Radiation and Thermal Stability of Solid Radwaste After Immobilization in Polymer Matrix - 13504

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ABSTRACT

The paper will illustrate results of the various experiments on radiation and thermal stability of polymer matrixes after solutions solidification including aqueous and organic solutions and mixed waste.

It was shown that- after irradiation the specimen and after solidification the mixture with oil and TBP hydrogen has been observed (less 1%) and some others gases have been detected.

Results of the performed experiments and the radiation stability data of the polymer compositions allow the conclusion that the technological process of immobilizing the above mentioned aqueous solutions and solutions with organic products into polymers at room temperature is the explosion- and flameproof as well as the storage thereof.

INTRODUCTION

Various methods, including an application of polymer materials which can solidify liquid radioactive waste (LRW) with chemically stable product formation, can be used to solve this problem.

At present in literature there is available information related to the use of third-generation high-tech polymer introduced by Nochar Company (US). This material has a broad spectrum of application in nuclear industry [1-4].

When selecting the LRW solidification technique the properties of the final solid waste forms and the intended storage or disposal conditions must be taken into consideration.

Taking into account the fact that the radioactive waste after solidification is to be transferred to the long-term storage, it was necessary to obtain experimental data on the radiation stability of polymer materials.

The processes of destruction occurred in the polymers under the impact of radiolysis could result in the formation of gaseous products capable of getting inflamed when contacted with air.

In addition, the process of LRW solidification should be fire- and explosion-proof, and not accompanied by generating of sizeable quantity of secondary RW.

From the literature reference analysis we have managed to find just a few publications containing the data on the radiation stability of polymer materials intended for the LRW immobilization. However the data on the composition and yield of the gaseous products were not available.

From other hand, to evaluate the thermal stability of mixtures of the organic products with oxidants, especially nitric acid and nitrates it is necessary to get the information on maximum gas yield rates, initial temperatures of the exothermal oxidation processes, and specific volume values for the gaseous products generated by that process.

From the common knowledge of the radiation chemistry of polymers one may say that the interaction on the ionizing radiation with organic compounds is accompanied by the formation of the intermediate active particles - radicals, by destruction, oxidation, cross-linking, gas formation, and de-polymerization. The substances containing C—F, C—Si, and C—O bonds possess the low radiation stability. The presence of double and conjugated bonds, benzene and heterocyclic rings in the molecule increases the radiation stability. The most considerable changes in the structure of polymer materials under the impact of ionizing radiation occur during the destruction and cross-linking of polymer molecules.

When a polymer is irradiated up to the absorbed dose of 10^4 Gr the irreversible changes, as a rule, are negligible. The polymer materials are subject to the radiation ageing produced by the chemical reactions of the generated free radicals with the atmospheric oxygen.

Therefore in the course of research a task was set to analyze the composition of the gaseous phase arisen under the impact of radiation during the long-term storage of waste in the polymer matrix.

In addition to investigations on radiation stability, the differential thermal analysis were carried out on the purpose of thermal stability determination.

RESULTS OF EXPERIMENTS AND DISCUSSION

During the experiment program planning the task was set to use the samples most interesting from the standpoint of safety during the solidification process and the long-term storage safety, too.

Perhaps the nitric acid is the most common oxidation agent present in LRW. Taking that fact into account we have set for irradiation the following samples of polymer No.960 after solidifying the nitrate containing solutions:

→ Polymer No.960 after the contact with 1M HNO_3 solution, solid to liquid ratio of S/L=2/1. An aliquot 33.3 g weight of the polymer was mixed with 16.7 g of the nitric acid solution. The sample was dried in the air during 1 month; the sample mass amounted 38.7 g.

→ Polymer No.960 after the contact with 5M HNO_3 solution, solid to liquid ratio of S/L=1/5. The obtained gel was set to irradiation without drying; the sample mass was 2.86 g.

→ Polymer No.960 + 1M HNO_3 solution with the cement additive. An aliquot 4.01 g weight of the polymer was mixed with 20 g of the nitric acid solution and 5.2 g of cement. The sample was dried before irradiation; the sample mass amounted 5.29 g.

The experimental results on the irradiation of those samples are given in Table I.

The most important result of the experiments (see Table I) for us was in the course of irradiation of the polymers intact, without the incorporated LRW components, no considerable quantities of the gaseous products have been detected. We failed to accurately measure the gas volume in those experiments; the radiolysis gas mass estimate did not exceed $2 \cdot 10^{-5}$ g per 1 g of the polymer.

From the result of this stage of work it has been concluded that the presence in the system of an aqueous phase containing a strong oxidizer (HNO_3) does not cause an increased gas yield and, hence, does not decrease the radiation-chemical stability of polymer No.960.

It has been already noted that we failed to make a sufficiently accurate measurement of the gas volume in these experiments because the excessive pressure in the ampoules was below 2 mm Hg.

The analysis of the composition of radiolytic gases after irradiation of the initial polymer and the nitrate solution containing polymer allowed the conclusion that the explosive gas content does not constitute a hazard during the long-term storage of the solidified waste (see Table II.).

For the radiation stability tests of the solidified organic waste samples we first paid our attention to tributyl phosphate (TBP) containing solutions and TBP-oil mixtures.

As it has been noted before, no adverse affects associated with the gaseous product yield were revealed when solidifying aqueous solutions in the joint presence of the organic substance (the polymer matrix) and the oxidation agent (nitric acid).

Nevertheless, we were not sure the radiolysis would not cause a negative result in the presence of TBP and oil.

TABLE I. Irradiation conditions of the samples of polymer No.960 after solidification of the nitric acid solutions and the estimate of the gaseous phase volume after irradiation. (As the emission source the gamma-installation with Co^{60} has been used.)

No	Sample set for irradiation.	Absorbed dose, Gr	Results
1	Polymer No 960, sample mass 5.46 g.	$9.6x10^5$	A slight yellowish-gray color appeared. Failed to measure the gas volume on account of the excessive pressure in the ampoule was less than 2 mm Hg.
2	Polymer No 910, sample mass 1,93 g.	$9.6x10^5$	The appearance of the sample after irradiation has not changed. Failed to measure the gas volume ($P \leq 2$ mm Hg).
3	Polymer No.960 after solidification of the 1M HNO3 solution, solid-to-liquid ratio = 2/1. The sample was dried prior to irradiation.	$3.9 x10^5$	A slight yellowish-gray color appeared. Failed to measure the gas volume on account of the excessive pressure in the ampoule was less than 2 mm Hg.
4	Polymer No.960 after solidification of the 2M HNO_3 solution, solid-to-liquid ratio = 1/5. Freshly prepared sample.	$9.8 x10^4$	A slight yellowish-gray color appeared. Failed to measure the gas volume ($P \leq 2$ mm Hg).
5	Polymer No.960 after solidification of the 1M HNO_3 solution, solid-to-liquid ratio = 1/5 with cement.	$9.6x10^5$	The appearance of the sample after irradiation has not changed. Failed to measure the gas volume ($P \leq 2$ mm Hg).

TABLE II. The gaseous phase composition after irradiating compositions with polymer No.960.

The gas mixture components.	The gaseous phase composition after irradiating, mass. %.The absorbed dose of 960 kGr.	
	Polymer No.960 + 1M HNO_3 solution + cement	Polymer No.960 (original)
Hydrogen	0.1300	0.3700
Methane	0.0053	0.0051
Ethane	0.0004	0.0017
Ethene	0.0002	-
Propane	-	0.0003

For an obvious reason the issues associated with the extraction system behavior under the ionizing radiation used to attract much attention and to date vast experimental data is accumulated on the radiation stability of the extractants, primarily TBP [5].

The detailed description, let alone the experimental studies of the TBP destruction processes under irradiation are far beyond the scope of our work. However in our report we believed worthwhile to outline the main peculiarities of the process that we would be able to demonstrate a rather good match of our results with those reported in literature.

Under irradiation of the individual TBP the processes of dealkylation, polymerization and the gaseous products formation occur, H_2 and light C_1 – C_4 hydrocarbons were being detected. Among the latter the *n*-butane and butenes prevail over the others. The maximum radiation yield for hydrogen is 1.2 molecules per 100 eV and the radiation yield for the sum of hydrocarbons is 1.75 molecules per 100 eV, respectively.

The liquid phase products of TBP radiolysis are dibutylphosphoric acid (DBP), monobutylphosphoric acid (MBP), and poly-recombination products.

At the TBP irradiation dose of $<10^6$ Gr the DBP and MBP are accumulated linearly with the G(DBP)/G(MBP) ratio of 7-8, which witnesses the independent ways of these radiolytic product formation. The radiation-chemical yield of DBP and MBP in the mixtures of TBP and aliphatic hydrocarbons depends on the TBP concentration.

A considerable reduction of the radiolytic product yields is inherent to the solutions of TBP in aromatic hydrocarbons. Phosphoric acid is detected in the irradiated TBP at the dose over 10^6 Gr and its radiation yield does not exceed 0.01 molecules per 100 eV.

Irradiation of TBP in two-phase systems is accompanied by the re-distribution of its radiolytic products between the phases and depends on the composition thereof. In the two-phase systems a stronger effect of oxygen, the nitric acid concentration, metal salts, and the irradiation dose is observed on the TBP decomposition rate. The liquid phase products of TBP radiolysis are dibutylphosphoric acid (DBP), monobutylphosphoric acid (MBP), and poly-recombination products.

Taking into account the above said, for irradiation we set the following samples of polymer No.910 after solidifying solutions of the following composition:

→ Polymer No.910 was mixed with 12.5 g of engine oil, S/L=1/5. The mass of the sample used in the run was 8.69 g;

→ Polymer No.910 was mixed with 6.25 g of TBP and 6.25 g of oil, S/L=1/5.5. The mass of the sample used in the run was 4.91 g. The sample of this composition was used two times at the different irradiation dose.

→ A 2.5 g aliquot weight of polymer No.910 was mixed with 3.75 g of TBP and 8.75 g of oil, S/L=1/5. The mass of the sample used in the run was 8.97 g.

The experimental results on the irradiation of those samples (polymer No.910) are given in Table III.

TABLE III. The composition and irradiation conditions of polymer samples and the gas volume estimate after irradiation.

No	Sample set for irradiation.	Absorbed dose, Gr	Results
1	The polymer No 910 +oil, S:L = 1:5	5.2×10^4	The appearance of the sample after irradiation has not changed. Failed to measure the gas volume on account of the excessive pressure in the ampoule was less than 2 mm Hg. Gas volume was approximately less than 8 ml.
2	The polymer No 910 + oil + TBP (50% TBP + 50% oil) S:L = 1:5	5.2×10^4	The sample became yellow in color, wet by visual. The amount of the yielded gas was small, estimated approximately less than 8 ml. Failed to measure the gas volume on account of the excessive pressure in the ampoule was less than 2 mm Hg.
3	The polymer No 910 + oil + TBP (30% TBP + 37% oil) S:L = 1:5	5.2×10^4	Two phases are present in the ampoule. Failed to measure the gas volume on account of the excessive pressure in the ampoule was less than 2 mm Hg.
4	The polymer No 910 + oil + TBP (50% TBP + 50% oil) S:L = 1:5	9.6×10^5	Two phases are present in the ampoule. The volume of gas phase - 259 ml, average velocity until D 280 KGr was - 0,075 ml/h·g, and after that D 960 KGr – 0,029 ml/h·g

It follows from the data given in Table III that as the result of irradiating the solidified TBP – oil mix under the maximum absorbed dose of $9.6 \cdot 10^5$ Gr the formation of the second phase and the considerable gaseous product yield was observed in one experiment only. The total volume of the yielded gas was 259 ml, or about 50 ml/g.

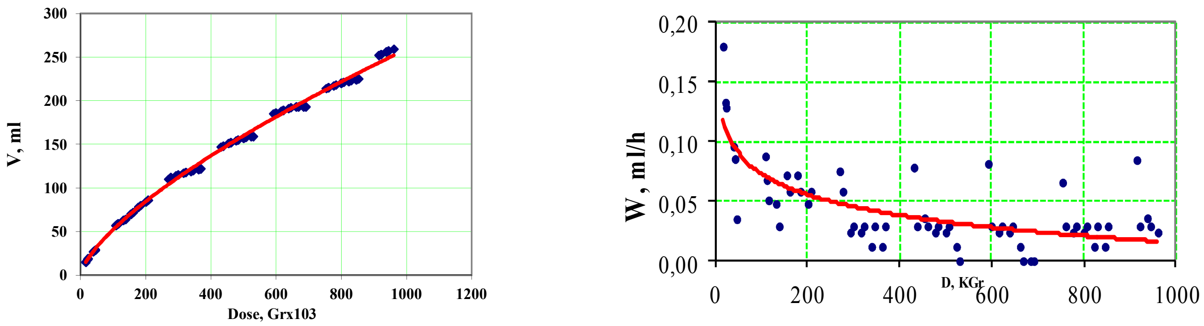
During this experiment we managed to obtain data on the gas yielding process dynamics under irradiation. (The radiolytic gas yield dynamics was evaluated using glass cylinder-shaped ampoules connected airtight with the volumetric gas burette.)

The experimental results characterizing the gas accumulation dynamics under irradiation of Sample No.4 (see Table III) are given in Fig. 1.

As it follows from the data obtained, the maximum gas yield rate is observed in the initial period. The values obtained for the gas yield rate were in the range of 0.08 thru 0.06 ml/hr under the absorbed dose D of $2.0 \cdot 10^5$ Gr. Under the further irradiation the gas yield rate is stabilized at the level of 0.02 thru 0.03 ml/hr.

Along with the data on the gas yield dynamics from the samples under irradiation, the gas composition constitutes the not least factor taken into consideration during the assessment of safety conditions. The experimental results characterizing the composition of gases formed under irradiation are given in Table IV.). 1

(The composition of gases formed under irradiation was determined by sampling gases from the ampoules containing the irradiated samples.)



A B

Fig. 1. The gas accumulation dynamics during irradiation of the sample (A) and the variation in the radiolytic gas yield rate as a function of the integral dose (B) of the following composition: polymer No.910 + 50% TBP + 50% oil.

TABLE IV. The gaseous phase composition after irradiating polymer No.910 based compositions.

The gas mixture components	Gaseous phase composition after irradiating, % vol		
	Polymer No.910 (original), the absorbed dose of 9.6x10^5 Gr	Polymer No.910 +50% TBP + 50% oil mix , S/L=1/5, the absorbed dose of 5.2 x10^4 Gr	Polymer No.910 +70% TBP + 30% oil mix , S/L=1/5, the absorbed dose of 5.2 x10^4 Gr
Hydrogen	1.16	0.14	0.13
Methane	0.08	0.019	0.003
Ethane	0.77	0.019	0.0044
Ethene	-	0.037	0.0072
Propane	0.013	0.016	0.0039
Propene	-	-	0.0003
Acetylene	0.0006	-	-
Isobutane	0.0150	0.0002	-
Butane	0.0160	0.0240	0.0069
Oxygen	5.0	8.0	14.0
Nitrogen	67.0	87.0	80.0

Taking into account the low gas yield rates and flammable gas concentrations it may be concluded that the immobilization of radioactive waste into polymers would not cause any complications associated with the provisions for the fire-proof and explosion-proof conditions in the course of the long-term storage.

Summarizing this work section it is necessary to address one more important issue, namely, the choice of dose value in our experiments, how far it is justified, whether it corresponds to the actual conditions of the long-term waste storage or not.

Therefore, along with the sample irradiation campaign, the specialists of Radium Institute have made the calculations of the integral doses absorbed by the material after solidifying it into the polymer matrix and during the following long-term storage in the repository.

From our point of view, the understanding of those issues is directly associated with the choice of the waste immobilization conditions and with the justification of the maximum activity level of the feed waste. The results of the calculations are given in Table V.

TABLE V.
The calculations of the integral doses to be absorbed by the material during the long-term storage after the immobilization of radionuclides ^{137}Cs, ^{90}Sr/^{90}Y and ^{241}Am into the polymer matrix.

Nuclides	The waste category	Specific activity, Bq/кg	The dose to be absorbed by the waste during the storage in the repository (burial site), Gr			
			1 month	1 year	50 years	100 years
^{137}Cs	HLRW	$>10^{10}$	$>1.7\cdot10^3$	$>1.87\cdot10^5$	$>6.2\cdot10^5$	$>8.1\cdot10^5$
	ILRW	10^6 - 10^{10}	0.2 - $1{,}7\cdot10^3$	19 – $1.87\cdot10^5$	62 - $6{,}2\cdot10^5$	81 – $8.1\cdot10^5$
	LLRW	$<10^6$	<0,2	<19	<62	<81
^{90}Sr/^{90}Y	HLRW	$>10^{10}$	$>4.7\cdot10^3$	$>5.6\cdot10^4$	$>1.6\cdot10^6$	$>2.2\cdot10^6$
	ILRW	10^6 - 10^{10}	0.47 - $4{,}7\cdot10^3$	56 – $5.6\cdot10^4$	$1.6\cdot10^2$ - $1.6\cdot10^6$	$2.2\cdot10^2$- $2.2\cdot10^6$
	LLRW	$<10^6$	<0.47	<56	$<1.6\cdot10^2$	$<2.2\cdot10^2$
^{241}Am	HLRW	$>10^8$	$>2.35\cdot10^2$	$>2.8\cdot10^3$	$>1.35\cdot10^5$	$>2.6\cdot10^5$
	ILRW	10^5 - 10^8	$2.35\cdot10^2$	$2.8\cdot10^3$	$1.35\cdot10^5$	$2.6\cdot10^5$
	LLRW	$< 10^5$	0.23- $2.35\cdot10^2$	2.8 - $2{,}8\cdot10^3$	135 – $1.35\cdot10^5$	2.60 - $2{,}6\cdot10^5$

From the data of Table V one might conclude that apart from the possibility to solidify the LLRW and ILRW categories into the polymer matrix, the polymers could be also used for solidifying the HLRW category.

However, one must not forget another very important factor. Existing techniques of forecasting the radiation stability of materials including the polymer ones are based upon the accelerated irradiation of samples and, therefore, are not perfect. Very often the irradiation conditions at the facility in the laboratory are very far from the actual operating conditions of various material types. Besides, the forecasting methods frequently do not take into consideration the specifics of the initial polymer structure and composition. The numerous facts witness that the radiation stability values for materials irradiated under the conditions inherent to the actual operation, such as the low dose rate, air medium could be 2-3 orders of magnitude less than those obtained in the accelerated experiment.

Experimental determination of the thermal stability resulted in the following.

Heating the polymer No.960 based samples containing 0.1 M HNO_3 and 50 g/L of either sodium or ammonium nitrate up to the temperature of 200°C is accompanied by a slight release of gas without exothermic effects.

When heating the polymer No.960 based sample containing 5 M HNO_3 up to the temperature of 200°C it is decomposed with the steady gas release at the low-level rate of 0.1-0.15 L/min per 1 kilogram of the sample. In the compacted state the sample decomposition is accompanied by the exothermic reaction: at 180-185°C the abrupt temperature change of 50-55°C is detected, and the gas release rate increases up to of 3.3 L/min per 1 kilogram of the sample, respectively.

The polymer No.960 based sample containing 5 M HNO_3 and 100 g/L of sodium nitrate begins to decompose at the temperature of 200°C with the exothermic effect accompanied by the 30-35°C warm up.

CONCLUSIONS

Results of the performed experiments and the radiation stability data of the polymer compositions allow to conclude that the technological process of immobilizing the above mentioned aqueous solutions and solutions with organic products into polymers No. 960 and 910 at room temperature as well as the storage thereof are the explosion- and flameproof.
All the data obtained were passed for use in the process of the polymer certification and for the justification of the waste disposal safety.

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