DECONTAMINATION OF FIBERGLASS FILTER PAPER

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The paper presents the results of fiberglass filter paper decontamination. The study establishes that nitric acid solutions provide fairly complete extraction of target element from the filter material. Three-fold ultrasonic treatment of fiberglass filter paper resulted in 98% Pu transfer into solution. The study shows that the developed decontamination method provides sufficiently complete recycling of the target component under the process flow chart and prevents nuclear material release into the environment at further radioactive waste management stages under long-term storage conditions. The study demonstrates that ultrasonic treatment implemented under the considered process of Pu recycling from spent fiberglass filter paper yields 3-fold decrease in the time of the dissolution process in nitric acid solution with an addition of fluoride-ion.

Keywords: *radioactive waste, decontamination, regeneration, radioactive decontamination, alpha-radionuclides, filter element, fiberglass filter paper, purification grade, ultrasound, ultrasonic bath.*

Nuclear facility operation necessitates the treatment of radioactive substances from gas-aerosols released by process units. Therefore, efficient and reliable operation of gas treatment systems is required to provide the radiation safety of personnel and the public.

Currently, Petryanov filters are widely used to treat exhaust ventilation air and process vents at FSUE PA Mayak. However, the materials applied in this equipment are flammable due to the polymer base and gauze substrate involved. Therefore, this equipment cannot be used at the operational stages implying some strict requirements imposed on the filters. For this reason, in the coming years the enterprise will have to replace the Petryanov filters completely with those made of non-combustible materials.

Previously implemented laboratory and pilot-production tests have shown that glass fiber paper can be considered as a material potentially meeting all safety requirements and providing highly effective treatment of ventilation air. Given optimal filtration rate, fog concentration, surface density of the filter layer, glass fiber paper may provide effective and long-term air treatment maintaining constant resistance [1]. Besides the non-flammability, another advantage of glass fiber paper elements is seen in their capability of operating under high-level humidity.

At present time, filters with a pore diameter of less than 0.5 μm (microfine), from 0.51 to 1.0 μm (ultrafine) and from 1.01 to 3.0 μm (superfine) are widely used at PA Mayak in treating exhaust ventilation air and process vents [1]. Their designs are based on artificial inorganic ultrathin glass staple fibers containing boron.

These filters have successfully passed the life tests and have demonstrated higher performance level with respect to aerosols containing plutonium than the Petryanov filters. In this regard, since 2006, they have been applied at several production sites where the industrial releases containing target components such as uranium and plutonium had to be treated.

Such filters require replacement every three months.

It's believed that the industrial need for these glass fiber paper filters in the next two years will be up to 1,000 pcs. per year.

To recycle plutonium extracted from such spent filters, FSUE PA Mayak currently applies a method involving nitric acid dissolution with preliminary alkaline treatment with a hot alkaline solution [2]—[4]. However, this method is considered time-consuming, labor- and energy-intensive. Thus, due to this decontamination method PA Mayak would annually accumulate a significant amount of glass fiber paper filters containing nuclear materials and considered as solid radioactive waste. In this regard, the method currently adopted to recover plutonium contained in these filters should be improved or a more advanced, less complicated and effective method should be developed to extract the target component. Glass fiber paper immersion into cleaning solution accompanied with ultrasonic treatment has been proposed as a possible option.

This paper evaluates the potential of the target component extraction from glass fiber paper implying two options: either with or without partially breaking their integrity by means of treating them with decontaminating solutions. It also overviews the experiments seeking to intensify the process of plutonium regeneration through the use of ultrasound.

Table 1 shows the approximate chemical composition of microfine glass fiber.

Table 1. Chemical composition of glass fiber

Component	Mass fraction of the component. %
SiO_2	61.0
B_2O_3	3.0
Na_2O	12.7
K_2O	1.8
CaO	8.0
ZrO_2	5.0
Fe_2O_3	7.0

Thanks to the structure of ultrathin glass fiber paper, the small fiber diameter, increased flexibility of individual filaments and crimp items made of this material have certain valuable properties that are considered inherent only to them:

- low bulk density ranging from 8 to 20 kg/m^3 at a specific pressure of 100 Pa. Such products contain from 99.0 to 99.7 % of air and only from 0.3 to 1.0 % of fiber, therefore, they are non-dusting, non-prickly and safe during installation operations;
- low thermal conductivity coefficient ranging from 0.030 to 0.033 W/m·K at a temperature of 20°;
- relatively good cold and temperature resistance (operating temperature ranges from 200 to 500 °C for products without a binder and from 150 to 180 °C for products impregnated with binders);
- high chemical resistance in water and various aggressive media, except for alkalis, which is explained by the chemical resistance of the original glass;
- good filtering properties due to the highly developed fiber surface;
- relatively low-level surface corrosion.

A 0.3 % aqueous solution of polyvinyl acetate dispersion (PVAD) or a mixture of PVAD with polyvinyl alcohol in a ratio of 1 : 1 (by dry residue) is used as a binder.

Items made of ultrafine glass fiber are non-toxic and non-explosive, and if no binders are applied, they are also non-combustible. With a mass fraction of synthetic resin ranging from 5 to 25 %, they become non-flammable. The filter efficiency amounts to 99.9999 %.

Chemical resistance of the filter material in glass fiber paper and its assessment

At the first stage, chemical resistance of the filter material in glass fiber paper filters to aggressive media was evaluated by the gravimetric method based on the changes in the mass of the sample before and after its treatment. Alkaline and acid solutions used to decontaminate equipment and products at the enterprise were used as aggressive media. This stage allowed to forecast the damage caused to the matrix during the decontamination process and to identify whether some additional filtering of spent decontaminating solutions is required.

The tests were carried out on glass fiber filter material samples with no radioactive contamination. Elementary samples being 0.05 × 0.05 m in their size were washed alternately with hot (T = 50 °C) and cold (T = 20 °C) water, squeezed and dried in a drying box at a temperature of (100 ± 4) °C to a constant weight. Then the samples were weighed on an analytical balance. The filter samples were processed by simulating the liquid decontamination process either considering the ultrasonic treatment stage or not. An ultrasonic bath of the UZV-18/200 TN brand with a rated power not exceeding 250 W was used as an ultrasonic vibration source.

The pretreated samples were placed into chemical beakers attached to purpose-designed holders (to prevent the samples from floating up) and filled with the prepared aggressive solutions. Solution consumption (cm^3) per one unit of the treated sample surface area (cm^2) was taken equal to 3 : 1. The

ratio of the solution volume (cm^3) to the filter mass (g) was 800 : 1.

The process was implemented both at room and elevated (up to 60 °C) temperatures in three cycles of 1 h each. Each subsequent treatment involved a fresh portion of aggressive solution.

After each cycle, the samples were washed under running cold water for 1 min, dried to constant weight and weighed.

The mass fraction of the dissolved material M_p was calculated by the formula:

$$M_p = \frac{m_0 - m_1}{m_0} \cdot 100\ \%, \qquad (1)$$

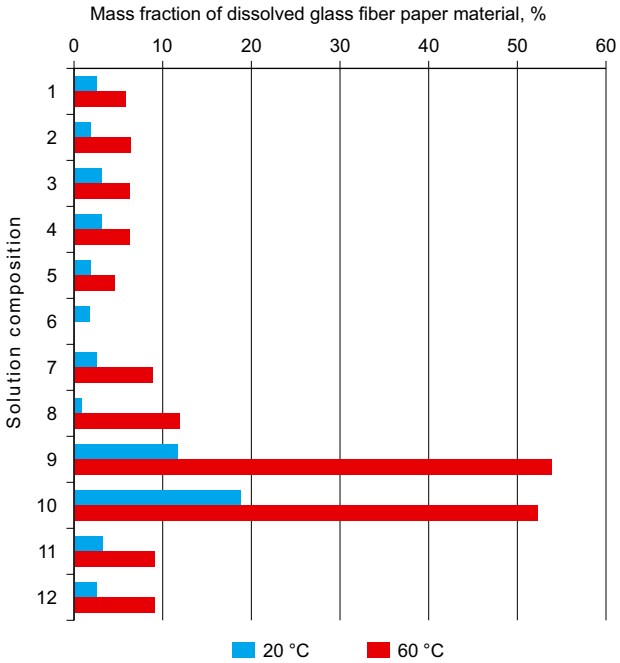
where m_0 is the mass of the sample before testing, mg; m_1 is the mass of the sample after testing, mg.

Figures 1—2 present the results of the chemical resistance testing involving the glass fiber paper material exposed to various acid solutions.

Figure 1 shows that nitric acid, nitric acid-oxalate and phosphate solutions have the least destructive effect at a room temperature. The amount of dissolved filter material after three treatment cycles did not exceed 2 %, whereas fluoride ion introduced to the nitric acid-oxalate solutions increased it up to two times.

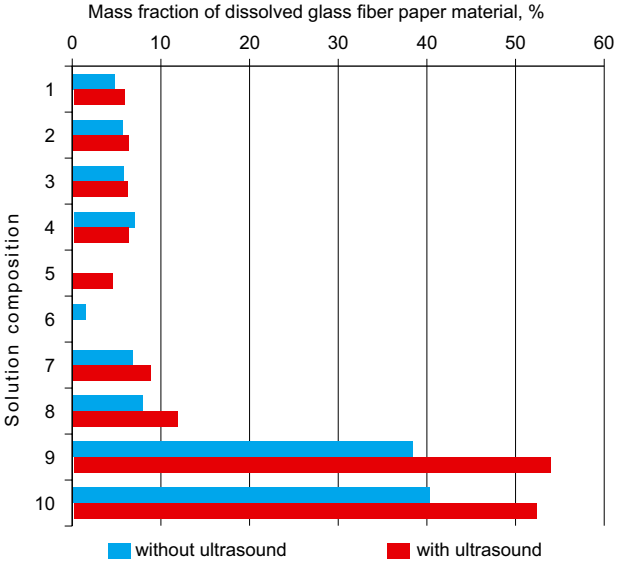
It should be noted that when the samples were kept in phosphoric acid solutions, the integrity of the material was disrupted (the samples were split into several parts). The experiments showed that the increase in the solution temperature to 60 °C reduced the chemical resistance of the glass fiber paper material from two to 20 times (Figure 1).

The ultrasound impact during similar tests had little effect on the integrity of the samples (see Figure 2). The mass fraction of the filter material dissolved at a room temperature was growing from 1.1 to 1.5 times when subjected to ultrasonic treatment and did not exceed 2.5 and 6.0% in nitric acid and nitric-oxalate solutions, respectively.



1 – 30 g/dm³ HNO_3; 2 – 100 g/dm³ HNO_3;
3 – 300 g/dm³ HNO_3; 4 – 450 g/dm³ HNO_3;
5 – 50 g/dm³ H_3PO_4; 6 – 100 g/dm³ H_3PO_4;
7 – 30 g/dm³ HNO_3 + 5 g/dm³ $H_2C_2O_4$;
8 – 100 g/dm³ HNO_3 + 5 g/dm³ $H_2C_2O_4$;
9 – 30 g/dm³ HNO_3 + 5 g/dm³ $H_2C_2O_4$ + 1 g/dm³ KF;
10 – 100 g/dm³ HNO_3 + 5 g/dm³ $H_2C_2O_4$ + 1 g/dm³ KF;
11 – 50 g/dm³ HNO_3 + 5 % H_2O_2;
12 – 100 g/dm³ HNO_3 + 5 % H_2O_2.

Figure 1. Mass fraction of dissolved glass fiber paper material in decontaminating solutions depending on the process temperature when exposed to ultrasound



1 – 30 g/dm³ HNO_3; 2 – 100 g/dm³ HNO_3;
3 – 300 g/dm³ HNO_3; 4 – 450 g/dm³ HNO_3;
5 – 50 g/dm³ H3PO4; 6 – 100 g/dm³ H_3PO_4;
7 – 30 g/dm³ HNO_3 + 5 g/dm³ $H_2C_2O_4$;
8 – 100 g/dm³ HNO_3 + 5 g/dm³ $H_2C_2O_4$;
9 – 30 g/dm³ HNO_3 + 5 g/dm³ $H_2C_2O_4$ + 1 g/dm³ KF
10 – 100 g/dm³ HNO_3 + 5 g/dm³ $H_2C_2O_4$ + 1 g/dm³ KF

Figure 2. Mass fraction of dissolved glass fiber paper material in decontaminating solutions with the use of ultrasound method and without it

In general, all studied decontaminating solutions, except for fluorine-containing ones, had a gentle effect on the structure of the filter material and could be considered suitable for glass fiber paper filter decontamination purposes.

Decontamination of glass fiber paper filters

Glass fiber paper filters were decontaminated in an ultrasonic bath UZV-18/20 in three cycles (1 hour each) with and without ultrasonic treatment.

Samples of spent glass fiber paper filters contaminated with plutonium dioxide were fragmented into elements weighing approximately 1 g. Then they were emplaced into chemical beakers attached to purpose-designed holders (to prevent samples from floating up) and filled with the prepared solutions. The ratio between the decontamination solution (cm^3) and the mass of the sample (g) was no less than 300 : 1.

The process was implemented both at a room and at elevated (up to 60 °C) temperatures in three cycles (1 h each). Each subsequent treatment was done in a fresh volume of the decontamination solution. After each cycle, a sample was extracted from the solution to measure the plutonium content.

To evaluate the effectiveness of glass fiber paper filter liquid decontamination using ultrasonic treatment, the filters were dissolved in 600 g/dm^3 HNO_3 + 10 g/dm^3 HF at a temperature of (85 ± 5) °C. The ratio between the solution volume and the mass of the treated glass fiber paper filter sample ranged from 200 to 250 cm^3 per 1 g of the filter, whereas the decontamination time varied from 20 to 180 min. After complete dissolution of the filter, the remaining volume of the solution was measured and the content of plutonium in it was calculated.

The decontamination degree of the glass fiber paper filter ω was calculated by the formula:

$$\omega = \frac{m_d}{m_f + m_d} \cdot 100\,\%, \qquad (2)$$

where m_d is the mass of plutonium in spent decontamination solutions, mg;
m_f is the mass of plutonium in solution after the dissolution of the decontaminated filter, mg.

Figure 3 presents the results of the experiments on filter decontamination at a temperature of 60 °C.

The figure demonstrates that filter treatment with nitric acid solutions with mass concentrations of 300 and 450 g/dm3 provides sufficiently complete separation of the target product from the filter material (up to 98%). Moreover, it should be noted that at equal mass concentrations of nitric acid (100 g/dm3), oxalic acid added to it decreases the efficiency of plutonium extraction from 3.3 to 6.5 times. On the contrary, under equal process conditions, hydrogen peroxide introduced to a nitric acid solution at a concentration of 50 and 100 g/l helped to increase the yield of the target component by 1.4 times.

It was also demonstrated that when heated from a room temperature to 60°C, the decontaminating solution increased the yield of the target component from 6 to 8%.

It was also shown that solution replacement after each cycle could increase the effectiveness of

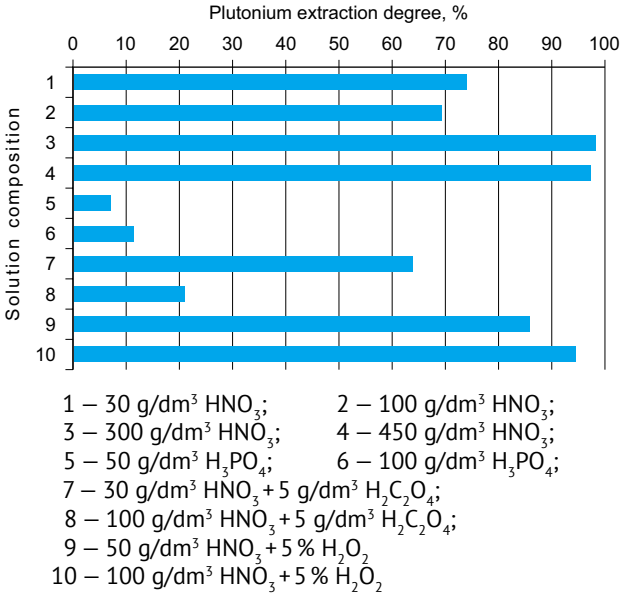


Figure 3. Dependence between the degree of plutonium extraction and the composition of the decontaminating solution at a temperature of 60°C

the decontamination process. Other experimental conditions being equal, continuous three-hour processing of the material in the working solution can decrease the plutonium yield into the solution by 1.5 times.

All decontaminated samples of glass fiber paper material were categorized as solid intermediate-level waste. However, the developed method involving the application of nitric acid solutions with a mass concentration of 300 to 450 g/dm^3 can provide a fairly complete recycling of the target component into the production process (for example, up to 9.8 kg of plutonium can be extracted from 100 kg of a spent filter material).

Optimization of the currently applied method for target component extraction from glass fiber paper filters

At the next stage of the study, the potential for a higher performance alkaline digestion and dissolution of glass fiber paper filters in a nitric acid-fluoride solution according to the current operational flowchart provided the use of ultrasonic treatment stage was evaluated.

The method currently applied to extract plutonium from spent glass fiber paper filters is considered quite laborious and time-consuming: only one filter can be treated per single work shift.

The tests were performed under conditions similar to the currently operated processing flowchart either involving the ultrasonic treatment or not.

Aqueous solution of sodium hydroxide with a mass concentration of 100 g/dm^3 was applied for

the alkaline digestion of the spent filter material: the ratio between the filter mass and the volume of the solution was taken equal to 1 g : 100 cm^3. The exposure time of the glass fiber paper material accounted for 3 hours:

- in a water bath at a solution temperature T = (60 ± 5) °C;
- in an ultrasonic bath at a solution temperature T = (60 ± 5) °C;
- on an electric stove at a solution temperature T = (80 ± 5) °C.

After cooling, the suspension was filtered through a Red Ribbon paper filter. The filter precipitate was washed with distilled water in a volume equal to the one of the alkaline solution.

At the next stage, the undissolved precipitate was treated with a mixture of aqueous solutions, namely, a 7 mol/dm^3 nitric acid solution, and a hydrofluoric acid solution with a molar concentration of 0.3 mol/dm^3 with a liquid and solid phase ratio of 300 cm^3/g at temperatures of 60 and 80 °C and at a temperature of 60 °C with the ultrasonic treatment applied. During the process, the time of complete suspension dissolution was monitored.

Table 2 summarizes the findings of the experiments.

Table 2. Results of experiments seeking to assess the potential for a higher performance extraction of the target components from spent glass fiber paper filters through the application of ultrasonic treatment

Experimental conditions	Without ultrasonic treatment		With ultrasonic treatment
Temperature of the solution, °C	60 ± 5	80 ± 5	60 ± 5
Treatment time with a hot alkaline solution, hours	3.0	3,0	3.0
Suspension dissolution time, min	> 1000	100	60
Mass fraction of the dissolved suspension, %	65	100	100

Table 2 shows that the rate of the filtered suspension dissolution during treatment in an ultrasonic bath is 1.7 times higher than the one at a temperature of 80 °C. If no ultrasonic treatment was applied during the decontamination of the glass fiber paper material at a temperature of 60 °C, it was not possible to attain complete dissolution of the suspension even after 20 hours of exposure. The mass fraction of the dissolved filter amounted to 65 %.

The experiments have demonstrated that the dissolution of the glass fiber paper filter suspension using the ultrasound method reduced the decontamination time to 1 hour.

Conclusion

The implemented tests were aimed at evaluating the potential for the extraction of the target component (plutonium) from glass fiber paper material constituting to spent aerosol filters of the gas treatment system. The potential for further upgrading of the existing method using the ultrasound treatment was evaluated.

The chemical resistance of the glass fiber paper material with respect to acidic decontaminating solutions was calculated. It was found that ultrasonic treatment produced only some negligible effect on the integrity of the filter material.

A method was developed providing the ultrasonic decontamination of glass fiber paper filters at a temperature of 60 °C. It involved the application of nitric acid solutions with a mass concentration of 300 and 450 g/dm3. It was shown that this method provided plutonium extraction from glass fiber paper material at a level of up to 98%.

It has been demonstrated that the developed decontamination method provides fairly complete recycling of the target component into the production process.

It was also shown that the use of ultrasound treatment with the currently applied method of plutonium recovery from spent glass fiber paper filters reduced the time of nitric acid-fluoride dissolution stage to 1 hour.

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