

Immobilization of Spent Ion-Exchange Resins in the Urea-Formaldehyde Matrix

S. V. S RAO,^{1,*} H. KOTHANDARAMAN,² M. SUDHAKAR,² K. B. LAL,¹ and R. V. AMALRAJ¹

¹Centralized Waste Management Facility, Nuclear Waste Management Group, Bhabha Atomic Research Centre, Kalpakkam, 603 102 India; and ²Department of Polymer Science, University of Madras, Madras, 600 025 India

SYNOPSIS

Studies have been carried out on the immobilization of spent ion-exchange resins produced in nuclear power plants in urea-formaldehyde matrix. The matrices were prepared by incorporating different types of ion-exchange resins in the pH range of 4.5 to 5.0, using boric acid as a catalyst. Characterization of the matrices was carried out with respect to dimensional changes, compressive strength, and leach resistance. The cumulative percentage weight loss and volume change were observed to decrease with the increase in boric acid concentration before attaining a plateau. The diffusion coefficients were in the order of 10^{-16} M²/s, and the compressive strengths were in the range of 0.83 to 12 MPa. Infrared spectral studies on the urea-formaldehyde matrices revealed that the rate and the extent of cure depended on the type of resin. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Ion-exchange resins are widely used in nuclear industry to remove radionuclides such as ¹³⁷Cs, ⁹⁰Sr, and ⁶⁰Co from the moderator, coolant, and wastewater streams. The spent resins need to be immobilized in a suitable medium before their disposal. Various matrices like cement, asphalt, and polymers were developed to incorporate spent resins.^{1,2} Polymer matrices like urea-formaldehyde (UF),³ polyester,⁴ and epoxy resins⁵ were observed to be good with respect to mechanical integrity and leach resistance in the presence of water compared to cement. The process temperatures were lower than that of asphalt.⁶

A review of the literature³ indicates that urea-formaldehyde matrix has good compatibility with many types of wastes such as sludges and ion-exchange resins. The process⁷ described therein stipulates the requirement of pH between 1 and 2 for curing where the reaction rates are significantly

high, resulting in the generation of excessive heat during solidification. It is also reported² that the liquid released from the UF matrix had a pH as low as 3, resulting in the corrosion of the containers. Therefore, an attempt was made in our earlier investigations⁸ to overcome the above problems by changing the conditions of polymerization, wherein studies were carried out with cation exchange resin (H⁺ form). Curing or solidification of the polymer matrix was done at 70°C.

In order to simplify the plant scale operation, the present studies are aimed at developing a method that obviates the need for stirring and heating during solidification. It is described in the literature⁹ that iron is essentially unaffected in the pH range of 4 to 10. In the present studies, the pH during solidification is maintained between 4.5 and 5.0, as compared to 4.0 in our earlier studies. Selection of pH in this region decreases not only the rate of reactions¹⁰ but also the corrosion rate of container material, which is made of steel. Inasmuch as the UF matrix prepared at low pH yields brittle products,¹¹ various buffer systems are recommended. In our studies, boric acid is employed as a buffer, which also serves as a catalyst.

* To whom correspondence should be addressed.

Table I Characteristics of the Ion-Exchange Resins

Characteristics	Na ⁺ Form	H ⁺ Form	MB 204 ^a		MB 206 ^a	
			Cationic	Anionic	Cationic	Anionic
1. Functional group	Sulphonic	Sulphonic	Sulphonic	Quaternary Ammonium	Sulphonic	Quaternary Ammonium
2. Form	Sodium	Hydrogen	Lithium	Hydroxy	Hydrogen	Hydroxy
3. Screen size (mesh)	16-50	16-50		16-50		16-50
4. Particle size (mm)	0.3-1.2	0.3-1.2		0.3-1.2		0.3-1.2
5. Temp. stability (°C)	120	120		120		120
6. Exchange capacity (mEq/mL)	1.8	1.8	1.8	1.0	1.8	1.0
7. Density (kg/M ³)	800-840	800-840	800-840	670-710	800-840	670-710
8. Moisture content (%)	52	52	52	60	52	60

^a Mixed bed resin contains 80% anion and 20% cation exchange resin by volume.

Urea is tetrafunctional with respect to formaldehyde, and the reaction mechanism is reported to be complicated.¹² The products formed depend on the conditions of polymerization, such as monomer ratio, catalyst, temperature, etc. The kinetics of the condensation reaction has been reported by estimating the free formaldehyde content.¹³ Infrared (IR) spectroscopy is one of the instrumental techniques that have been developed for the analysis of UF resins.^{11,14} Generally, the region 1000-1700 cm⁻¹ is chosen because the observed bands beyond this region were either too weak or too broad to permit quantification. In order to understand the curing mechanism, the decrease in the methylol group concentration owing to condensation reaction was estimated.

This paper describes the preparation of polymer matrices or specimens incorporated with mixed bed resins and cationic resins, and their characterization with respect to density, waste/matrix ratio, compressive strength, homogeneity, leach resistance, and dimensional changes. In addition, the IR spectroscopic study was carried out on the polymer specimens.

EXPERIMENTAL

Materials

Urea (GR grade, Sarabhai Chemicals); formaldehyde (GR grade, Sarabhai Chemicals, 37% w/v solution in water); boric acid (S. D. Fine Chemicals); cesium chloride (AR grade, BDH Ltd.); sodium acetate (GR grade, Sarabhai Chemicals); liquor ammonia (AR grade, S. D. Fine Chemicals); ion-exchange resins (nuclear grade, Thermax Ltd.).

Preparation of the Polymer Matrices

Preparation of polymer matrices or specimens involved three steps viz. (a) preparation of the ion-exchange resin, (b) synthesis of urea-formaldehyde prepolymer, and (c) preparation of polymer matrix.

a. Preparation of Ion-Exchange Resin

The resins studied in these experiments include mixed bed resins (1) MB 204, (2) MB 206, cation exchange resins, (3) sodium form (Na⁺ form), and (4) hydrogen form (H⁺ form). The characteristics of the resins are given in Table I. The resins were washed with demineralized (DM) water to a con-

Table II Properties of the Matrices

1. Density (kg/M ³)	1010-1018
2. Waste/matrix ratio (weight %)	0.23-0.62
3. Compressive strength (MPa)	0.81-12.3
4. Cumulative percentage volume change	
a. With boric acid (6 g) and without heating (after 3.4 × 10 ⁶ s)	25.1
b. With boric acid (30 g) and without heating (after 7.7 × 10 ⁶ s)	0.7
c. Without boric acid and with heating (after 3.4 × 10 ⁶ s)	55.8
5. Cumulative percentage weight loss	
a. With boric acid (6 g) and without heating (after 3.4 × 10 ⁶ s)	34.3
b. With boric acid (30 g) and without heating (after 7.7 × 10 ⁶ s)	1.2
c. Without boric acid and with heating (after 3.4 × 10 ⁶ s)	52.4
6. Diffusion Coefficient (M ² /s)	
a. H ⁺ form in DM water	2.03 × 10 ⁻¹⁶
b. H ⁺ form in ground water	1.85 × 10 ⁻¹⁴

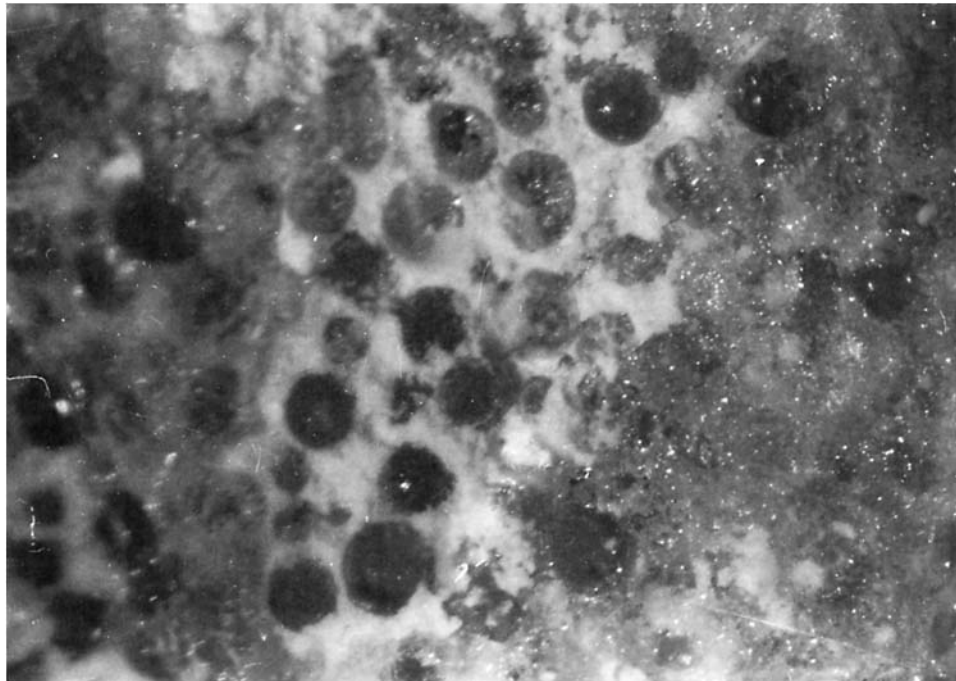


Figure 1 Microscopic view of cross-section of UF matrix (10 times magnification).

stant pH before loading with cesium chloride (inactive) or radioactive cesium (^{137}Cs). Hydrogen ion released from the resin and traces of cesium left in the supernatant liquid were removed by washing

with DM water. The required amount of boric acid was added to the resins to adjust the pH.

b. Synthesis of UF Prepolymer

The details of the process are given in our earlier report.⁸ In all the experiments, the molar ratio of urea and formaldehyde was maintained at 1 : 1.5. Urea weighing about 60 g was added to the mixture of formaldehyde, sodium acetate, and ammonia, and the contents were heated at a temperature in the range of 60 to 65°C. Heating was discontinued when the specific gravity of the syrup reached around 1.2.

c. Preparation of UF Matrices

The polymer matrices were prepared in right cylindrical molds with a diameter of 6 cm. UF syrup was added to the ion-exchange resin and allowed to cure in the molds at an ambient temperature of 28°C. After curing for about a month, the specimens were removed from the molds for characterization.

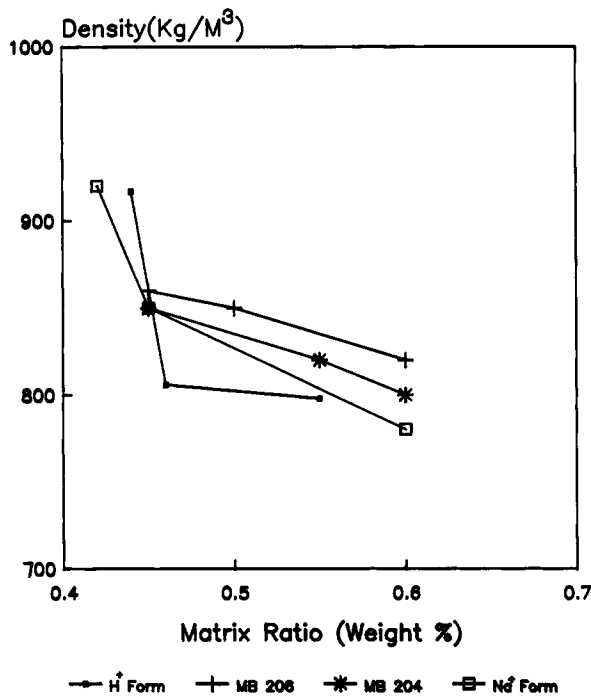


Figure 2 Matrix ratio vs. density of UF matrices.

Characterization of the Matrices

Compressive Strength

The polymer specimens prepared with different waste/matrix ratios were subjected to compressive strength testing. Measurements were carried out on

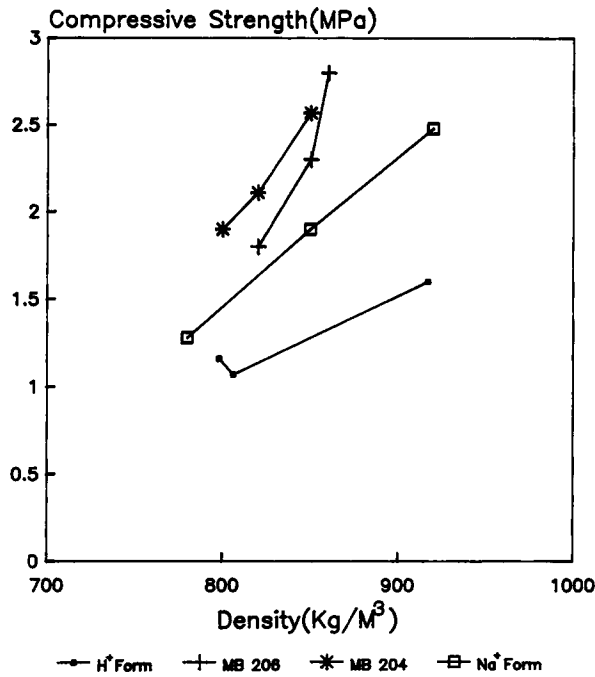


Figure 3 Density vs. compressive strength of UF matrices.

an FIE (Fuel Instruments and Engineers Pvt. Ltd.) compression testing machine conforming to the grade "A" of BS: 1610 : 1964.

Dimensional Changes

The dimensional changes of the specimens prepared with different concentrations of boric acid at am-

bient temperature were measured at different time intervals. These values were compared with those of the specimen prepared at 70°C without boric acid.

Leaching Studies

Leaching studies were carried out in accordance with the American Nuclear Society (ANS) 16.1 standard leach test method.² The leachants used in these experiments were DM water and ground water (GW); the pH and the total hardness as calcium carbonate of GW were 7.8 and 68 mg/L, respectively. The specimens containing inactive cesium were immersed in DM water, whereas the ones containing ¹³⁷Cs were kept in ground water. The ratio of the leachant volume to the surface area of the specimen was maintained at 10. Leachant samples were collected and analyzed periodically for cesium. Inactive cesium was analyzed using Atomic Absorption Spectrophotometer (GBC Model 902), while the active cesium was analyzed using a gamma counter. Leach rate (LR) was calculated using the following equation.

$$LR = (\Sigma A/A_0) \times (V/S) \times 1/\Sigma T \quad (1)$$

Where

$\Sigma A/A_0$ = cumulative leach fraction

A_0 = initial concentration of cesium

A = concentration of cesium at any time
 T (seconds)

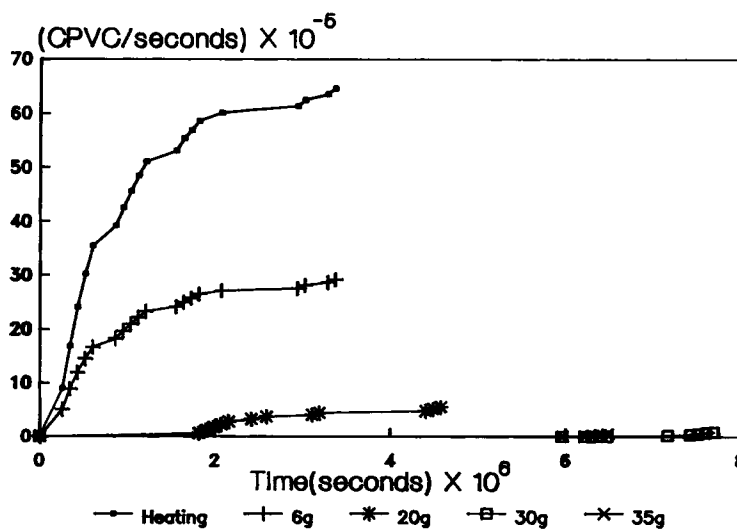


Figure 4 Cumulative percentage volume change/time vs. time with different amounts of boric acid.

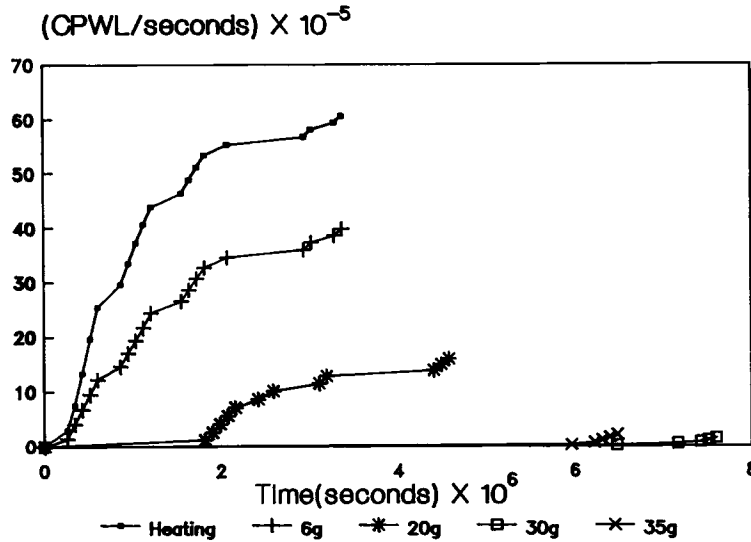


Figure 5 Cumulative percentage weight loss/time vs. time with different amounts of boric acid.

V = volume of the specimen (M^3)
 S = surface area of the specimen (M^2)
 ΣT = cumulative time (seconds)

area at 1650 cm^{-1} ($C=O$ of amide) in the absorption spectrum.

IR Studies

The infrared spectra of the polymer specimens at various time intervals were obtained using KBr pellets and a Hitachi Model 270-30 spectrophotometer. The rate of curing of UF polymer containing resin was determined by comparing the ratio of peak area at 1020 cm^{-1} ($O-H$ group of methylol) to the peak

RESULTS AND DISCUSSION

Table II gives the physical properties of the polymer matrices. The densities were in the range of 1040 to 1180 kg/M^3 . The compressive strengths were in the range of 0.81 to 12.3 MPa , and these values were higher than the minimum value of 0.36 MPa as stipulated in the 10 CFR 61 regulations.¹⁵ Figure 1

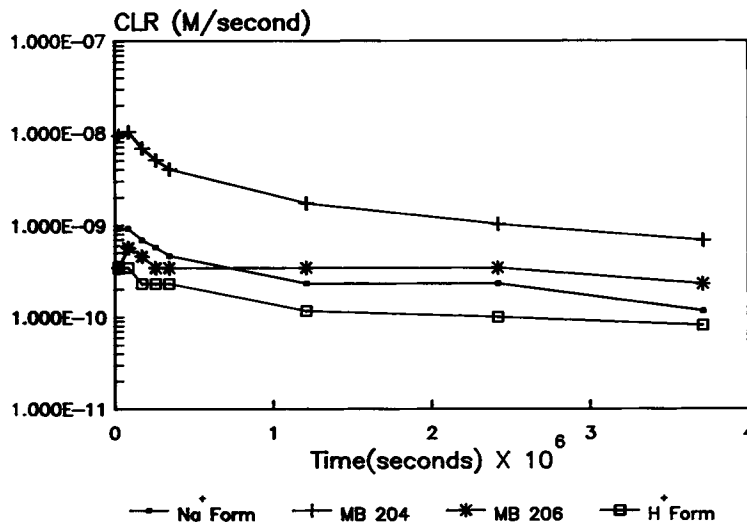


Figure 6 Cumulative leach rate vs. time of UF matrices.

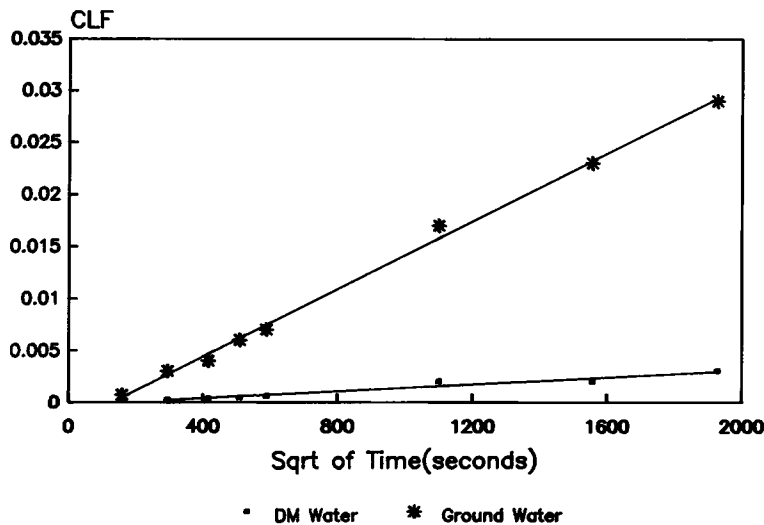


Figure 7 Cumulative leach fraction vs. square root of time of H⁺ form matrix.

shows the microscopic view of the UF matrix cross section. It is evident from the figure that the ion-exchange resin beads are distributed uniformly in the matrix. Microscopic examination also revealed the presence of UF polymer within the pores of the ion-exchange resin.

In order to find out the relation between the density and compressive strength, measurements were carried out on the polymer specimens with different waste to matrix ratios. These specimens were cured for a period of approx. one year. It is assumed that in this long period the weight of the specimens attain a constant value. Figure 2 shows the density of the specimens against the waste to matrix ratio. It is observed from the figure that the values of the density decrease with increase in the waste to matrix ratio. The compressive strength for the corresponding polymer specimens against density is shown in Figure 3. It is evident that the compressive strength values increase with increase in density.

The dimensional changes of the waste form do not present a problem to the waste container, but large shrinkages could cause cracking of the waste forms. In general, polymer matrices undergo shrinkage during curing. It is more prominent in the case of urea-formaldehyde due to the loss of water formed during condensation reaction. Cumulative Percentage Weight Loss (CPWL) and Cumulative Percentage Volume Change (CPVC) were calculated. In Figures 4 and 5, the ratio of CPVC and CPWL to time are plotted vs. time for the specimens prepared with different amounts of boric acid. The volume changes and weight loss were observed to decrease with increase in the boric acid concentra-

tion. The CPWL and CPVC values were observed to increase initially and then attained a plateau. When these values for the specimen containing 30 g boric acid were compared with those of the specimen prepared by heating at 70°C in the absence of boric acid, they showed 40 to 78 times lower values, respectively. It is reported¹⁶ that boric acid tends to

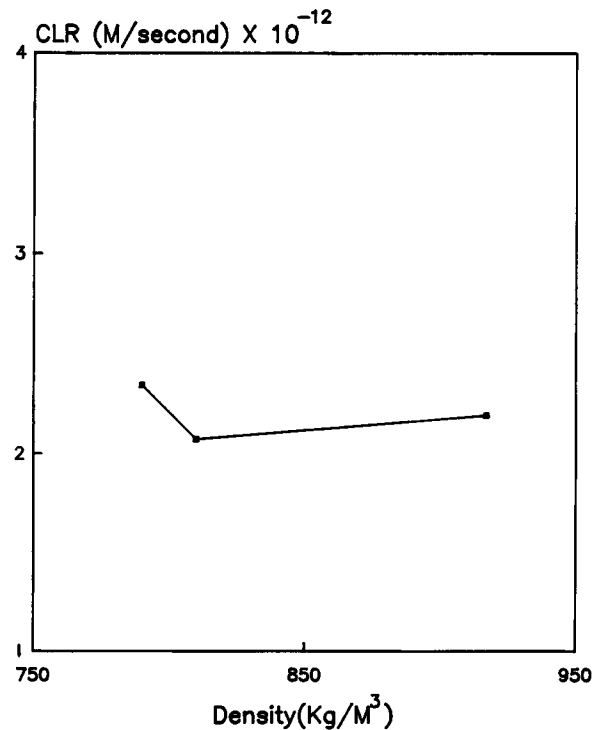


Figure 8 Density vs. cumulative leach rate of H⁺ form matrix.

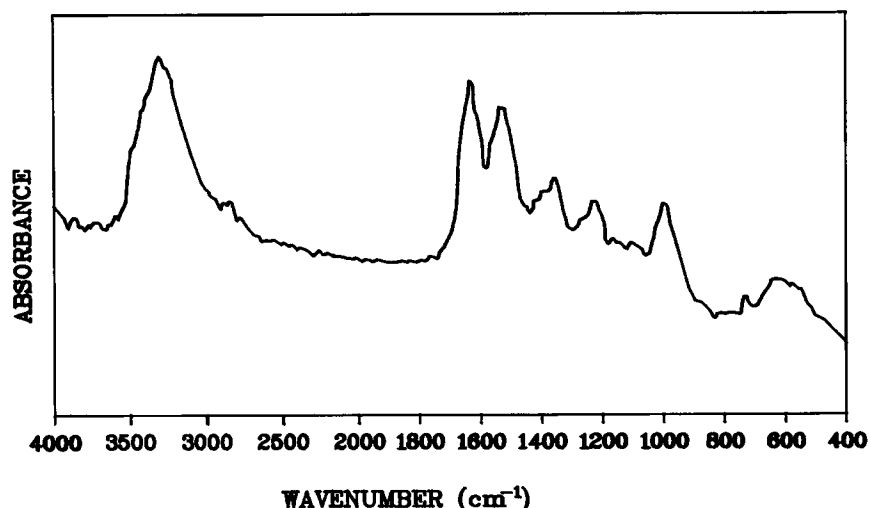


Figure 9 IR absorption spectra of UF polymer.

reduce the reaction rates. The slow release of water may be the cause of reduction in the shrinkage rate of the matrix.

The cumulative leach rates (CLR) were calculated using eq. (1). Figure 6 shows the CLR of the specimen containing radioactive cesium (^{137}Cs) kept in ground water. The leach rates of the specimen containing H^+ form resin were lower than those of the other specimens. On the other hand, their values were observed to be high for the specimen containing MB 204 resin with lithium form of cation exchange resin. Figure 7 shows the cumulative leach fraction (CLF) of cesium plotted against the square root of days. The diffusion equation employed in these studies is derived by assuming cylindrical plane

source model with the surface concentration as zero at the leachant/solid interface at time > 0 .¹⁷

$$D = \pi/4 \times (V/S)^2 \times M^2 \quad (2)$$

where M is the slope of the plot given in Figure 7.

The diffusion coefficients (D) of cesium from the matrix containing H^+ form resin in DM water and ground water are given in Table II. In DM water, the diffusion coefficient was 100 times lower than in ground water. It is also observed that the D values in DM water were lower than those of the UF matrix reported in our earlier studies. Furthermore, the leach rates were observed to show a slight variation with the densities of the specimens. Figure 8 shows

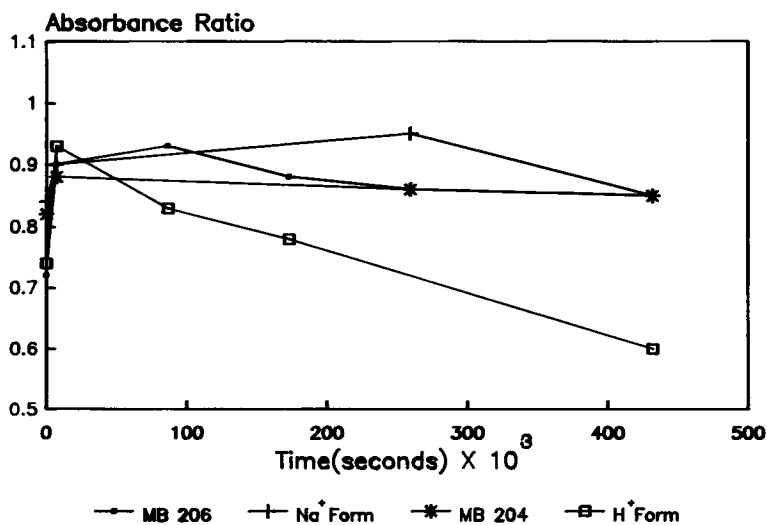


Figure 10 IR absorption ratio vs. time of UF matrices.

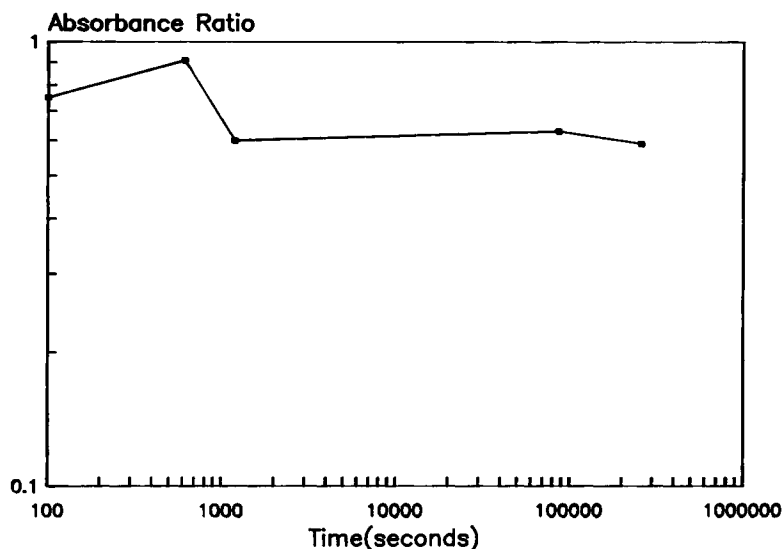


Figure 11 IR absorption ratio vs. time of H^+ form matrix at $70^\circ C$.

the CLR of H^+ form resin (after 7.7×10^6 s) against density of the specimens. It was observed that there was no change in the order of the CLR values with the change in the density of the specimens.

The IR spectra of urea-formaldehyde prepolymer is given in Figure 9. The band at 1650 cm^{-1} is reported to remain constant during cure. In our studies the peak area obtained at 1020 cm^{-1} (O—H group in methylol) was compared to that of the 1650 cm^{-1} (C=O in amides) with respect to the same base line. Figure 10 shows a plot of the ratios of peak area of UF specimens against time. In all the cases, there was an increase in the absorbance ratio before it showed a decreasing trend. The increase in the ratio is attributed to the formation of methylol groups and the decreasing trend is due to the condensation reactions. It was observed that the rate of methylol group formation and its disappearance was higher in the case of H^+ form resin, whereas these values were lower for MB 204 with Li^+ form cation exchange resin. The increase in the rate of curing may be due to the presence of H^+ ion in the ion-exchange resin. The minimum absorption ratio attained in the case of H^+ form resin is attributed to the increased crosslinking of the UF polymer. The leach rates, therefore, were observed to be low in H^+ form resin.

Similar IR studies were carried out on the specimen containing H^+ form resin at $70^\circ C$ (in the absence of boric acid). Figure 11 shows the absorption ratio curve at different time intervals. The curve showed a similar trend as in the above case and the rates, as expected, were observed to be high because of the low pH and high temperature. However, the

leach rates and the diffusion coefficients were comparatively lower for the matrix prepared with boric acid (ambient temperature). This is attributed to the low porosity of the matrix resulting from the slow release of water which, in turn, reduced the formation of channels or interconnecting pores.

CONCLUSION

The UF polymer matrices prepared at ambient temperatures were found to have good leaching characteristics and moderate compressive strengths. The slow curing rates facilitated the slow release of water and thereby reduced the permeability and shrinkage of the matrix. The leach rates and curing rates were found to depend on the type of resins. As this process does not release any corrosive liquid nor does it require much handling of the spent resin, it can be safely adopted in the plant scale operation.

The authors express their thanks to Shri. M. K. T. Nair, Director, NWMG for his guidance during the conduct of this study. The authors are also greatly indebted to Shri. Susheel Kumar Sharma for his help in drawing figures, and to Smt. R. Lakshmi and Smt. P. Kamali for their technical assistance.

REFERENCES

1. G. Arnold, P. Colombo, and R. Doty, Brookhaven National Laboratory, 51615 (1982).
2. A. A. Moghimsi, H. W. Godbee, and S. A. Hobart,

- Radioactive Waste Technology*, The American Society of Mechanical Engineers, New York, 1986.
3. M. W. Carter, A. A. Moghissi, and B. Kahn, *Management of Low level Radioactive Waste*, Vol. 1, Pergamon Press, New York, 1979.
 4. N. E. Ikaladious, N. K. Ghattas, and S. B. Eskander, *Nucl. Chem. Waste Management*, **6**, 101 (1986).
 5. S. G. Burnay, *Nucl. Chem. Waste Management*, **6**, 139 (1986).
 6. N. Moriyama, S. Dojiri, S. Emura, T. Sugo, and S. Machi, *J. Nucl. Sci. Technol.*, **12**, 362 (1975).
 7. A. A. Moghissi, H. W. Godbee, M. S. Ozker, and M. W. Carter, *Nucl. Power Waste Technol.*, The American Society of Mechanical Engineers, New York, 1978.
 8. S. V. S. Rao, K. B. Lal, and R. V. Amalraj, *Waste Management*, **12**, 337 (1992).
 9. F. H. Cocks, *Manual of Industrial Corrosion Standards and Control*, American Society for Testing and Materials, Philadelphia, 1973.
 10. Kirk-Othmer, *Encyclopedia of Chemical Technology*, 3rd ed., Vol. 2, Wiley, New York, 1978.
 11. B. Meyer, *Urea Formaldehyde Resins*, Addison-Wesley, Reading, MA, 1979.
 12. G. Allen, *Comprehensive Polymer Science*, Vol. 5, p. 649, Pergamon Press, New York, 1989.
 13. L. E. Smythe, *J. Am. Chem. Soc.*, **51**, 369 (1947).
 14. G. E. Myers, *J. Appl. Polym. Sci.*, **26**, 747 (1981).
 15. Radioactive Waste, Proceedings of the Twenty-First Annual Meeting of the National Council on Radiation Protection and Measurements, Vol. 7, 49, 1980.
 16. J. I. Duffy, *Treatment, Recovery and Disposal Processes for Radioactive Wastes*, Noyes Data Corporation, Park Ridge, NJ, 1983.
 17. M. Nishikawa, H. Kido, *Nucl. Chem. Waste Management*, **5**, 101 (1984).

Received May 11, 1993

Accepted November 3, 1993