Dual Solidification Process of BN-350 Liquid Radioactive Waste Using High Technology Polymers and Newly Designed Encapsulation Techniques

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ABSTRACT

Application of high technology polymers #910 and #960 manufactured by NOCHAR, USA, for treatment of liquid radioactive waste (LRW) have demonstrated good results at test sites worldwide. At the BN-350 site (Aktau, Kazakhstan), the tests were conducted successfully with contaminated oil, alkaline and salt containing LRW. This paper represents the results of immobilization of NOCHAR polymers, saturated with LRW, into solid matrix to comply with Kazakhstan regulatory requirements for long term storage and/or disposal (Table 1).

1. EXPERIMENTAL

There are two significant LRW issues for the BN-350 fast breeder reactor located in Aktau, Kazakhstan, which is being transferred to 50 years SAFSTOR status. The first issue involves the handling of sodium coolant that should be converted into sodium hydroxide at the sodium processing facility (SPF). The technology of the following sodium hydroxide immobilization is a geocement matrix comprised of cheap materials such as blast furnace slag, kaolin clay and bergmeal (diatomite) [1]. The matrix is capable of isolating radionuclides, predominately Cs-137, thereby preventing its release into the environment during long term storage or disposal.

The second issue involves the processing of LRW accumulated during the operation life of the BN-350 reactor. The LRW streams include contaminated pump oil, alkali, high content salt solutions and slug.

The designed LRW processing facility is planned to be constructed, however a sizable portion of LRW cannot be processed through it because cementation technology is considered as a final stage of processing and some of the waste streams are incompatible with cementation.

Table 1. Regulatory requirements of Kazakhstan to solidified LRW compound

Leaching rate (for Cs-137), not more than	$1 \cdot 10^{-3}$ g/(cm^2 day),
Mechanical strength (compressive strength), not less than	4,9 (50) MPa (kg/cm^2)
Radiation stability under irradiation,	$1 \cdot 10^6$ Gr
Frost resistance (number of freezing /melting cycles), not less than	30 cycles
Resistance to durable stay in water	90 days

1.1. Immobilization into geocement, slag cement and diatomite-cement matrices

The following components were used in experiments at different ratios:

- Portland cement M400;
- Granulated blast-furnace slag and construction lime subjected to mutual grinding until the specific surface of not less than 3500 cm^2/g has been achieved. Bulk density of slag-lime mixture was 1.1 g/cm^3;
- Enriched kaolin dried up to 1% of residual moisture used as a clay mineral. Milling provided the production of homogeneous loose mass and fineness of grinding;
- Diatomite used as mineral admixtures. Diatomite, consisting of diatomite shells for over 50% and containing over 70% of soluble silica, of a high porosity, low bulk density and high absorbency properties characterized by enhanced selectivity to cesium and strontium ions. Natural diatomite was dispersed down to complete pass through the sieve 0.14 (70-74 μm).
- 35% sodium hydroxide modeling the primary sodium processing product;
- Nochar polymer # 910 saturated with real oil LRW (1:3);
- Nochar polymer # 960 saturated with real LRW (1:3) and treated at temperatures 250-300 C to prevent water absorption after saturation with LRW.

Experiments started with samples 2x2x2 cm for all the compositions (geocement, slag cement and diatomite-cement). Experiments revealed that the slag cement samples did not pass the tests to comply with the regulations, so up-scaled tests with samples 10x10x10 cm were carried out only for diatomite-cement and geocement compounds.

Table 2. Composition of diatomite-cement and geocement compounds.

Compound with NOCHAR #910	**Type of LRW**	**Weight ratio of the components**
Diatomite-cement (D)	Oil LRW (upper level B-02/6)	LRW – 3 parts, polymer #910 – 1 part, water – 25 parts, diatomite – 12,5 parts, cement M400 – 25 parts
GCS+10 vol.% LRW (G)	Oil LRW (upper level B-02/6)	LRW – 3 parts, polymer #910 – 1 part, 35% solution NaOH – 12,5 parts, diatomite – 2,5 parts, kaolin – 2,5 parts, slag – 20 parts

Fig. 1 Sample of diatomite cement 10x10x10 cm

Fig. 2 Sample of geocement 10x10x10 cm

1.2. Immobilization into sulfur compound matrix

Experiments on immobilization of NOCHAR polymer #910 and #960 into sulfur compound saturated by model solutions and real LRW (oil) were carried out. The objective was to achieve sulfur polymerization for to obtain good mechanical properties and leachibily. The following components were used in sulfur compound experiments:

- NOCHAR polymer #910 saturated with real oil LRW (1:3);
- NOCHAR polymer #960 saturated with real LRW (1:3) and treated at temperatures 250-300 ^{0}C before immobilization into sulfur compound to prevent water absorption after saturation with LRW.

Experiments on Cesium-137 release from #960 polymer were carried out with real LRW at elevated temperatures. The objective of the tests with thermal treatment of the polymer was to stop water absorption that results in degradation of compounds mechanical properties. Table 3 provides data on changes in the activity of cesium-137 after exposure to temperatures 250 – 300 ºC within 30 minutes.

Table 3. Cesium 137 release from NOCHAR #960 samples at elevated temperatures

No	Sample mass, Initial/treated	Temperature of treatment, ^{0}C	Initial activity by ^{137}Cs, Bq	Activity after treatment ^{137}Cs, Bq	Decrease in activity, %
1	570/573	250	100562	100412	0
2	854/855	260	103155	102720	0,5
3	854/856	270	103155	100742	2,5
4	854/857	280	103155	97490	5,5
5	854/858	290	103155	94912	8
6	570/574	300	100562	72226	28,2

Analysis of the data in Table 2 shows that increasing of treatment temperature up to 270-300 ^{0}C, results in significant cesium release from NOCHAR #960 polymer. Unfortunately, this temperature is crucial to stop water absorption and prevent compound degradation.

The following mixtures were prepared and tested in sulfur compound experiments: sulfur - 40%, barite - 20%, shale ash – 40% with reinforcing chrysotile-asbestos additive, plasticizer and modifier. Different amounts of the polymer #910 saturated with LRW (oil) were introduced to this mixture. Samples for testing were prepared using standard hot pressing molds after heating at 140°C. Oil LRW content in the samples varied from 5.5% to 35%.

2. RESULTS

2.1. Immobilization into Geocement and diatomite-cement matrices

Results of saturated polymer #910 immobilized into diatomite cement and geocement compounds tests on mechanical properties and leachibility are represented in Table 4 and Fig 3 and 4. It is obvious, that the samples of NOCHAR #910 polymer immobilized into diatomite cement compound comply with Kazakstan regulatory requirements for mechanical properties and leachibility and may be recommended for future LRW immobilization. Samples of diatomite cement and geocement with #960 polymer did not survive water resistance and leachibility tests.

Table 4. Mechanical properties of diatomite cement and geocement compounds

Type of compound	Strength, MPa		
	Initial sample (after 28 days ageing)	After tests for frost resistance	After tests for prolonged stay in water
D -Diatomite-cement	8.9	7.6	8.0
	9.2	7.4	8.5
	8.1	6.6	9.5
	9.07	7.2	8.67
G – GCS +10 vol.% LRW	4.2	3.0	5.3
	4.0	2.6	4.8
	3.7	2.2	4.4
	3.97	2.6	4.83

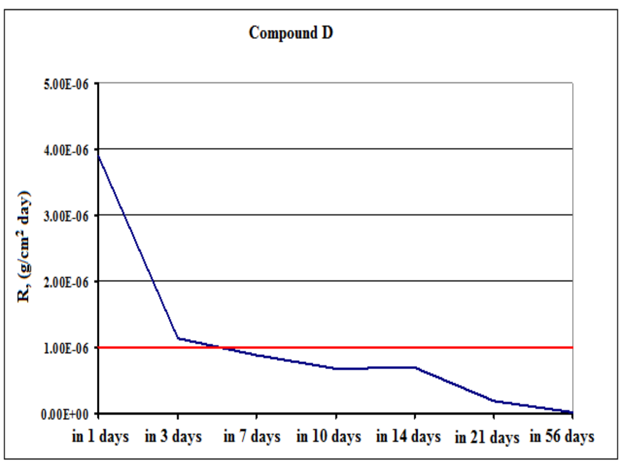

Fig. 3 Leachibility test of #910 polymer, immobilized into diatomite cement compound

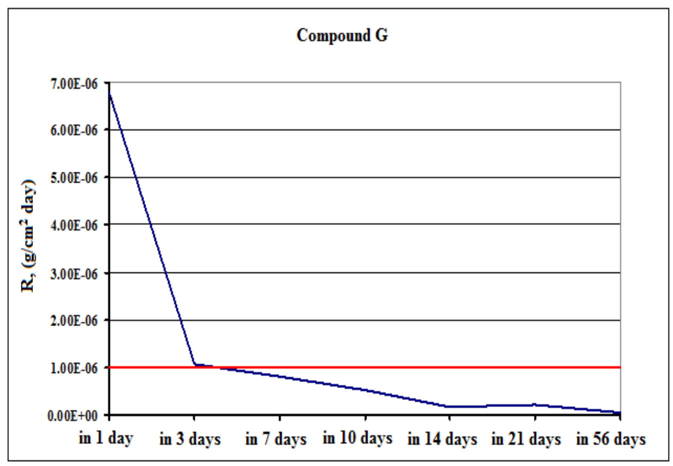

Fig. 4 Leachibility test of #960 polymer, immobilized into geocement compound

2.2.Immobilization into sulfur compound matrix

Fig. 5 and 6 show the results of tests for the sample of sulfur compound based on 125 g of NOCHAR polymer #910 + 375 ml of real LRW (oil) + 1100 g of mixture (40% sulfur, 20% barite, 40% shale ash with modifying additive) obtained by hot pressing in a special mold after heating at 140°C within 2 hours. Results of the experiments have showed that NOCHAR polymer #910 saturated with oil LRW provides for co-polymerization of sulfur that resulted in rubber like compound structure with good leachibility.

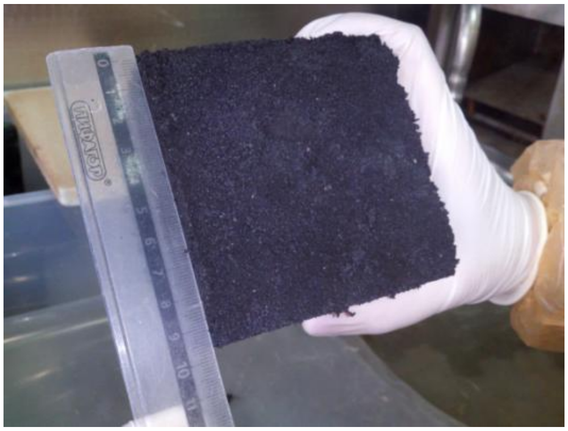

Fig. 5 Sulfur compound sample 10x10x10 cm

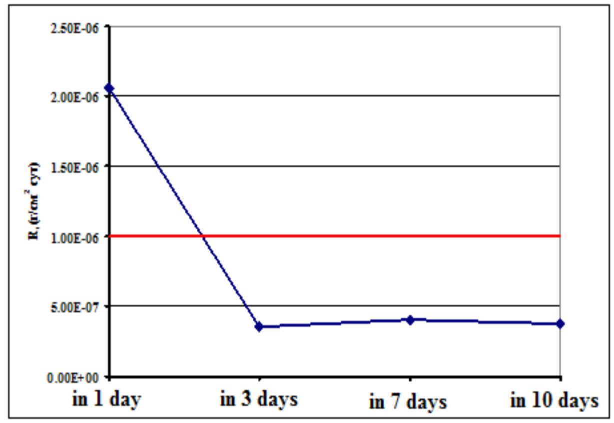

Fig 6 Leaching test of sulfur compound

Mixtures of 5g of polymer #960 with LRW solutions (all mass ratios #960:LRW are 1:3): 450 g/l - (#960+450), 150 g/l - (#960+150), and 2% NaOH - (#960+2%NaOH) were heated at 300°C within 30 min, after cooling they were grounded in a mortar and on their basis there were prepared mixtures of sulfur (S), diatomite (D), diatomite saturated with LRW in the ratio 1g:1ml (D1), double saturated diatomite in the ratio 1g:2ml (D2) and specially prepared mixture of sulfur shale ash and barite concentrate (C). The mixtures prepared and tested are shown in Table 5.

Table 5. Mechanical properties of different sulfur compound mixtures

Sulfur compound samples	Compressive strength, MPa	Water resistance, W%
10g (#960+450) + 25g S	16,43	3
5g (#960+450) + 5g D1 + 5g C + 50g S	7.716	0.6
10g (#960+450) + 5g D2 + 5g C + 50g S	19.173	0.5
10g (#960+150) + 25 g S	10.199	3
10g (#960+150) + 5g D1 + 5g C + 50g S	9.267	0.6
10g (#960+150) + 5g D2 + 5g C + 50g S	16.004	0.5
5g (#960+2%NaOH) + 5g D1 + 5g C + 50g S	21.304	0.8
5g (#960+2%NaOH) + 5g D2 + 5g C + 50g S	22.456	0.7
5g (#960+450) + 5g C + 25g S	19.147	0.2
5g (#960+150) + 5g C + 25g S	14.503	0.2

Results of the experiments confirm that sulfur compounds prepared on the basis of NOCHAR #960 polymer, saturated with LRW and then heat treated at 300^0C provides good mechanical properties and water resistance.

CONCLUSIONS

1. The possibility is shown for immobilization of NOCHAR #910 saturated with oil into diatomite-cement compound that complies with the regulatory requirements of Kazakhstan.
2. Experiments conducted demonstrated feasibility and reasonability of developing technology of LRW immobilization into NOCHAR polymer followed by immobilization into sulfur compound matrix for long-term storage.

3. NOCHAR #910 saturated with oil provides for the co-polymerization of sulfur in sulfur compound matrix.
4. The samples of sulfur compound obtained in experiments carried out on immobilization of NOCHAR #910 saturated with real LRW (oil) in sulfur compound matrix show high water and leaching resistance meeting the requirements for long term storage and/or disposal.
5. NOCHAR #960 saturated with LRW (high concentration salt solutions) and treated at temperature 300°C can be successfully immobilized into sulfur compound matrix that meets regulatory requirements

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