the feed solution varied from 12 to 20 l/h, the flow rate of the reagent varied from 1.7 to 4.8 l/h, discharge coefficient CH$_2$O/HNO$_3$ varied from 0.3 to 0.65 mol/mol. Pressure and temperature control was carried out by the use of manometers and thermometers mounted on the equipment. During the operation of the evaporation stand, the nitric acid concentration was determined in the samples of the bottom solution and distillate. The concentration of nitric acid was determined by titration with 0.1 mol/l NaOH (fixanal), with a 0.1 % phenol red indicator (20 % alcohol-water solution).

3. Results
The Table 1 shows the results of experiments on the decomposition of nitric acid on an experimental evaporator stand. When feeding a formaldehyde solution with a concentration of 6.5 mol/l, at a molar the discharge coefficient CH$_2$O/HNO$_3$ (in relation to the initial amount of nitric acid) 0.3, 0.5, and 0.6, the stationary concentration of nitric acid in the bottom solution was 5.1, 3.8, and 3.2 mol/l.

The calculation of the material balance and the results obtained demonstrate the decomposition of nitric acid turned out to be close and position to ~ 40 %. However, with an increase in the discharge coefficient from 0.3 to 0.5 CH$_2$O/HNO$_3$, the regeneration of nitric acid in the absorption column decreased from 36 to 14 %. Decreased regeneration of nitric acid indicates an increase in the loss of nitric acid with the vapour-gas phase from 9 to 24 %, which can be explained by an increase in the formation of nitrous oxide.

4. Conclusion
As a result of work on a full-scale evaporator stand, denitration modes with different molar discharge coefficient CH$_2$O/HNO$_3$ (in relation to the initial amount of nitric acid) were tested. The tested modes make it possible to destroy nitric acid and maintain a stationary concentration of nitric acid in bottom solution at a level of 5.1-3.2 mol/l. The results obtained show the possibility of reducing the acid concentration in bottom solution, which will allow the HLW to be evaporated with a higher degree of evaporation without the risk of precipitation. However, the question of the possibility of simultaneously optimizing the regeneration of nitric acid and reducing the concentration of nitric acid in the bottom solution in the evaporator below 4 mol/l requires more careful study.

Experimental studies carried out on a full-scale evaporator rig confirm the scalability of the process and the choice of optimal design choices when creating reliable equipment.
Table 1. Results of experiments on the decomposition of nitric acid on an experimental evaporator stand.

| t, min | Flow rate, L/h | Reagent (formaldehyde 6.5 mol/L) | Concentration HNO₃ (concentrate), mol | CH₂O/HNO₃, mol/mol | Removal of HNO₃ from the absorber, % |
|--------|----------------|----------------------------------|-------------------------------------|---------------------|-------------------------------------|
| 40     | 15.0           | 2.8                              | 4.2                                 | 0.49                |                                     |
| 60     | 17.0           | 2.8                              | 3.9                                 | 0.46                |                                     |
| 80     | 16.0           | 2.8                              | 3.8                                 | 0.44                | 14                                  |
| 100    | 20.0           | 2.8                              | 3.5                                 | 0.37                |                                     |
| 120    | 12.0           | 2.8                              | 4.0                                 | 0.61                |                                     |
| 140    | 15.0           | 2.8                              | 4.0                                 | 0.49                |                                     |
| 160    | 17.0           | 2.8                              | 3.8                                 | 0.43                |                                     |
| average | 16.0           | 2.8                              | 3.83                               | 0.48                |                                     |
| 200    | 12.0           | 1.7                              | 4.1                                 | 0.37                |                                     |
| 220    | 15.0           | 1.7                              | 4.2                                 | 0.29                |                                     |
| 240    | 15.0           | 1.7                              | 4.45                                | 0.29                |                                     |
| 260    | 16.0           | 1.7                              | 5.0                                 | 0.28                |                                     |
| 300    | 17.0           | 1.7                              | 4.8                                 | 0.26                |                                     |
| 320    | 15.0           | 1.7                              | 5.2                                 | 0.29                | 36                                  |
| 340    | 12.0           | 1.7                              | 5.3                                 | 0.37                |                                     |
| 360    | 18.0           | 1.7                              | 5.1                                 | 0.25                |                                     |
| 400    | 15.0           | 1.7                              | 5.3                                 | 0.29                |                                     |
| 420    | 15.0           | 1.7                              | 4.9                                 | 0.29                |                                     |
| average | 15.4           | 1.7                              | 5.1                                 | 0.29                |                                     |
| 90     | 17.0           | 4.0                              | 3.0                                 | 0.61                |                                     |
| 110    | 16.0           | 4.0                              | 3.15                                | 0.65                |                                     |
| 130    | 18.0           | 4.2                              | 3.2                                 | 0.61                |                                     |
| 150    | 19.0           | 4.8                              | 3.3                                 | 0.66                |                                     |
| 170    | 19.0           | 4.8                              | 3.0                                 | 0.66                |                                     |
| 190    | 19.0           | 4.8                              | 3.1                                 | 0.66                |                                     |
| average | 18.8           | 4.7                              | 3.2                                 | 0.64                |                                     |

References
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