



Technical Note

A study of thermolysis of irradiated diamide-containing extraction systems with nitric acid

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ABSTRACT

The dynamics of gas release at thermal oxidation of extraction systems on the basis of diamides of dicarboxylic acids in fluorinated sulphones with 14 mol/L HNO₃ was investigated. The effect of pre-irradiation of the mixtures with accelerated electrons on the kinetics of their thermolysis was determined. The mixtures were heated in an autoclave at temperatures of 170 and 200 °C and irradiated using an electron accelerator to absorbed doses of 0.1, 0.5, and 1.0 MGy. It has been shown that no conditions for autocatalytic oxidation at thermolysis of extraction mixtures irradiated up to a dose of 1 MGy were developed.

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1. Introduction

The identification of the causes of explosion and fire accidents at the nuclear facilities plays an important role in nuclear and radiation safety warranty. The most dangerous among them are spent nuclear fuel (SNF) reprocessing facilities using the processes of extraction/re-extraction of the target components from nitric acid media with organic reagents in various diluents—PUREX (the Plutonium Uranium Redox EXtraction) and UNEX (UNiversal Solvent EXtraction). Interaction of organic solutions and nitric oxidizers represents a potential danger due to risk of uncontrolled exothermic reactions which already resulted to explosions at radiochemical plants in Russia and other countries [1–4].

To validate the possibility of application of the fluorinated diluents in radiochemical processes additional studies are required. Previous studies have shown that fluorinated diluents have rather high flash point (90 °C [5], 79 °C [6]) that is more than 10 °C higher than the recommended values [7]. Due to low probability of flammability of gaseous phase the given compounds are of interest for

practical application in extraction processes. Currently trifluoromethylphenylsulphone (FS-13) diluent is actively investigated for the possibility to be used in the Grouped ActiNide Extraction (GANEX) process in order to substitute for fire-dangerous cyclohexanone [8]. No essential exothermic effects under contact of the unirradiated FS-13 diluent with nitric acid with a concentration of up to 14 mol/L and a temperature of up to 120 °C have been found [5–11]. Therefore, the data on thermal and radiation stability of this diluent in complex extraction mixtures under high radiation doses especially in the solutions containing alpha-emitting isotopes (Pu, Am, Cm, etc) are extremely relevant.

In order to improve the fire safety and radiation stability of the UNEX process the possibility of replacing carbomailphosphine oxides with phosphorus free extractants, for example diamides of heterocyclic dicarboxylic acids [12–14] is under investigation. Among them high extraction capacity with respect to ²⁴¹Am and ¹⁵²Eu is a characteristic of di (N-ethyl-4-hexylanilide) 2,2'-bipyridyl-6,6' dicarboxylic acid (DYP-7) [15,16]. The aim of the present work was to study of explosion and fire stability of extraction mixtures based on diamides of heterocyclic dicarboxylic acids in the FS-13 and meta -nitrobenzotrifluoride (F-3) diluents.

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2. Experimental

Three diamides were proposed as extractants for use in the UNEX process for high level waste (HLW): di (N-ethyl-4-ethylanimid) 2,2'-bipyridin-6,6'-dicarboxyl acid (DYP-9); di (N-ethyl-4-hexylanimid) 2,2'-bipyridin-6,6'-dicarboxyl acid (DYP-7) and di (N-ethyl-4-fluoranimid) 2,6-pyridinedicarboxyl acid, Et (pFPh)DPA. The chemical structures of the diamides are shown in Fig. 1. As potential diluents, two polar compounds were tested: FS-13 and F-3.

The extractants and diluents (as many as 95% of target component), reagent-grade nitric acid, HNO₃, and distilled water (Russian Standard 6709–72) were used in the experiments.

The prepared organic phases (organic solvents) had the following compositions:

- 1) 0.1 mol/L DYP-7 in FS-13;
- 2) 0.1 mol/L DYP-7 in F-3;
- 3) 0.05 mol/L DYP-9 in FS-13;
- 4) 0.05 mol/L DYP-9 in F-3;
- 5) 0.05 mol/L Et (pFPh)DPA in FS-13;
- 6) 0.05 mol/L Et (pFPh)DPA in F-3.

The prepared organic solvents were three-fold agitated with 14 mol/L nitric acid solution (the highest concentration used in radiochemical processes) at a phase volume ratio of 1:1 for 30 min to an equilibrium concentration of HNO₃ in extractant of 1.3 mol/L. Saturation of organic solvents with 14 mol/L nitric acid prior to irradiation was performed with the aim to simulate conditions of extraction of metals from the nitric acid solutions during the HLW processing. The prepared organic solvents were irradiated using a UELV-10-10-C-70 linear electronic accelerator (CCU FMI IPCE RAS) with energy of electrons 8 MeV to absorbed doses of 0.1, 0.5, and 1.0 MGy. Radiation doses absorbed by the acid-saturated organic solutions were calculated using data received with a film dosimeter based on phenazine dye.

The samples of organic solvents for thermolysis were contacted with a 14 mol/L nitric acid solution at a volume ratio of 1:2. Both the as-prepared two-phase systems and those kept for 2 weeks followed by separation of organic and aqueous phase and repeated intermixing of organic phase with 14 mol/L HNO₃ were subject to thermolysis. Under these conditions, the easily oxidized products of radiolysis react with nitrates and nitric acid thus the thermal stability of extractant increase.

Thermolysis of the pristine and pre-irradiated 10 mL samples was conducted under atmospheric pressure, using a metal unit described in Ref. [17]. The cells with samples were put in the thermostat that was activated for heating up to temperature 150 °C with rate 1 °C/min and isothermal holding. Thereby the oxidation processes that occur in extraction systems at normal operation (less than 60 °C) and accident condition (at elevated temperatures) was

studied. During heating of samples the thermograms and volume profiles were measured.

Specific volume of the gases was calculated as the ratio of the total volume of released gas to the volume of the organic phase at the beginning of the experiment. The gas measuring system determines the volume of non-soluble gases at room temperatures. The error in determining the volume of gases released did not exceed 5%. The chemical composition of the released gas in this work was not determined.

Investigations under elevated pressure were performed in a thermostat with 300 cm³ autoclave containing the 30 mL sample (10 mL of organic phase and 20 mL of aqua phase) [18]. Firstly, the sample was placed into a cold autoclave and after sealing, the autoclave was put into a hot thermostat. During heating the samples in the closed volume the thermo-gram and pressure-profile were measured. The uncertainty of the pressure measurement was 5%. Total duration of the experiment was for 5 h. Temperatures at all experiments were measured by chromel-alumel thermocouples in stainless steel protected covers and errors do not exceed 2 °C.

3. Results and discussion

3.1. Thermolysis of extraction systems under atmospheric pressure

All the above-listed two-phase diamide-bearing extraction systems were examined.

Experimental results at a temperature in thermostat of 150 °C have shown that in all the cases, heating of the extractant samples pre-treated with nitric acid were not accompanied with a sharp rise in their temperature due to exothermic processes and the release of the cell contents and exhaust of the cell containment due to gas release intensification.

By measuring the volume of gases released by heating samples, the total gas volume was determined and recalculated per 1 L of the initial liquid sample. The data on the specific volume of gases released by thermolysis of the pre-irradiated two-phase diamidic extraction systems are shown in Figs. 2 and 3. Fig. 2 illustrates values of specific volume of released gases for two different diamides in the same diluent FS-13 as a function of the radiation dose. The values of specific volume of gases released during thermolysis of unirradiated two-phase samples are at the level of 40 L_g/L_l. For the samples irradiated to absorbed dose of 1 MGy the values were found to be higher by nearly one order of magnitude than those for the unirradiated samples. Moreover, it has been established that with the increase of the radiation dose, the discrepancy in the volume of gases released during thermolysis of various diamide-containing extractants increases (Fig. 2).

The data on the effect of the nature of diluents at thermolysis of DYP-9 extractant solutions are shown in Fig. 3. For all the extraction systems studied the maximum gas release rates during thermolysis

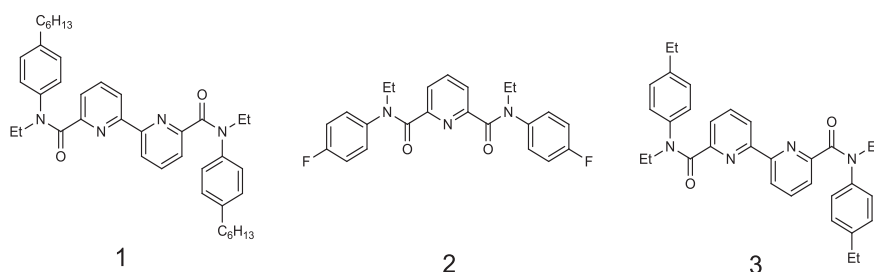


Fig. 1. The chemical structures of di (N-ethyl-4-hexylanimid) 2,2'-bipyridin-6,6'-dicarboxyl acid, DYP-7 (1); di (N-ethyl-4-fluoranimid) 2,6-pyridinedicarboxyl acid, Et (pFPh)DPA (2); di (N-ethyl-4-ethylanimid) 2,2'-bipyridin-6,6'-dicarboxyl acid, DYP-9 (3).

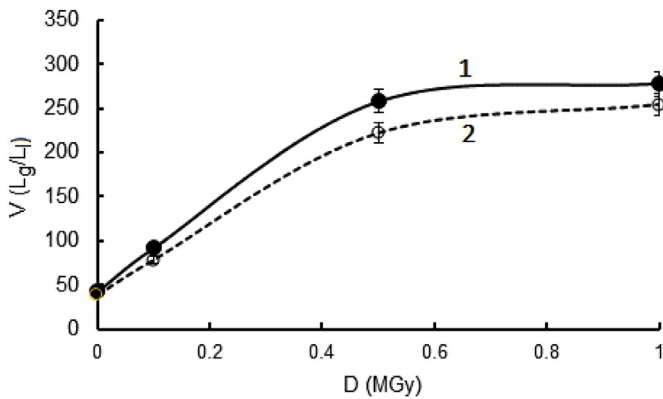


Fig. 2. The dependence of specific volume of the gases release (Liter of gas/Liter of liquid) from absorbed dose at thermolysis of the extraction systems 0.1 mol/L DYP-7 in FS-13–14 mol/L HNO₃ (1) and 0.05 mol/L of Et (pFPh)DPA in FS-13–14 mol/L HNO₃ (2).

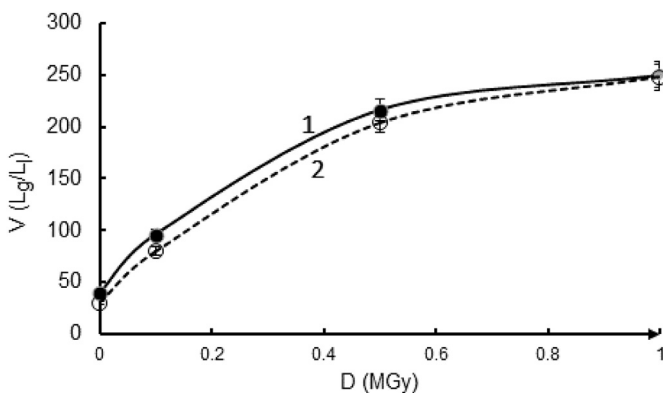


Fig. 3. The dependence of specific volume of the gases release (Liter of gas/Liter of liquid) from absorbed dose at thermolysis of the extraction systems 0.05 mol/L of DYP-9 in FS-13–14 mol/L HNO₃ (1) and 0.05 mol/L of DYP-9 in F-3–14 mol/L HNO₃ (2).

have been calculated. During the process of thermolysis, the organic solvents prepared with the FS-13 diluent produced some higher amount of gaseous products than those with the F-3 diluent.

The maximum gas release rate for thermolysis of two diamide-containing extraction systems in FS-13 was studied as a function of absorbed dose, and the observed changes are plotted in Fig. 4. Within the range of absorbed dose from 0 to 1 MGy, the maximum

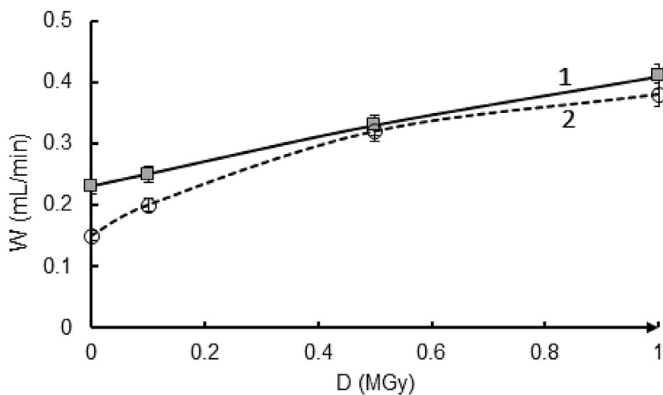


Fig. 4. The dependence of specific volume of the gases release (Liter of gas/Liter of liquid) from absorbed dose at thermolysis of the extraction systems 0.05 mol/L of Et (pFPh)DPA in FS-13–14 mol/L HNO₃ (1) and 0.1 mol/L of DYP-7 in FS-13–14 mol/L HNO₃ (2).

gas release rates smoothly increases by about two-fold with increasing absorbed dose for both the extraction systems studied. Comparison of the obtained results with reference data for extraction systems based on tributyl phosphate (TBP) under close thermolysis conditions [7,19] allows to make the following conclusions:

- thermolysis of unirradiated, two-phase samples of diamides in FS-13 (F-3) containing 14 mol/L HNO₃ solution and the TBP bearing systems with 12 mol/L HNO₃ produce the same specific volumes of gaseous products;
- specific volume of gaseous products released during thermolysis of the irradiated two-phase diamide-based extraction systems is by 3–5 times higher as compared to the values measured for the TBP-based extraction systems;
- the maximum gas release rate at thermolysis of irradiated samples of diamide-containing and TBP based extraction systems were found to be similar.

3.2. Thermolysis of extraction systems in a closed volume

Experiments on determination of characteristics of thermolysis were conducted for all the sources, chemically-treated, and irradiated two-phase diamide-containing samples were for all the extraction systems.

The two-phase samples were heated in a thermostat at two temperatures of 170 and 200 °C. For the unirradiated extractants in the FS-13 and F-3 diluents a notable gas release occurs at 130 °C and 110 °C, respectively. No appreciable exothermic effects were observed during sample heating. Maximum deviation on temperature curve did not exceed 10 °C.

The values of maximum pressure developed in the closed volume and the pressure build-up rate during the thermolysis process in the autoclave have been determined from the experimental data on the variation of pressure with heating time. The extreme dependences of the maximum pressure developed during thermolysis in a closed volume of autoclave of the organic solvent samples irradiated by the electron beam with a dose of the range 0–1 MGy were determined (Fig. 5). For the unirradiated samples, the maximum pressure value during thermolysis of extraction systems in a closed volume was found to be within the range of 1.8–2.1 MPa (18–21 atm). According to the data obtained, when the temperature in the thermostat increased from 170 °C to 200 °C, the

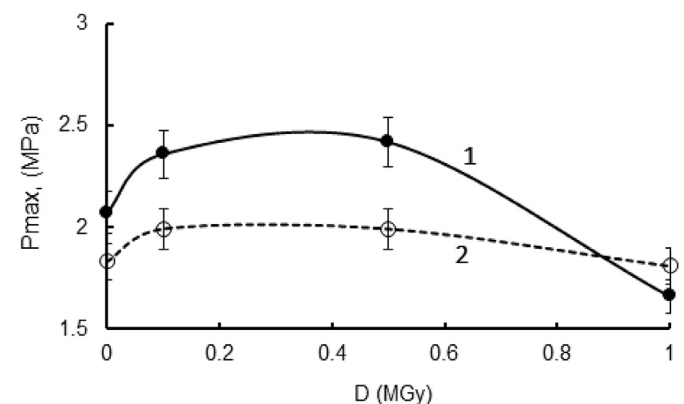


Fig. 5. The dependence of maximum pressure in autoclave from absorbed dose at thermolysis to 170 °C of the extraction systems 0.05 mol/L of DYP-9 in FS-13–14 mol/L HNO₃ (1) and 0.05 mol/L of Et (pFPh)DPA in F-3–14 mol/L HNO₃ (2).

maximum pressure achieved in the autoclave as a result of thermolysis increased for all investigated extraction diamide-containing systems, but in a significantly different extent for each of them. The data obtained are shown in Fig. 6 (bars 1 and 2) on the example of three extraction systems.

Under similar conditions, experiments were carried out with samples of diamide-containing extraction systems, which were in a 2-week contact with a 14 mol/L solution of nitric acid before thermolysis that simulate longtime contact of degraded extractant with nitric acid solutions during normal operation of HLW processing. As it is shown on the example of heating of two-phase samples to 170 °C (Fig. 6) such pretreatment of samples by a strong oxidizer led to a decrease in the maximum pressure developed during thermolysis. This was observed for all investigated diamide-containing extraction systems.

The results of determining the change of the maximum rate of pressure during thermolysis of diamide-containing extraction systems in general form are shown in Fig. 7. An increase in the heating temperature of two-phase samples from 170 °C to 200 °C leads to an increase in the rate of pressure change in the autoclave. In relation to samples pre-treated with 14 mol/L solution of nitric acid for 2 weeks the pressure change rate is shown in Fig. 7, (lines 2 and 3). Under comparable conditions, the rate of pressure increases during thermolysis for the samples pre-treated with concentrated nitric acid was higher than that for untreated samples of the diamide-containing extractants (lines 1 and 2 in Fig. 7). As seen from the obtained data, the long-term contact with concentrated nitric acid diamide-containing extraction systems irradiated with accelerated electrons leads to a decrease in the maximum pressure during their long stay in a closed volume and to an increase in the rate of pressure growth in the initial heating period.

Comparison of the results with the data in Refs. [7,19] obtained for similar conditions in relation to extraction systems containing TBP with 12 mol/L nitric acid solution notes that:

- thermolysis of the diamide-containing extraction systems in the closed volume is accompanied by significantly less exothermic effects (3–7 °C) than those for the extraction systems containing TBP, where it can exceed 100 °C;
- values of the maximum pressure at thermolysis in the closed volume for unirradiated diamide-containing extraction systems (1.8–2.1 MPa) are significantly lower, than those for the extraction systems containing TBP (up to 6 MPa).

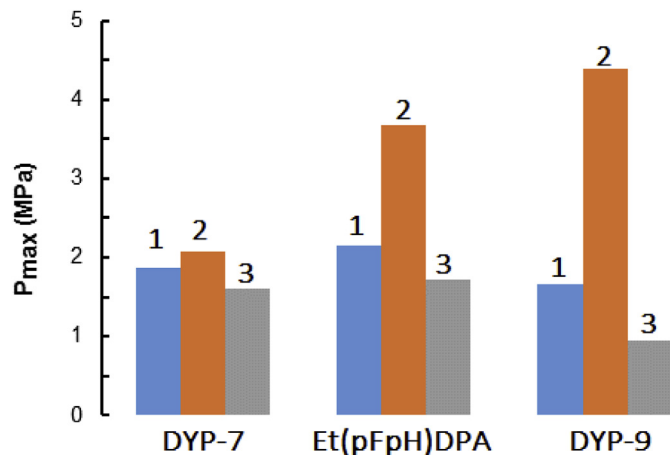


Fig. 6. The values of maximum pressure in autoclave at heating of the samples irradiated to a dose of 1 MGy at temperatures of 170 °C (1), 200 °C (2), and 170 °C pre-contacted with 14 mol/L HNO₃ (3) for two weeks.

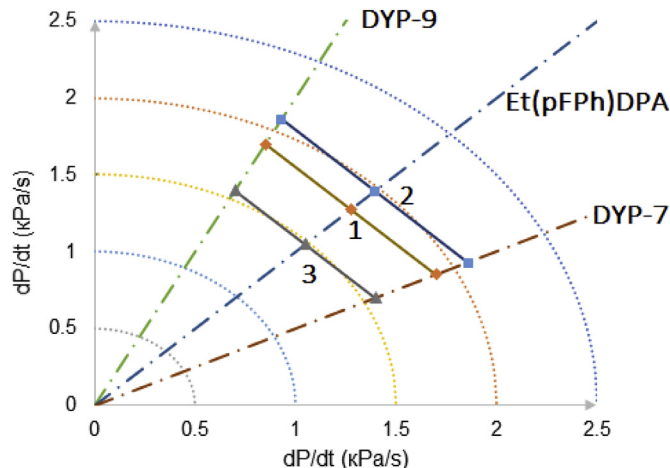


Fig. 7. The values of pressure variation rate at heating of irradiated (1 MGy) samples of extraction systems to temperatures of 200 °C (1), 200 °C pre-contacted with 14 mol/L HNO₃ (2), and 170 °C pre-contacted with 14 mol/L HNO₃ (3).

4. Conclusion

Comparative study of thermal stability of diamides of 2,6-pyridindicarboxylic and 2,2'-bipirili-6,6' dicarboxylic acids in FS-13 and F-3 diluents has been shown as follows:

- under atmospheric pressure, keeping at 150 °C in contact with 14 mol/L HNO₃ all the irradiated diamides (DYP-7, DYP-9, and Et (pFpH)DPA) in heavy potentially fire- and explosion-safe diluents (FS-13 and FS-3) have acceptable thermal stability for practical purposes. Even in the case of radiation degradation they do not pose increased risk compared with the data for the extraction systems based on TBP used in practice;
- under conditions of closed volume in autoclave, heating up to 170 °C, in contact with 14 mol/L nitric acid, all studied irradiated extraction systems with diluents FS-13 and F-3 have an acceptable thermal resistance for practical application. Thus, the recorded pressure values (18–21 atm) during heating of samples in the autoclave for FS-13 were lower than in the case of heating of extraction systems containing TBP under comparable conditions (up to 60 atm); the achieved overheating of the samples due to exothermic processes (3–7 °C) was significantly lower as compared to extraction systems containing TBP (more than 100 °C);
- at long-term contact of pre-irradiated extraction mixtures with concentrated nitric acid (14 mol/L), partial oxidation of the products of radiation degradation occurs. As a result, in the conditions of heating of the obtained samples to 170 and 200 °C in a closed volume of the autoclave, all studied irradiated extraction systems with diluents FS-13 and F-3 demonstrated a decrease in the intensity of oxidizing processes in comparison with the same samples without long-term contact of the components of extraction systems. Thus, long-term contact of extraction mixtures with concentrated nitric acid to some extent increases the thermal stability of the investigated extraction systems.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.net.2018.07.011>.

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