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China's Scientific Investigation for Liquid Waste Treatment Solutions

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ABSTRACT

Post World War II created the nuclear age with several countries developing nuclear technology for power, defense, space and medical applications. China began its nuclear research and development programs in 1950 with the establishment of the China Institute of Atomic Energy (CIAE) located near Beijing. CIAE has been China's leader in nuclear science and technical development with its efforts to create advanced reactor technology and upgrade reprocessing technology. In addition, with China's new emphasis on environmental safety, CIAE is focusing on waste treatment options and new technologies that may provide solutions to legacy waste and newly generated waste from the full nuclear cycle.

Radioactive liquid waste can pose significant challenges for clean-up with various treatment options including encapsulation (cement), vitrification, solidification and incineration. Most, if not all, nuclear nations have found the treatment of liquids to be difficult, due in large part to the high economic costs associated with treatment and disposal and the failure of some methods to safely contain or eliminate the liquid. With new environmental regulations in place, Chinese nuclear institutes and waste generators are beginning to seek new technologies that can be used to treat the more complex liquid waste streams in a form that is safe for transport and for long-term storage or final disposal. [1]

In 2004, CIAE and Pacific Nuclear Solutions, a division of Pacific World Trade, USA, began discussions about absorbent technology and applications for its use. Preliminary tests were conducted at CIAE's Department of Radiochemistry using generic solutions, such as lubricating oil, with absorbent polymers for solidification. Based on further discussions between both parties, it was decided to proceed with a more formal test program in April, 2005, and additional tests in October, 2005. The overall objective of the test program was to apply absorbent polymers to various waste streams to determine leach rates, stability (immobilization), effective bonding ratios, compression capability, waste minimization and effects of irradiation on the solidified samples.

INTRODUCTION

It has been more than fifty years since China began its nuclear research and nuclear industry; the achievements of technology development for power, defense, space and medical applications are significant. During this period of nuclear development, a large amount of solid and liquid radioactive waste has been generated. A portion of this waste can be treated and disposed of immediately; however, some of the waste cannot be treated due to unreliable treatment methods and technologies. As a result these waste types are accumulated and, over time, containers begin to corrode with the risk of leaks into the environment. Proper treatment of these waste types will ensure that safeguards are put in place to protect the environment and to promote the long-term growth of China's nuclear industry.

Since the inception of China's nuclear industry, large volumes of radioactive liquid waste have been produced; these waste types include strong alkaline and nitric acidic solutions, TBP/OK (purex), vacuum pump oil, scintillation fluid, etc. [2] With maintenance and decommissioning work at some facilities, the treatment of liquid waste has become a critical issue. With the wide diversity of liquid compositions and activity levels, it is important to note that many of these compositions cannot be treated with standard products and technologies. [3]

The formal test program conducted at CIAE involved the application of high technology polymers manufactured by Nochar®, Inc. (Indiana, USA) to a variety of complex waste streams. [4] The primary objective of the scientific research was to solidify, through an absorption process, the liquid waste streams with polymer formulas. The tests were to provide data on stability, leaching, compression capacity, determining bonding ratios and the effects of irradiation on the solidified samples.

EXPERIMENTAL CONDITIONS

Six simulant waste streams were tested:

- Tri-butyl phosphate : 30% TBP / 70% kerosene
- Acidic solution: $NaNO_3$, 150g/L & HNO_3, 5M/L; less than 0 pH
- Alkaline solution: NaOH, 2 M/L; more than 14 pH
- Ion exchange resin: anion to cation 2:1, approximately 50% water
- vacuum pump oil
- scintillation liquid

Polymers used were N 910, for oil and organic liquid. N910 is hydrophobic. N960, for aqueous solutions. N990, a premium blend of polymers for oil / organic liquid and 20% or less of aqueous content. N910 and N960 can be blended if an organic / aqueous composition needs to be solidified. The solidification (bonding) ratio is determined by weight; i.e., liquid to polymer as indicated in Tables I-VI. [5] Solidification ratios of waste to polymer varied between 1:1 and 3:1 for all tests except ion exchange resin which was performed at 5:1.

To conduct the experiments the necessary items included: glass beakers, glass stirrer, polymers, simulant waste solutions and a weight scale.

EXPERIMENTAL RESULTS

Table I. Solidification of TBP/OK

Test number	Liquid waste (g)	Polymer (g)	Remarks	Stir [a]	After 6 weeks
1-1	8g	8g N910	Waste added to the polymer. Rapid reaction, about 20 seconds Not fully consumed	no	No significant variance (Fig. 1.)
1-2	24g	8g N910	Waste added to the polymer. Rapid reaction. Not fully consumed. Small amount of dry polymer at bottom of beaker	no	Become translucent like glass; elasticity increase
1-3	24g	8g N910	Waste added to the polymer. Rapid reaction Polymer not fully consumed	yes	Become translucent like glass; elasticity increase

Table II. Solidification of Acidic Solution [b]

Test number	Liquid Waste (g)	Polymer (g)	Remarks	stir	After 6 weeks
2-1	13g	13g N960	Waste added to the polymer. Rapid reaction, about one third polymers have not been consumed	yes	Free liquid appears
2-2	54g	18g N960	Waste added to the polymer. The reaction is a bit slow, the surface of the waste form is wet	yes	Becomes yellow liquid , polymer gradually disappears

Table III. Solidification of Alkaline Solution

Test number	Liquid Waste(g)	Polymer (g)	Remarks	stir	After 6weeks
3-1	11g	10g N960	Waste added to the polymer. About half polymers have not been consumed; more compact than the acidic absorbed polymer	no	No significant variance on the appearance, elasticity increase

Table IV. Solidification of Vacuum Pump Oil

Test number	Liquid Waste(g)	Polymer(g)	Remarks	stir	After 6 weeks
4-1	11g	9g N910	Polymer added to the waste. About half polymers have not been consumed. Fluffy particles are not bonded together	yes	Spongy particles
4-2	30g	10g N910	Polymer added to the waste. Polymer fully consumed, fluffy. Pass the Paint Filter Test [c]	yes	Spongy particles
4-3	20g	10g N990 [6]	Polymer fully consumed, fluffy.	yes	Spongy particles

Table V. Solidification of Ion Exchange Resins

Test number	Liquid Waste(g)	Polymer(g)	Remarks	stir	After 6 weeks
5-1	100g (about 50% water)	20g N960	Resin particles are embedded in the polymer mass	yes	No significant variance (Fig. 2.)

Table VI. Solidification of Scintillation Liquid

Test number	Liquid Waste(g)	Polymer(g)	Remarks	stir	After 6 weeks
6-1	12g+10g+10g	10g N910	Waste added to the polymer. Fluffy particles. The surface is wet	no	volatilization of the naphthaline
6-2	16g + 13g	10g N910 3g N960	Waste added to the polymer. Fluffy particles. The surface is wet	no	volatilization of the naphthaline
6-3	16g	10g N910 5g N960	Waste added to the polymer. Fluffy particles. The surface is dry.	no	volatilization of the naphthaline

Notes:

a. The reaction is so rapid that a large amount of the polymer was not exposed to the liquid waste; slow stirring is needed sometimes to obtain the full contact of polymer to liquid.
b. Solidification of acidic solution failed, supplementary tests were performed.
c. Paint Filter Test (EPA SW-9095) is applied to a waste or waste form to determine whether the material meets the U.S. EPA definition of solid. The material is placed in a paint filter identical to those used to remove lumps from paint. The amount of liquid that passes through the filter is recorded. If drainage is observed from the filter, the material fails the test for a solid waste form.
d. Over time the vapor phase (odor) is reduced significantly.

Fig. 1.TBP/OK SolutionFig. (Table I, No. 1-1)

2. Ion Exchange Resin Solidification (Table V, No. 5-1)

SUPPLEMENTAL EXPERIMENT

As a result of a high concentration of H+, the solidification of the nitric acid solution failed. When the pH level is in the 0-2 range, the solution will have a negative affect on the solidification process. In order to achieve a proper solidification, the pH level must be raised to 2 or above. Sodium carbonate was added to the acidic solution to raise the pH to acceptable levels. The solidification results are indicated in Table VII.

Table VII. Supplementary Tests

Simulant waste	Liquid Waste (g)	Polymer (g)	Remarks	After 6 weeks
2.5M HHO_3 Less than 0 pH	20g	10g N960	Rapid reaction, jelly-like mass	No significant variation
1M HHO_3 Less than 0 pH	20g	10g N960	Rapid reaction, jelly-like mass	No significant variation

IRRADIATION TESTS

Solidified waste forms will be packaged and placed for final storage in repositories**.** The stability of the solid waste is critical as the effects of radiation on the waste may cause degradation of the waste form. Irradiation tests are conducted to test for leaching and durability of the waste. The solidified waste forms were sealed in individual ampoules (reference Figures 3 & 4). A Cobalt-60 gamma irradiator was used with a dose rate of 1 x 10^5 rad / hour. The total dose rate applied to all samples was 1 x 10^7 rad or 70 million rad. The samples and results are presented in Table VIII.

Table VIII. Irradiation Test Results

NO	Samples*	Weight(g)	result
1	1-1	1.0	Drier in appearance, no free liquid is present.
2	1M HNO_3	1.2	No significant vary in appearance
3	3-1	1.5	No significant vary in appearance
4	4-1	1.0	No significant vary in appearance
5	6-3	1.0	No significant vary in appearance
6	N910	0.5	No significant vary in appearance
7	N960	1.0	No significant vary in appearance

- Note: after 100 days setting and then sealed into the ampoule.

Fig. 3. Vacuum Pump Oil before Irradiation (Table IV. No. 4-1)

Fig. 4. Vacuum Pump Oil after Irradiation (Table IV. No. 4-1)

Included in the irradiation tests were the two polymers, N910 and N960 (No. 6 and No. 7) in Table VIII. Polymers are checked before and after irradiation. A spectra-graph analysis confirms that the polymers are stable products to use in the irradiation tests.

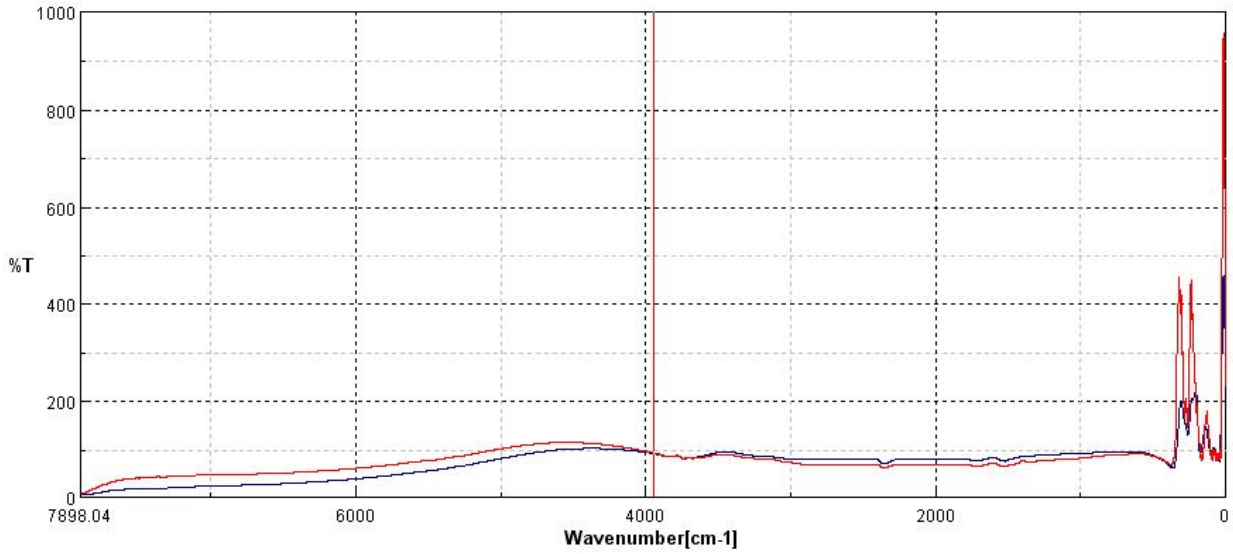

Fig. 5. IR Spectra-graph of Polymer N910
(Red represents after irradiation, blue represents before irradiation)

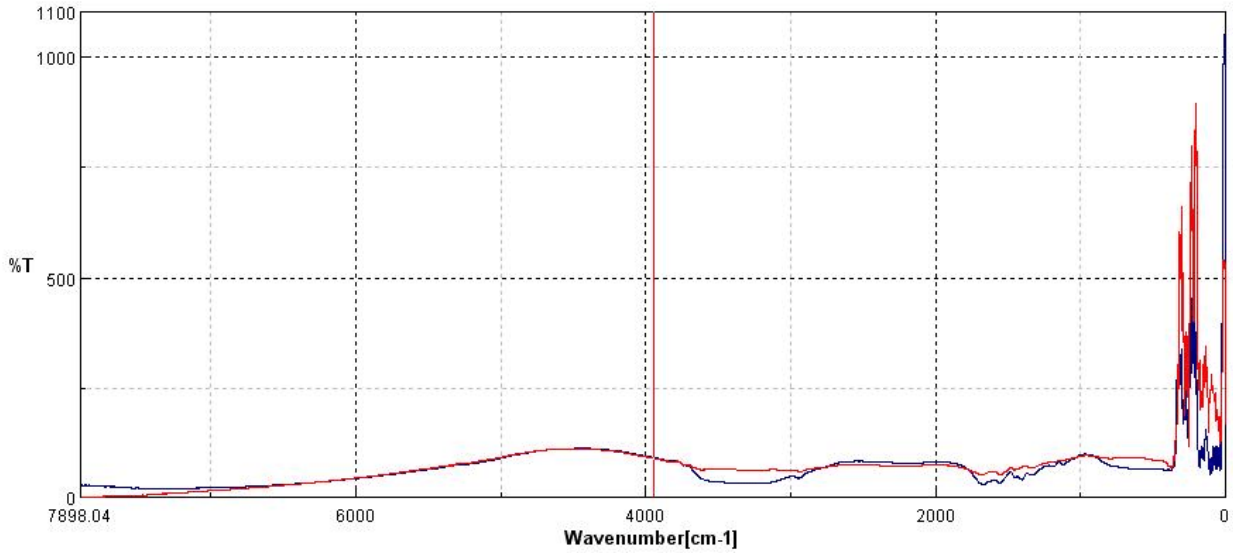

Fig. 6. IR Spectra-graph of Polymer N960
(Red represents after irradiation, blue represents before irradiation)

CONCLUSIONS

Based on the results of these experiments, we can make the following conclusions:

- Nochar polymers can absorb and solidify, effectively, most types of radioactive liquid waste including complex aqueous and organic solutions.
- Test results indicate that the optimum ratio of liquid waste to polymer, by weight, is 2:1 to 3:1. The bonding ratios offer economic advantages to waste generators.
- Based on the performance of the solidification waste forms following irradiation tests, the waste forms are suitable for long-term or final storage. Packaged in special designed containers, the solidified waste can be safely transported and stored without the possibility of leaching.
- This innovative absorption technology is safe and easy to apply. The polymers can be applied to large and small volume waste streams and have applicability in all nuclear sectors including medical facilities, research institutes, uranium mining operations, etc.
- We can conclude from the experiments, with the exception of the ion resin waste, that the final waste form, whether it be sponge-like, granular or very hard, has no relationship to its ability to remain stable. The critical factor with solidification is its ability to remain stable, without leaching or breakdown, for a long or indefinite period of time.
- A second test program could be advanced that considers various options for packaging the solidified waste. This program would focus on production methodologies of large volume liquid waste and design criteria for containers.

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