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Dynamics of gas release during thermal oxidation of TBP solutions in Isopar-M in two-phase system

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ABSTRACT

The dynamics of the gas release at thermal oxidation of the two-phase systems of 30% solution of tri-n-butyl phosphate (TBP) in isoparaffinic diluent Isopar M – aqueous solution of 4.3, 8.2 and 12 mol/L of HNO_3 has been investigated within the temperature range from 70°C to 110°C. The effect of pre-irradiation of the system TBP–Isopar-M–HNO_3 on the kinetics of its thermolysis has been determined. All of the samples were irradiated with an electron accelerator at a dose rate of 10 kGy/h up to integrated doses of 0.5, 1 and 2 MGy. The parameters of heat and gas emission during thermolysis of the tested extraction system in an open apparatus have been determined experimentally. It has been demonstrated, that there are no conditions for extension of autocatalytic oxidation under heat treatment of two-phase extraction systems in open vessels.

INTRODUCTION

At the current moment, recycling of the spent nuclear fuel (SNF) is one the priorities in the radiochemical industry. The aim of the recycling is decrease the radiation hazard of SNF, safe dispose of unused components and extraction of valuable elements for further use. The core of technology for SNF reprocessing in radiochemical plants all over the world is PUREX-process that provide the high degree of extraction of plutonium and uranium. As in Russia, and abroad almost all types of extraction technology of SNF reprocessing involve the use of tributyl phosphate (TBP) as an extractant for the recovery of target components. TBP adequately meets all the process requirements, such as high boiling temperature, resistance to chemicals and to radiation, immiscibility with water, regenerability. Generally, TBP is used in mixtures with various inert diluents in different ratios. Aliphatic hydrocarbons with a linear chain, their mixtures, mixtures of isoparaffins and kerosene are used as diluents [1,2].

The intensity of oxidation processes is significantly affected by radiation and thermal effects during the extraction reprocessing of SNF. The oxidation processes in extraction systems depend on conditions and can proceed with a relatively constant rate of liquid and gaseous products formation or can proceed in autocatalytic regime resulting in self-heating of the mixture and dramatically accelerating gas release. There are several known accidents at radiochemical plants in many countries including Russia that were a result of thermal explosion caused by interaction between oxidants and extraction systems affected by radiation and heat [3-9]. Therefore, it is critical to investigate thermal stability of the considered extraction system under irradiation.

An important parameter to characterize fire and explosion safety of substances and materials is the gas release, namely, the volume of gaseous products of oxidation and the rate of their release. Since a working medium is a steam and gas phase in the case of destruction of the equipment, it is necessary to estimate the capacity of the gas lines and to provide the withdrawal of the released products of interaction. This must be done for several reasons: first, there is the direct threat of equipment rupture due to pressure increase in the case of limited withdrawal of steam and gas phase, second, rising pressure often initiated accelerates oxidation processes in condensed phases, changes the oxidation mechanism that results in even faster acceleration of gas release. Thus, investigating new extraction systems it is crucial to estimate the onset temperature of exothermic processes and the maximum acceptable concentration of nitric acid.

The aim of this work is to study the effect of ionizing radiation on the fire and explosion safety of extraction mixtures based on solutions of TBP in a branched hydrocarbon diluent Isopar-M.

EXPERIMENTAL

The samples investigated were 30% solutions of TBP in Isopar-M saturated with 4.3, 8.2 and 12 mol/L nitric acid. TBP has been preliminary purified with potassium permanganate in basic solution with subsequent washing with oxalic acid supplemented with 0.3 mol/L HNO_3 (to remove MnO_2), further treatment with 10% aqueous solution of sodium hydroxide and repeated washing with water until neutral. The organic solution, to be subjected to thermolysis, was stirred three times for 20 min. with an equal volume of 4.3, 8.2 and 12 mol/L nitric acid in a separating funnel with a helical stirrer.

Experiments on thermal oxidation of the two-phase system were carried out in the temperature range from 70°C to 110°C. The rate of gas release was determined with a specially designed equipment (Fig. 1). The volume of studied sample was 10 mL. The temperature of the solution was controlled permanently during the thermolysis.

Preliminary irradiation of the TBP samples in Isopar-M saturated with nitric acid was carried out on a linear electron accelerator UELV-10-10-S-70 (the energy of electrons 8 MeV, pulse duration 6 μs, pulse repetition frequency 300 Hz, average beam current ≤800 μa, scan width 245 mm, scanning frequency 1 Hz) of the Center for collective use of IPCE RAS. Schematic diagram of irradiation is shown in Fig. 2. The beam of accelerated electrons was scanned along the vertical axis of the 55 mm in diameter, 200 mL volume vessel filled with liquid equipped with the hydraulic lock and installed on a turntable rotated at a rate of 140 mm/s. 4 mol/L HNO_3 was used as a tempered liquid. Temperature of the solutions was measured after each passage of an electron beam through the sample using a pyrometer avoiding overheating of samples. The average dose rate depending on the density of the sample and the speed of its passage through the electron beam was 1.2 kGy/s. Organic solutions were irradiated up to doses of 0.5, 1 and 2 MGy.

During the thermolysis of unirradiated samples the gas release preceded by a certain induction period of time τ_{ind}, its duration depends on temperature and concentration of nitric acid. After the induction period the gas release starts and its rate reaches maximum value W_{max} after time τ_{max}. W_{max} value also depends on temperature and concentration of nitric acid. After τ_{max}, there is a slow decrease of the rate of gas release to almost constant value W_{st}.

RESULTS AND DISCUSSION

The upper temperature border for the investigated two-phase systems is limited by the boiling point of aqueous phase in open vessel which is 110-115°C for the used nitric acid solutions. In unirradiated two-phase systems of TBP in Isopar-M – aqueous solution of HNO_3 the notable gas release has been observed already at concentrations of nitric acid less than 8 mol/L and temperatures below 90°C. The maximum rate of gas release increases slightly with increasing nitric acid concentration, but increases in order of magnitude with temperature increase (Table I).

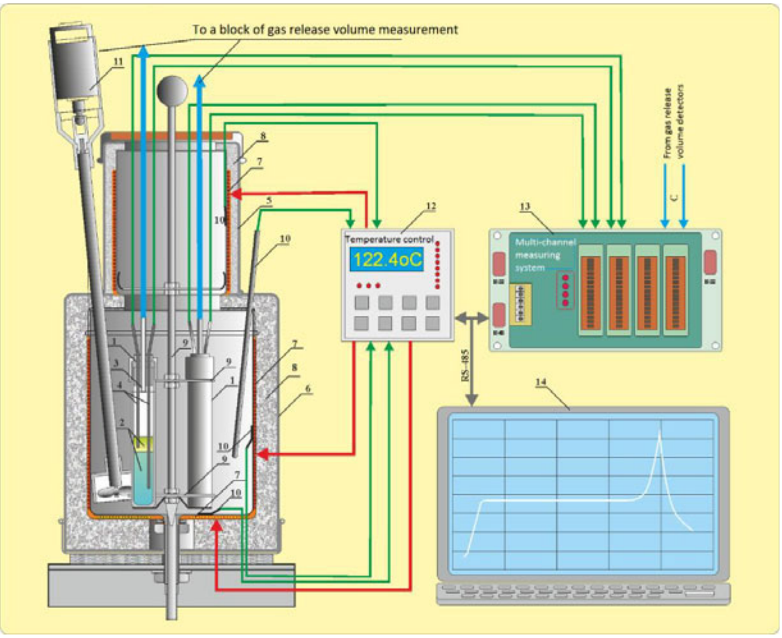

Figure 1 – Schematic diagram of apparatus for study of thermal stability under conditions of open vessel:

1 – cell (reaction vessel); 2 – components of the studied mixture; 3 – connection for output of the released gases; 4 – thermocouple thermometers; 5,6 – upper and lower units of thermostat; 7 – heater; 8 – insulation; 9 – parts of the equipment to load cells into the thermostat; 10 – temperature sensors; 11 – mixer; 12 – multichannel temperature controller; 13 – multichannel measurement system (direct measurements – temperature, voltage; functional – multichannel analog to digital conversion, digital input/output); 14 – control computer.

The volume of released gases increase significantly with increasing temperature and concentration of nitric acid, reaching the value 36 L_g/L_l at C_{HNO3} = 12.0 mol/L, that is 4 times higher than the gas release for the system with the diluent C13 under similar conditions. However, the maximum rate of gas release for Isopar-M is much less than for C13 diluent [10].

The maximum volume of released gaseous products of oxidation has been observed at a heating temperature 110°C. At this temperature under experimental conditions the maximum volume is proportional to concentration of nitric acid ~ 3 $L_g/(L_l*[HNO_3])$.

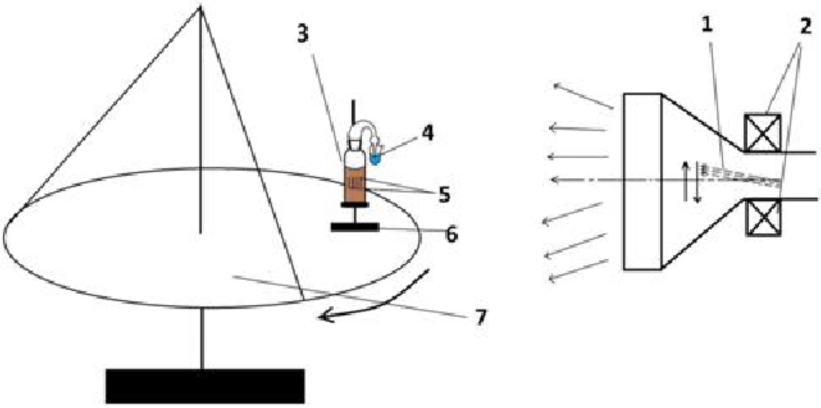

Figure 2 - Schematic diagram of irradiation of organic liquids

1 – electron beam, 2 – electromagnet deviating the beam with a frequency of 1 Hz, 3 –glassy cell with solution (specimen), 4 - gate, 5 –dosimetry films, 6 - support, 7 – turntable (carousel).

Preliminary irradiation of 30% solution of TBP in Isopar-M decreases the temperature of notable gas release down to 70°C, there is no induction period, as for single-phase systems, but the gas release is significantly enhanced (Fig. 3).

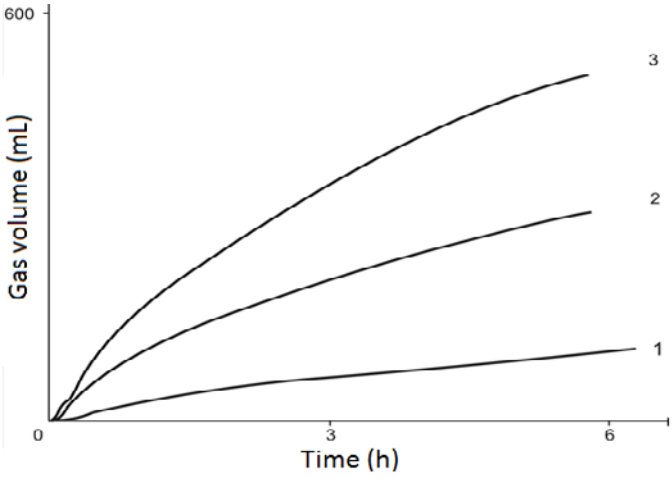

Figure 3 – Temperature dependence of the released gas volume in two-phase system of TBP in Isopar-M saturated with 12 mol/L HNO3 and irradiated up to a dose of 1 MGy: 1 – 70°C, 2 – 90°C, 3 – 110°C.

The most important parameters of gas release in two-phase systems of TBP/Isopar-M – HNO_3 (4.3, 8.2 and 12.0 mol/L of nitric acid in aqueous phase) are shown in Tables II-IV. The maximum specific rate of gas release increases with the heating temperature, as in the case of unirradiated samples; it is several times higher for solutions irradiated up to a dose of 2 MGy than for unirradiated systems. Overall, the increase of radiation dose from 0 to 2 MGy at 110°C increases the specific volume of gas released barely twice.

Volumes of the gaseous products slightly increase at temperatures 70 and 90°C. Variation of nitric acid concentration affects the volumes of the gas released less, than increase of temperature. Thus, the temperature increase from 70°C to 110°C enhances the gas release in 2-6 times at the same doses.

The investigation of the considered irradiated systems shows no linear correlation between the volume of the gaseous products and concentration of nitric acid in solutions, that indicates a more complex mechanism of interaction. Table V shows data for unirradiated two-phase systems based on TBP solutions in various diluents in contact with 12 mol/L nitric acid solution. There is almost no gas release at concentrations of nitric acid lower than 12 mol/L and temperatures below 100°C. While for industrial diluents, like RED-1 and especially RJ-3, the gas release has been observed already at concentration of HNO_3 in organic phase of 0.55 mol/L [11], that is equal to ~4 mol/L nitric acid in equilibrium aqueous phase.

Table I. Temperature dependencies of the maximum rate of gas release (W_{max}), time to reach it (τ_{max}), and the total volume of gas released (V) during thermolysis of unirradiated 30% solution of TBP in Isopar-M in contact with nitric acid of different concentrations

	τ_{max}, sec			$W_{max,}$ $L_g/(hour\times L_l)$			V, L_g/L_l		
	t °C			t °C			t °C		
C_{HNO3}, mol/L	70	90	110	70	90	110	70	90	110
4	810	745	850	0.3	1.2	8.0	0.2	1.3	11.4
8	395	500	650	1.8	2.8	8.1	1.3	14.6	26.3
12	375	400	350	1.5	3.2	9.1	5.3	23.0	35.9

Table II. Temperature dependencies of the maximum rate of gas release (W_{max}), time to reach it (τ_{max}), and the total volume of gas released (V) during thermolysis of irradiated up to dose of 2 MGy 30% solution of TBP in Isopar-M in contact with nitric acid of different concentrations

	τ_{max}, sec			$W_{max,}$ $L_g/(hour\times L_l)$			V, L_g/L_l		
	t °C			t °C			t °C		
C_{HNO3}, mol/L	70	90	110	70	90	110	70	90	110
4	945	735	565	14.7	9.7	23.8	6.2	7.2	10.1
8	815	615	380	13.0	38.9	62.8	11.2	15.7	34.0
12	765	600	485	13.4	45.7	80.7	15.1	35.4	55.5

Table III. Temperature dependencies of the maximum rate of gas release (W_{max}), time to reach it (τ_{max}), and the total volume of gas released (V) during thermolysis of irradiated up to dose of 1 MGy 30% solution of TBP in Isopar-M in contact with nitric acid of different concentrations

	τ_{max}, sec			$W_{max,}$ $L_g/(hour\times L_l)$			V, L_g/L_l		
	t °C			t °C			t °C		
C_{HNO3}, mol/L	70	90	110	70	90	110	70	90	110
4	655	580	420	1,1	6,2	28,8	1,4	11,7	28,5
8	680	560	430	2,1	14,5	60,9	1,6	25,4	62,2
12	655	490	400	5,9	21,3	30,7	6,2	31,6	35,1

Table IV. Temperature dependencies of the maximum rate of gas release (W_{max}), time to reach it (τ_{max}), and the total volume of gas released (V) during thermolysis of irradiated up to dose of 0.5 MGy 30% solution of TBP in Isopar-M in contact with nitric acid of different concentrations

	τ_{max}, sec	$W_{max,}$ $L_g/(hour\times L_l)$	V, L_g/L_l

	t°C			t°C			t°C		
C_{HNO3}, моль/л	70	90	110	70	90	110	70	90	110
4	1850	850	480	1,3	3,5	22,1	1,3	4	8,9
8	1675	1100	950	2,8	5,6	22,3	3,9	7,9	48,7
12	900	845	780	2,2	38,4	72,0	7,4	26,8	37,6

Table V. Comparison of explosion safety parameters (the induction period (τ_{ind}), the maximum rate of gas release (W_{max}), time to reach it (τ_{max}) and the steady-state rate of gas release (W_{st})) during the thermolysis of two-phase systems in open vessels

System	t° C	τ_{ind}, min.	τ_{max}, min.	$W_{max,}$ $L_g/(min.\times L_l)$	$W_{st,}$ $L_g/(hour\times L_l)$
TBP – 12 mol/L HNO_3 [12]	90	60	180	0.04	0.02
	110	10	30	0.50	0.16
TBP in Isopar-M – 12 mol/L HNO_3	70	-		0.025	
	90	-		0.05	
	110	-		0.15	
TBP in C13 – 12 mol/L HNO_3[10]	70	-	-	0.05	
	90	60	195	0.14	
	110	6	15	0.62	
TBP in dodecane – 12 mol/L HNO_3[12]	90	50	160	0.11	0.090
	110	10	30	0.7	0.250
TBP in HCBD – 12 mol/L HNO_3[13]	90	240	270	0.0024	0.002
	100	60	220	0.028	0.020
	110	30	45	0.112	0.070
	115	20	45	0.165	0.140

Parameters of the gas release are very close for the unirradiated systems containing organic solutions of TBP in diluents C-13 and dodecane. Solutions of TBP in hexachlorobutadiene (HCBD) and in Isopar-M demonstrate higher thermal stability as compared to systems of unbranched hydrocarbon diluents.

The differences in the gas release for single- and two-phase systems are demonstrated by the data in Table VI with the example of mixture 30% solution of TBP in Isopar-M – aqueous solution of 12 mol/L HNO_3 at 110°C. In single- and two-phase systems the gas release starts without the induction period, maximum rates of gas release are not high, however for two-phase systems they are three times higher, than for single-phase systems. The total volume of the released gases in two-phase systems is seven times larger, than for single-phase systems. The latter is the result of both contributions to the gas release of oxidation products, organic components dissolved in aqueous phase, and compensation of oxidant consumption in organic phase by transfer of nitric acid from aqueous phase. The diffusion of nitric acid from aqueous to organic phase balances the consumption of acid in oxidation processes at temperatures below 90°C. At temperatures above 110 °C the rate of these processes in organic phase and acid consumption exceeds the rate of acid transfer in from aqueous phase that results in slow decrease of HNO_3 concentration in organic phase and, as a consequence, decrease of gas release. Boiling of nitric acid at temperatures above 110°C also results in heat loss.

Table VI. Parameters of gas release in single-phase and two-phase systems based on 30% solution of TBP in Isopar-M at 110°C and 12 mol/L HNO_3

System	τ_{max}, sec.	W_{max}, $L_g/(min.\times L_l)$	V, L_g/L_l
Single-phase	480	0.05	5.6
Two-phase	350	0.15	35.9

CONCLUSIONS

The results of this work indicate that heating of two-phase extraction system in open vessels does not provide the conditions for the release of intensive autocatalytic oxidation despite of significant amount of oxidant (nitric acid). In open vessels the great heat losses take place due to boiling and evaporation of system components, wherein the mixing of the phases with releasing gaseous products prevents autocatalytic exothermic processes accompanying with mixture self-heating in organic phase. Furthermore, there is no accumulation of significant quantities of oxidants in organic phase during heating in open vessel due to the removal of active oxidizer – nitrogen dioxide – into gas phase.

It was found that thermolysis of both unirradiated and irradiated solutions of 30% TBP in Isopar-M saturated with nitric acid is characterized by volley gas release at temperatures above 100°C without induction period, with high peak values, which values increase with increasing temperature and dose of preliminary irradiation, with a fast decay until the complete disappearance of nitric acid.

The mass transfer of nitric acid from aqueous to organic phase balances the acid consumption in oxidation processes at thermolysis temperatures below 90°C. At temperatures above 110°C the rates of oxidation processes in organic phase exceed the rate of acid diffusion from aqueous phase that results in slow decrease of HNO_3 concentration in organic phase and, as a consequence, decrease of the gas release.

With respect to uncontrolled chemical exothermic reactions (thermal explosion), extraction systems based on diluents HCBD and Isopar-M demonstrate better explosion safety, however strong corrosive properties of HCBD towards construction materials and its high toxicity are questioning its use, despite of small amounts of products deteriorating the extraction properties. Thus, Isopar-M can be considered as a promising diluent in the extraction reprocessing of SNF.

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