



Technical Note

Thermal stability of nitric acid solutions of reducing agents used in spent nuclear fuel reprocessing



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ABSTRACT

The thermal stability of carbohydrazide, hydrazine nitrate, acetohydroxamic acid in nitric acid solutions has been studied at atmospheric pressure and above atmospheric pressure. The volumes of gaseous products of thermolysis and the maximum rate of gas evolution have been determined at atmospheric pressure. It has been shown that, despite the high rate of gas evolution and large volumes of evolved gases, the conditions for the development of autocatalytic oxidation are not created. Exothermic processes are observed in a closed vessel in the temperature range of 50–250 °C. With an increase in the concentration of nitric acid, the temperatures of the onset of exothermic effects for all mixtures decrease, and the values of the total thermal effects of reactions increase, to the greatest extent for solutions with carbohydrazide.

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1. Introduction

Mixtures of reducing agents and/or complexing agents with nitric acid oxidants are used in technological operations at radiochemical plants (RCP) during the reprocessing of spent nuclear fuel (SNF) [1,2]. They are used to change the valence of metals; are part of solutions for the destruction (neutralization) of HNO₃ and ammonia mother solutions; are added to dissolve slurries and deposits during waste storage. Reducing agents can be contained in liquid waste and accumulate on filters together with oxidizing agents. One of the usual operations in the RCP technology is the evaporation of nitric acid solutions at temperatures of 90–120 °C. The potential danger of such operations is the possibility of exothermic oxidation processes, accompanied by evolution of heat and gases, which can lead to the release of the contents of the apparatus or its deformation. An even greater danger is the drying of nitric acid solutions containing reducing agents, since when a certain temperature is reached, these mixtures are capable of self-ignition. In some cases, the process of mixing of reducing agents with oxidizing agents due to intense heat and gas evolution is also dangerous.

In the practice of Russian enterprises, there are cases of

accidents caused by intense exothermic reactions of reducing agents with nitric acid [3,4]. The thermal explosion of dry acetate-nitrate salts formed during the drying of liquid waste with subsequent heating due to the heat of radioactive decay of nuclides caused partial destruction of a number of industrial buildings with contamination of the plant's territory and the formation of a nuclear trace (FSUE « Production Association « Mayak», 1954). A thermal explosion upon contact of formic acid with 10.9 mol L⁻¹ nitric acid was accompanied by rupture of the technological apparatus, partial destruction of the chamber and radioactive contamination in and out of the chamber (FSUE « Production Association « Mayak», 1959). Due to the increasing intensity of operation of technological mixtures and the use of modified fuel for fast neutron reactors, the main attention is paid to ensuring the natural safety of all processes, including spent nuclear fuel reprocessing, through development of underpinned safety cases based on defense-in-depth and regulatory oversight.

For the existing SNF reprocessing technologies, the properties of nitric acid solutions of reducing agents, such as hydrazine derivatives [5–10], carbamides, organic acids, formaldehyde, hydroxylamine [11,12], and their thermal stability have been studied. Kinetic models that predict the stability of hydroxylamine nitrate (HAN) in aqueous solutions containing nitric acid and plutonium have been developed [13–15], and the application of these models to process vessels in the simulation of standard and emergency modes has been studied [15]. Currently, new water-soluble organic

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compounds are being introduced as reducing agents and/or complexing agents for separating uranium from plutonium, neptunium and technetium. These include acetohydroxamic acid (AHA), which is used for the reduction and complex formation of plutonium and neptunium to reduce their distribution in the organic phase of tributyl phosphate (TBP) [16–19] and carbonylhydrazide (CH), a promising effective reducing agent for Pu(IV) and Np(VI), which does not form salt-containing products and has antinitrite properties [20–22]. The aim of this study is to assess the thermal stability of carbonylhydrazide, hydrazine nitrate (HN), acetohydroxamic acid and their mixtures under the conditions of their use in the technological process.

2. Experimental methods

The thermal stability of the following reducing agents has been studied: carbonylhydrazide 97% («ACROS»), acetohydroxamic acid 98% (JSC «V.G. Khlopin Radium Institute»), hydrazine nitrate, and their mixtures. HN was prepared by mixing of hydrazine hydrate (HH) 100% (Pariteks LLC) with nitric acid. The solutions of reducing agents were prepared with three concentrations of nitric acid: 0.8, 1.6, and 3.2 mol L⁻¹ of the high purity grade. These concentrations of reducing agents correspond to the conditions of their use in the extraction technology of spent nuclear fuel processing, in which solutions containing 1–3 mol L⁻¹ of HNO₃ are used. The concentration of nitric acid was determined by potentiometric titration. Each concentration of HNO₃ corresponds to its own concentration of the studied substances (Table 1).

Reducing agent solutions were prepared by mixing of the required concentration with nitric acid in the above proportions. To obtain solutions of mixtures of reducing agents, the required amount of 0.8, 1.6, or 3.2 mol L⁻¹ nitric acid was mixed with the calculated amount of HN, then AHA or CH was added and stirred until the crystals were completely dissolved.

To determine the characteristics of exothermic processes occurring in the studied samples at a pressure above atmospheric, a DSC-500 differential scanning calorimeter (manufactured by Samara State Technical University) was used. The sample mass was 11 ± 2 mg (10 µL). An aliquot of the solution was placed in a steel sealed crucible and heated at a rate of 2 and 5 K/min in a temperature range of 50–250 °C; the heating time was 40–110 min, depending on the heating rate. An empty crucible served as a reference sample. To process the results, the Proteus software package (Netzsch) was used, in which the temperature of the onset of the exothermic effect (T_{st}), the maximum temperature reached in the reaction (T_{max}), and the value of the specific thermal effect (J/g) were determined using the Proteus Analysis environment.

A decrease in the heating rate of the sample from 5 to 2 K/min has little effect on the position of exothermic effects; therefore, the article presents thermograms at a heating rate of 5 K/min. However, with a change in the heating rate, the character of the heat flow curve changes (Fig. 1). Comparison of thermograms of two heating rates shows that some exothermic processes are complex, i.e. several reactions take place and their effects are superimposed on each other. Due to the large number and proximity of temperature

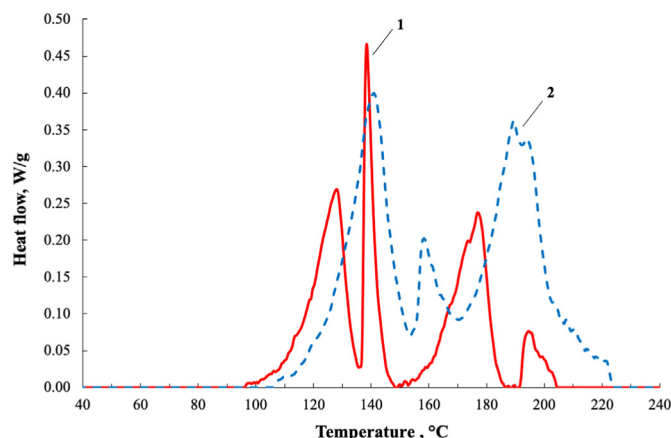


Fig. 1. Change in heat flow during heating of the HN with 3.2 mol L⁻¹ HNO₃ at different heating rates (K/min): 1–2; 2–5.

ranges, it is difficult to separate them; therefore, in the article we present the total thermal effects of the reactions.

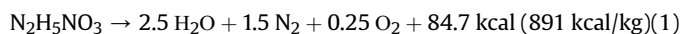
To study the thermal stability at atmospheric pressure, a «Thermoflame-2» unit was used [23], samples with a volume of 2 ml were kept for 6 h at a thermostat temperature of 100 °C. During thermolysis, the temperature and the volume of the evolved gas in the system were monitored. The values of the maximum gas evolution rate (W_{max}), the volume of evolved gases (V_g); temperature of the onset of the exothermic reaction T_{st} were determined. The method error is less than 5%.

3. Results and discussion

3.1. Evaluation characteristic of oxidative reaction of reducing agents by nitric acid

The maximum evolution of heat and gases is achieved in solutions with a stoichiometric ratio of a reducing agent and an oxidizing agent, oxidation of hydrogen to H₂O and carbon to CO₂. Real technological nitric acid solutions contain significantly less reducing agents than mixtures of stoichiometric composition. Emergency situations with technological mixtures of reducing agents and oxidizing agents can occur when they are heated to a critical temperature (T_{st}), which depends on the concentration of the components and the reactivity of the reducing agents. If the boiling point of the solutions is higher than T_{st}, then intense exothermic reactions are possible only at above atmospheric pressure.

Hydrazine nitrate melts at a temperature of 70.7 °C, sublimates at 140 °C, begins to decompose intensively at temperatures of 200–220 °C, flares up at 270 °C [24]. Its decomposition occurs according to the equation:

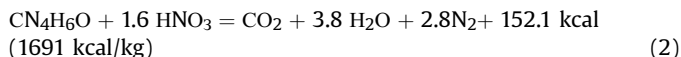


The specific volume of gaseous reaction products (V_{sp}) is about 1000 L per 1 kg of HN, its characteristics are close to trinitrotoluene (TNT). In aqueous solutions, the temperature of its exothermic decomposition cannot be reached, but isothermal decomposition is possible with the release of 412 L of gases per kg of HN.

Oxidation of carbonylhydrazide to final products occurs according to the equation:

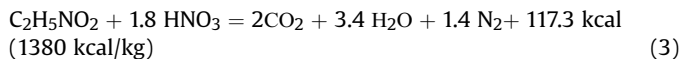
Table 1
Compositions of the mixtures used in the experiments.

HNO ₃ concentration, mol · L ⁻¹	Reducing agent concentration, g/l (mol · L ⁻¹)		
	AHA	HN	CH
0.8	3 (0.04)	5 (0.05)	5 (0.06)
1.6	6 (0.08)	10 (0.11)	10 (0.11)
3.2	12 (0.16)	20 (0.21)	20 (0.22)



with the release of 1890 L (H₂O_v) or 946 L (H₂O_l) per kg of CH, where v–vapor, l–liquid.

The reaction between acetohydroxamic and nitric acids can be represented by the following equation:



with the release of 2030 L of gaseous products (H₂O_v) or 1015 L (H₂O_l) per kg of AHA. The mass ratio of the components in this mixture of AHA:HNO₃ g/g is 1:1.512.

However, the interaction of reducing agents with nitric acid solutions can occur not only according to the equations presented above. The degree of phlegmatizing action of water is also unknown. Therefore, it is not possible to calculate the possibility of the occurrence of potentially hazardous exothermic reactions in nitric acid solutions of reducing agents; experimental studies are needed.

3.2. Study of thermal stability at above atmospheric pressure

For solutions of individual reducing agents with 0.8, 1.6, and 3.2 mol L⁻¹ nitric acid, it has been found that linear heating in sealed crucibles is accompanied by a number of exothermic effects differing in intensity, thermal effect, and temperature of the onset of the exothermic reaction (Table 2).

Nitric acid solutions of AHA undergo changes accompanied by exothermic effects in the temperature range from 76 to 142 °C (Fig. S1). Regardless of the concentration of nitric acid, exothermic reactions are characterized by a sharp jump to the maximum temperature; however, the specific thermal effects of these reactions are small. Heat evolution for AHA solutions ends after the end of the exothermic reaction, and no exothermic effects occur up to 250 °C. Nitric acid solutions of CH and HN are characterized by a gradual change in heat evolution with two or three exothermic effects, which begin at higher temperatures, but their total value is several times higher than for solutions with AHA (Figs. 2 and 5).

In solutions of CH with a nitric acid concentration of 1.6 and 3.2 mol L⁻¹, exothermic reactions begin at close temperatures of 110–109 °C, respectively (Fig. 3). The specific thermal effect of the exothermic reaction increases with an increase in the concentration of HNO₃, for 3.2 mol L⁻¹ HNO₃ its sharp jump is observed,

Table 2
Temperature of the onset of exothermic reaction (T_{st}) and maximum temperature (T_{max}) for reducing agents and their mixtures, depending on the concentration of HNO₃.

Reducing agent	Temperatures	C(HNO ₃), mol·L ⁻¹		
		0.8	1.6	3.2
AHA	T _{st} , °C, ±3%	142	133	76
	T _{max} , °C, ±3%	145	135	78
CH	T _{st} , °C, ±3%	136	110/165 ^a	109/204 ^a
	T _{max} , °C, ±3%	162	144/194 ^a	149/210 ^a
HN	T _{st} , °C, ±3%	181	160	102/154 ^a /169 ^b
	T _{max} , °C, ±3%	186	183	141/158 ^a /189 ^b
AHA + HN	T _{st} , °C, ±3%	166	108/176 ^a	91/156 ^a
	T _{max} , °C, ±3%	176	158/193 ^a	125/180 ^a
CH + HN	T _{st} , °C, ±3%	138	117	91/120 ^a
	T _{max} , °C, ±3%	182	163	96/158 ^a

^a Data for the second exothermic effect.

^b Data for the third exothermic effect.

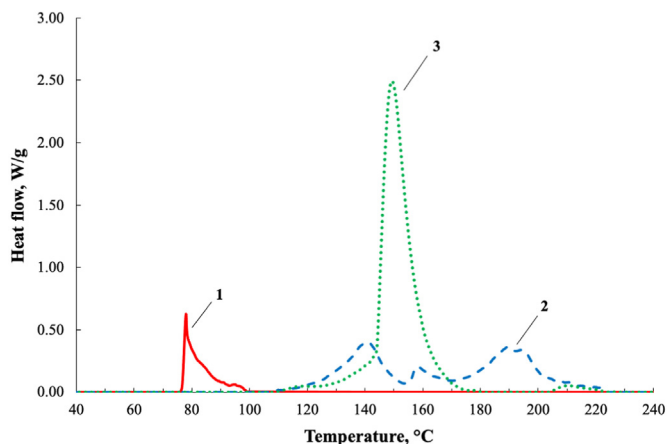


Fig. 2. Change in heat flow during heating with 3.2 M HNO₃ of: 1 – AHA; 2 – HN; 3 – CH.

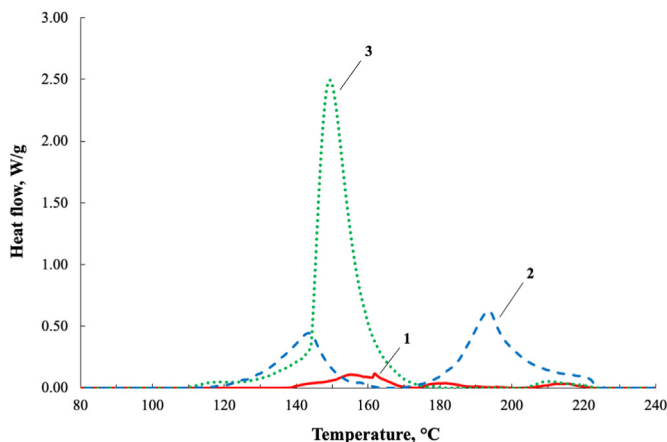


Fig. 3. Change in the heat flow during heating of the CH depending on the concentration of HNO₃ (mol·L⁻¹): 1–0.8; 2–1.6; 3–3.2.

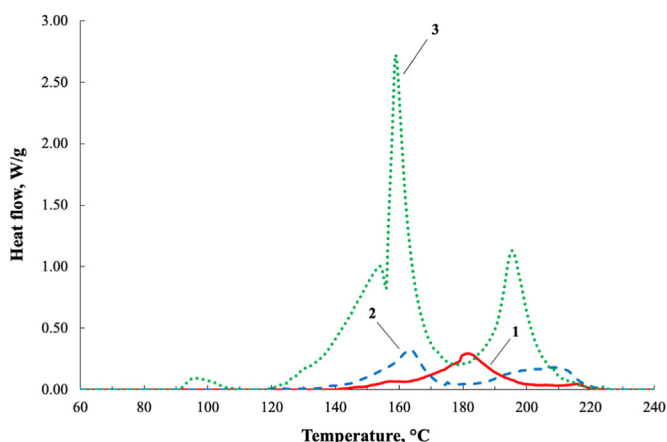


Fig. 4. Change in heat flow during heating of CH with HN depending on the concentration of HNO₃ (mol·L⁻¹): 1–0.8; 2–1.6; 3–3.2.

which amounted to 374 ± 15 J/g, which is several times higher than for solutions with AHA. For the CH solution with 1.6 mol L⁻¹ HNO₃, two exothermic processes were observed with a total thermal effect of 223 ± 10 J/g, which is much less than for 3.2 mol L⁻¹ HNO₃. A

similar character of the change in the specific thermal effect depending on the concentration of nitric acid is also observed for AHA solutions, however, its maximum value does not exceed 70 J/g.

Thus, for all studied solutions of reducing agents, with an increase in the concentration of nitric acid, the temperatures of the onset of exothermic effects decrease and the values of the total thermal effects of reactions increase. A particularly strong decrease in the temperature of the onset of the exothermic reaction is typical for an AHA solution with 3.2 mol L⁻¹ HNO₃, the value of T_{st} was 76 °C, which is significantly lower than the temperatures of the evaporation process. The total thermal effect of this reaction was 67 ± 5 J/g.

Solutions of HN and CH at a nitric acid concentration of 3.2 mol L⁻¹ have similar temperatures for the onset of exothermic effects of oxidation – 102 and 109 °C (Fig. 2). In this case, further thermolysis of HN and CH was accompanied by a number of reactions with the heat evolution. This raises the question of how these reducing agents affect each other in a mixture. Whether the presence of HN will shift the initial temperature range towards an increase in temperature or other reducing agents can initiate the oxidation of HN. Therefore, the values of thermal effects have been determined for mixtures of HN with AHA and HN with CH (Table 2) under the same experimental conditions.

For solutions of a mixture of HN with CH (Fig. 4), exothermic processes occur in the temperature range from 90 to 225 °C; for a mixture of HN with AHA, an abrupt exothermic effect was observed in the range from 90 to 210 °C (Fig. S2). For nitric acid solutions of mixtures of reducing agents, as well as for individual reducing agents, with an increase in the concentration of HNO₃, the values of the total thermal effect of the reaction increase, and the temperatures of the onset of exothermic reactions decrease (Table 2).

The specific thermal effect (Fig. 5, S1-S2) of the exothermic reaction at 166 °C for a solution of AHA with HN in 0.8 mol L⁻¹ HNO₃ was 53 ± 5 J/g. The exothermic effect of a mixture of AHA with HN in 1.6 mol L⁻¹ HNO₃ is complex and consists of two peaks. Analysis of the exothermic effect at 108 °C showed that its heat was 50 ± 5 J/g, and at 176 °C – 20 ± 5 J/g. For a solution of AHA with HN in 3.2 mol L⁻¹ HNO₃, two exothermic effects were observed. The value of the specific thermal effect of the first process was 114 ± 5 J/g, of the second – 22 ± 5 J/g. Specific thermal effects of exothermic reaction for nitric acid solution of a mixture of CH with

HN are: for 0.8 mol L⁻¹ HNO₃ at a temperature of 138 °C – 86 ± 5 J/g; for 1.6 mol L⁻¹ HNO₃ at 117 °C – 123 ± 5 J/g; for 3.2 mol L⁻¹ HNO₃, two exothermic effects were observed, the total value of which was 631 ± 5 J/g, which is 494 ± 5 J/g more than in the nitric acid solution of AHA with HN under the same conditions. Thermal effects for CH and its mixture with HN sharply increase with an increase in the concentration of nitric acid and significantly exceed the values for the mixture with AHA, which affects their thermal stability.

Thus, at nitric acid concentrations of 0.8 and 1.6 mol L⁻¹, all the considered reducing agents and their mixtures are thermally stable. AHA solutions based on 3.2 mol L⁻¹ HNO₃ decompose at temperatures below the evaporation temperatures of technological solutions, but have a low thermal effect. Solutions of CH with 3.2 mol L⁻¹ HNO₃ decompose at higher temperatures, but at the same time the total thermal effect of the reaction increases by several times.

3.3. Study of thermal stability at atmospheric pressure

In the technological process, liquid radioactive waste containing reducing agents is formed at the RCP, and they are evaporated to minimize their volume. The creation of excess pressure in the apparatuses due to the evolved gaseous oxidation products can be considered potentially dangerous. To estimate the volumes of the evolved gases, the solutions were held at atmospheric pressure and a temperature of 100 °C, which is lower than the boiling point of the mixture. The choice of this temperature value makes it possible to estimate the volume of gaseous oxidation products and the possibility of uncontrolled exothermic reactions in the condensed phase.

To simulate process upsets, the concentrations of 25 and 50 g/L in 12 mol L⁻¹ HNO₃ were taken for AHA, CH, HN solutions, and the gas evolution parameters were determined for them (Table 3). The volume of the samples was 2 ml, the tests were carried out at a temperature of 100 °C for 5 h.

At atmospheric pressure, the processes of gas evolution of mixtures of reducing agents with 12 mol L⁻¹ HNO₃ at 100 °C proceed for tens of minutes without visible exothermic effects, W_{max} does not exceed 16 ml/min. The characteristic dependence of the change in the temperature of the mixture and the volumes of the evolved gases is presented by the example of an AHA solution. As can be seen from Fig. 6, there are no exothermic effects. The volumes of evolved gases for mixtures containing AHA are significant, despite the absence of exothermic effects. The maximum gas evolution rate for the CH is two times higher than for the AHA (Table 3). After the end of heat evolution, the gas evolution also ends. For samples containing 50 g/L HN, the reaction with the evolution of gaseous products began even during the preparation process, then gas evolution was observed for an hour at a maximum rate of 16.0 ml/min, which is 3 times higher than for AHA solutions and 1.5 times higher than for CH (Fig. 7). The maximum rates of gas evolution and the volume of evolved gas are weakly dependent on the concentration of the reducing agent (Table 3).

Thus, at the temperatures of the technological process of reductive back-extraction, the interaction of the components of the solutions does not occur. At temperatures close to the temperatures of evaporation, exothermic processes are possible, but only if there is a sufficient amount of reducing agent, which is confirmed by the data of [10,25].

The nature of gas evolution for mixtures of AHA with HN of various concentrations turned out to be different from each other. For mixtures with a concentration of reducing agents of 25 g/L, gas evolution continued during the entire time of the experiment, whereas at a concentration of 50 g/L, the entire volume of gaseous products released in the first 10 min of the experiment. The

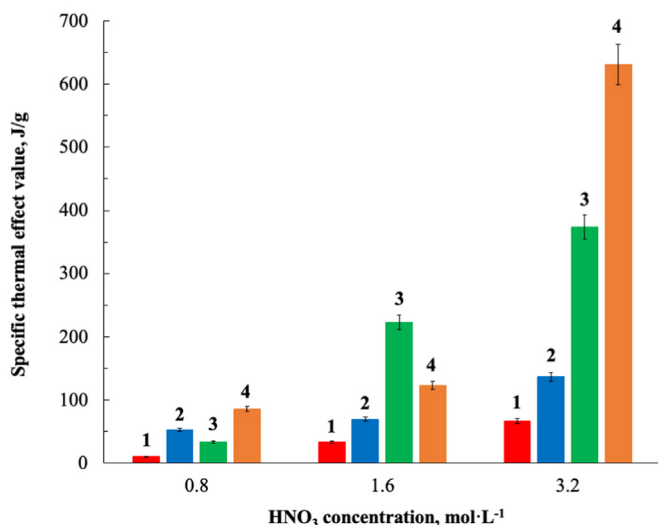


Fig. 5. Values of specific thermal effects of exothermic reactions for reducing agents at different concentrations of HNO₃: 1–AHA; 2–AHA with HN; 3–CH; 4–CH with HN.

Table 3
Maximum rate of gas evolution (W_{max}) and specific volume of gas (V_{sp}) during heating of nitric acid solutions of mixtures of reducing agents at a temperature of 100 °C.

Reducing agent mixture	Indicators	Reducing agent concentration	
		25 g/L	50 g/L
AHA	C, mol·L ⁻¹	0.33	0.67
	V _{sp} , L _g /L _l	50	59
	W _{max} , ml/min	4.2	4.6
	T _{st} , °C	no exothermic effect	no exothermic effect
CH	C, mol·L ⁻¹	0.28	0.56
	V _{sp} , L _g /L _l	44	39
	W _{max} , ml/min	10.7	9.6
	T _{st} , °C	86	84
HN	C, mol·L ⁻¹	0.26	0.53
	V _{sp} , L _g /L _l	44	50
	W _{max} , ml/min	15.4	16
	T _{st} , °C	no exothermic effect	87
AHA + HN	C _{AHA} + C _{HN} , mol·L ⁻¹	0.33 + 0.28	0.67 + 0.56
	V _{sp} , L _g /L _l	55	65
	W _{max} , ml/min	14.8	15.7
	T _{st} , °C	no exothermic effect	no exothermic effect
CH + HN	C _{CH} + C _{HN} , mol·L ⁻¹	0.28 + 0.26	0.56 + 0.25
	V _{sp} , L _g /L _l	44	56.5
	W _{max} , ml/min	5.6	6.5
	T _{st} , °C	98	87

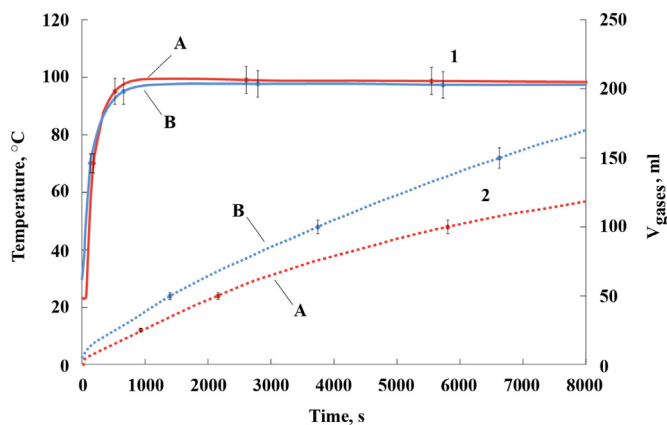


Fig. 6. Dependence of the sample temperature (1) and the volume of the evolved gas (2) on the thermolysis time for a mixture of AHA (A–25 g/L; B–50 g/L) with 12 mol L⁻¹ nitric acid.

maximum gas evolution rates were: 14.8 ml/min for a component concentration of 25 g/ml and 15.7 ml/min – for 50 g/L; no visible exothermic effects were observed (Table 3). For solutions with CH, gas evolution continued throughout the entire experiment with a maximum rate of 5.6 ml/min for a component concentration of 25 g/ml and 6.5 ml/min – for 50 g/L; the temperature of the onset of the exothermic reaction was 98 and 87 °C, respectively.

Experiments with nitric acid solutions containing HN with AHA, HN with CH have shown that during heating, the gas evolution processes occur in two stages: after the induction period, gas evolution begins at rates characteristic of the HN oxidation, and after the appearance of NO₂ in the gas phase, a period of intense gas evolution begins with self-heating of solutions. Obviously, HN is oxidized first of all and prevents the interaction of the second reducing agent with HNO₃, then the oxidation process proceeds much more intensively than with each reducing agent separately. Exothermic processes do not occur in mixtures of HN with AHA, despite the higher gas evolution rate and large volumes of evolved

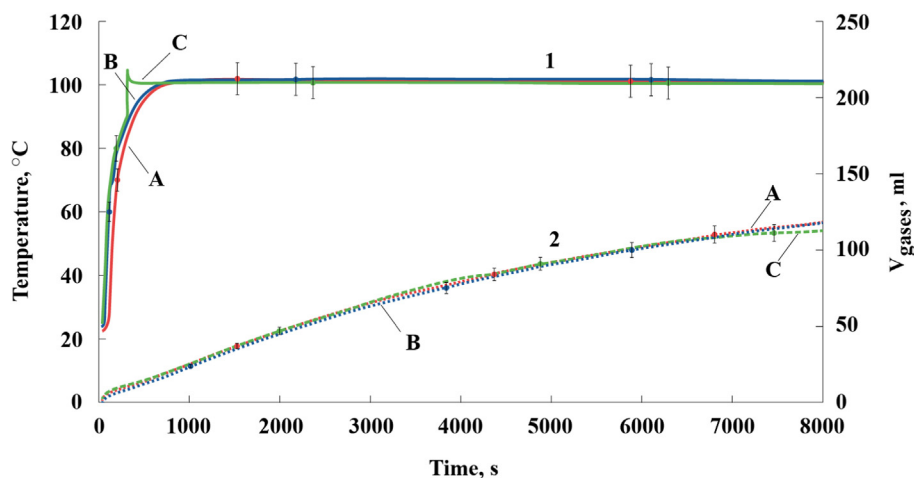


Fig. 7. Dependence of the sample temperature (1) and the volume of gases (2) on the thermolysis time for a mixture of 50 g/L reducing agents (A–CH; B–AHA; C–HN) with 12 mol L⁻¹ nitric acid.

gases.

4. Conclusions

A number of exothermic processes have been established in the study of thermal stability of solutions of reducing agents and their mixtures with nitric acid in the temperature range from 50 to 250 °C and above atmospheric pressure. Their effects differ in intensity, thermal effect, and temperature of the onset of the exothermic reaction. For all solutions, an increase in the concentration of nitric acid lowers the onset temperature of the exothermic reaction and increases the total thermal effect of the thermolysis reaction. AHA solutions are characterized by an abrupt change in the heat flow with a rapid achievement of the maximum temperature, while the heat evolution from nitric acid solutions of CH and HN occurs gradually, with the occurrence of two or three exothermic reactions. In the case of carbohydrazide, a sharp increase in the value of the total thermal effect with an increase in the HNO₃ concentration is observed both for a single-component solution and a mixture with hydrazine nitrate. The value of the total thermal effect for a solution of AHA and HN changes little with an increase in the concentration of HNO₃ and does not exceed 150 J/g, while for a mixture of CH with HN it increases more than 5 times, reaching a value of 630 J/g.

At nitric acid concentrations of 0.8 and 1.6 mol L⁻¹, the studied reducing agents and their mixtures are thermally stable. Although solutions of AHA in 3.2 mol L⁻¹ HNO₃ decompose at temperatures below the technological parameters of evaporation (76 °C), they have a low thermal effect. CH solutions with 3.2 mol L⁻¹ HNO₃ decompose at higher temperatures, but the total thermal effect of the reaction increases by many times. This is important to take into account in order to establish safe conditions for the evaporation process, since the concentration of HNO₃ occurs during evaporation.

At atmospheric pressure, the thermal stability of nitric acid solutions of reducing agents is determined by their reactivity. There are no intense exothermic processes of oxidation of AHA, CH, and HN at reductive back-extraction temperatures. During evaporation of nitric acid solutions containing macro amounts of reducing agents, exothermic processes are observed for CH, HN and their mixtures. The volume of evolved gaseous products is determined by the content of the reducing agent in solutions, as well as the rate of decomposition of nitric acid. Solutions of AHA with a high concentration of HNO₃, despite rapid gas evolution, are stable up to 100 °C, while HN reacts with HNO₃ at room temperature during the operation of mixing of the components.

Based on the data obtained, it is possible to assess the explosiveness of technological operations with nitric acid solutions containing the studied reducing agents. At temperatures below 70 °C, they do not pose a danger in relation to intense exothermic processes with gas evolution. The presence of significant amounts of water in the mixture greatly reduces the intensity of potentially dangerous exothermic processes.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.net.2022.03.034>.

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