Progress in Solidification of Radioactive Waste Resins Using Specific Cement

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ABSTRACT

A kind of special cement (Named as ASC) was used in radioactive spent resins solidification in China. A prescription of X ASC cement + 0.5X waste resins (50%water hold) + 0.35X water was obtained first. In order to control the temperature rise caused by hydration of cement in 200L solidification matrix, various supplementary materials were tried. Based on compressive strength tests and center temperature rise, super powered zeolite was selected. In addition, more resins were added to reduce the center temperature rise. A superior combination was obtained as ASC 35wt.%, zeolite 7wt.% to mix 42wt.% of resins(50%water hold) with 16wt.% of water. The microstructures of hydrated OPC, ASC and ASC with different zeolite addition were compared by means of Scanning Electron Microscopy (SEM). From the SEM pictures, the structures of the needles or spines can be seen in ASC matrices and the needles structure of ASC change into flake structure gradually with more zeolite added. The simulated leaching tests showed that inclusion of zeolite in ASC reduced the leaching rates of radionuclides significantly. From 200L matrix test, the centre temperature curve was measured, and the highest temperature was lower than 90□. No thermal cracks were found in the final solidified products.
Key words: Radioactive resins; cementation; solidification;

INTRODUCTION

Radioactive waste ion exchange resins comprise the major fraction of low and intermediate level radioactive wastes in nuclear facilities. These waste resins should be properly treated and disposed in order to minimize the potential danger to the environments. Cement solidification is a conventional technique to solidify radioactive wastes. Cement solidification has many advantages, such as requiring simple equipment, low working temperature, no trouble of gas cleaning, and low cost. Radioactive waste resin is one of the most difficult wastes to be cemented. The major problems are low loading of spent resins, low compressing strength and high leaching of radionuclides. Because there is no practicable treatment technology available, most of the waste resins were deposited in containers temporarily in China. These resins had to be solidified/stabilized in order to be finally disposed in permanent repository site. Most of the nuclear facilities have equipments for cementation of liquid radioactive wastes, and these equipments can be used for cementation of waste resins with none or little changes. So cementation seems to be the most practicable method for solidification/stabilization these radioactive waste resins.

In order to find a practicable technique, researches on effective cement solidification of waste resins had been carrying out, and a kind of special cement (ASC) was used in radioactive spent resins solidification in China recently. In this paper, the chemical composition and property of ASC were compared with ordinary Portland cement (OPC) and blast furnace slag cement (BFC). The effects of addition of zeolite on the strength and leaching rates of the resins cementation matrix were investigated. The microstructures of hydrated OPC, ASC and ASC with different zeolite addition were compared by means of SEM. The centre temperatures of 200L solidification matrix during hydration were measured.

Chemical composition and physical properties of ASC

ASC cement has a different composition from OPC and BFC as listed in Table I. Their physical properties are also different from each other as listed in Table II. It can be seen from the tables that ASC contained more Al and S than OPC and BFC and it is a kind of quick setting cement with high early strength. ASC is also a kind of expansive cement during hydration.

Table I. Chemical Composition of Different Cements*

Cement type	Average Composition as Oxides, wt.%								
	SiO_2	Al_2O_3	CaO	Fe_2O	MgO	SO_3	TiO_2	Loss	sum
ASC	9.21	31.36	40.90	3.28	3.79	9.45	1.21	0.55	99.75
OPC	23.40	4.52	63.70	4.55	1.76	0.68	0.40	0.71	99.72
BFC	24.35	8.05	57.57	3.78	3.94	0.58	0.80	0.35	99.42

*The China Institute of Building Material Science supplied the cement in Tables I and II.

Table II. Physical Properties of the Cements

Cement type	Setting time (min)		Specific surface (m^2/kg)	Compressive strength(Mpa)			Expansion rate of 28 d ( )
	Initial	Final		1 d	3 d	28 d	
ASC	26	60	480	42.5	55.0	68.0	0.055
OPC	65	300	320	8.5	28.0	54.5	-0.080
BFC	80	400	340	8.0	25.5	55.0	

Resins load and compressing strength of the cemented matrix using ASC

According to researches had been done by Natsuda, resins load in the solidification products of OPC should be controlled bellow 20% (volume of wet resins to solidification product) [1,2]. When resins load was higher than 20%, cracks were often engendered and the solidification products had lower stability. Resins expansion in water was also researched, and it was believed that the expansion of resins was one of the main reasons resulting in cracks. The range of expansion pressure was 0~50 MPa. The resins should be saturated in water before solidification in order to prevent cracks. Furnace slag and fly ash were added in cementation of radioactive resins by PAN[3]. The superior combination was obtained as furnace slag 24 wt.%, fly ash 24 wt.%, and OPC 8 wt.% to mix 24 wt.% of resin with 20 wt.% of water. The rate of resin to base material is about 43:100 (wt./wt.). Zeolite and OPC were also used resins cementation[4]. The prescription of 24ml resins, 55.9g OPC, and 37.3g zeolite were used. Assuming the weight of 24ml resins was 20g, the resins to base ratio was about 20:100(wt./wt.).

In the primary researches a prescription of X ASC cement + 0.5X waste resins(50wt.% water contained) + 0.4X water was obtained. For matrices obtained from this prescription, the load of resins was about 45(v/v). The 28d compressing strengths of the matrices were 18-20 MPa [5,6]. The resins to base ratio was about 50:100(wt./wt.)

The required compressing strength of cemented solids is 7 MPa in China. In order to increase the resins load and decrease the temperature rise from hydration heat, more resins were added and various supplementary materials were tried. Based on compressive strength tests and center temperature rise, super powered zeolite was selected. In addition, more resins were added to reduce the center temperature rise. A superior combination was obtained as ASC 35wt.%, zeolite 7wt.% to mix 42wt.% of resins(50%water hold) with 16wt.% of water. The 28d compressing strengths of the matrices were 12-13 MPa, and the matrices could meet the required compressing strength of finally disposed. The resins to base ratio was about 100:100(wt./wt.).

Leaching rate of matrices cemented by ASC

Leaching tests were carried out using the method recommended by the national standard GB7023[7]. In the course of leaching test, specimens were stored, air-tight PVC vessels that filled with 2-L of deionized water and covered with a lid. The specimens were hanging-up by a thread, and the size of the vessels ensured that the samples were surrounded with at least 10 mm of water on each side. The leaching rates R were calculated using

$$R=CLV/WFT_n \qquad \text{(Eq.1)}$$

Where: R is the leaching rate of cations, cm/d;

C is concentration of cations in the leacate, g/ml;

L is the leachant volume, ml;

V is the matrix volume, cm^3;

W is the cations loading in the simulated resin in the matrixs, g;

F is the matrix surface area, cm^2;

T_n is duration of the nth period, in days.

Heavy metals readily precipitate in the high pH environment of cements, but alkali metals, such as Cs, remain substantially soluble. Cs-loaded resins, when cemented, show one or two orders of magnitude higher leach rates than the resins themselves. So the leaching rates of Cs in matrices cemented by ASC and the impacts of zeolite addition were studied. The leaching rates of Cs were given in Fig. 1. The portions of Cs contained in matrices were shown in Fig. 2. For the figures it can be found that the addition of zeolite can reduce the leaching of Cs greatly.

Microstructure studies of ASC

By SEM analysis, the properties corresponding to the microstructures of resins solidification products made by ASC and zeolite had been studied and the microstructures of ASC matrices and OPC matrices were also compared. The results were shown in picture 2. From the pictures, the structures of the needles or spines can be seen in ASC matrices, and the structures of flakes can be seen in OPC matrices. The differences of structure reduce the performances of the matrices. The needles or spines structures can improve the compressing strength of the solidification products. It is the needles or spines structures that result in the high compressing strength of the solidification products. With the addition of zeolite, the needles or spines structures are grown thicker at first stage. And when the addition of zeolite was near 40% the needles-like structures are turned into flakes like structure gradually. There for, the addition of zeolite in little quantity will not decrease the compressive strength, but can reduce the leaching of radionuclides greatly.

Center temperatures in 200L mortar

Because ASC is a kind of quick setting cement with high early strength, the hydration heat of ASC is released in short time during hydration. Temperature rise resulted from ASC cement in resin cementation could induce thermal cracks in large-scale solidification. Previous researches showed that the highest temperature in 200L solidification using ASC cement was above 100℃. From results of compressive strength tests and considering about adding more zeolite in order to reduce hydration heat to prevent thermal cracks, the 20% zeolite added ASC cement were also used in large-scale experiments. The center temperature curve resulting from hydration heat was presented in Fig. 4. The highest temperature was lower than 90℃. No thermal cracks were found in the final solidified products.

Conclusion

The ASC cement is a promising material for cementation of radioactive spent resins due to its good property, such as low nuclides leaching rates, high spent resin loadings in the matrices, , high matrix strength, and easy solidification. Inclusion of zeolite in ASC can reduce the leaching rates of radionuclides significantly.

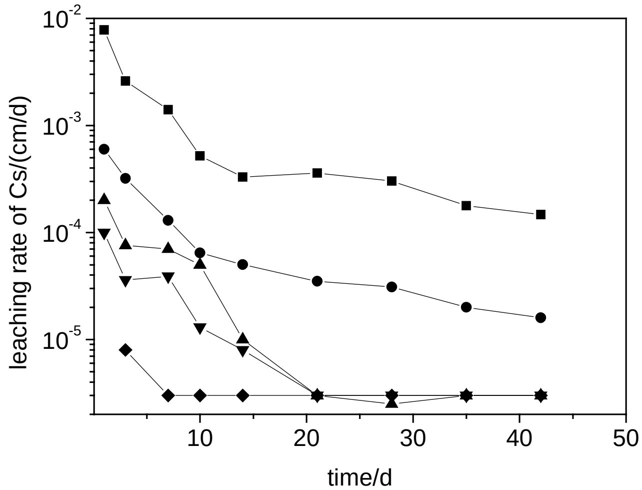

Fig. 1. Impacts of zeolite addition on Cs+ leaching rate

■—ASC ●—ASC with 10 zeolite ▲—ASC with 20 zeolite

▼—ASC with 30 zeolite ♦—ASC with 40 zeolite

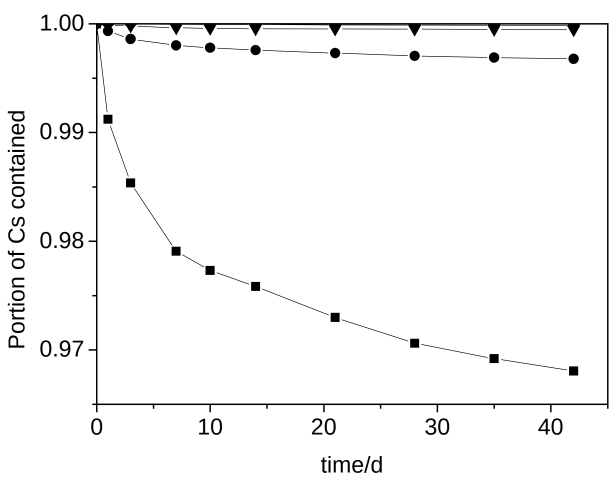

Fig. 2. Impact of zeolite addition on Cs+ contain

■—ASC ●—ASC with 10 zeolite ▲—ASC with 20 zeolite

▼—ASC with 30 zeolite ♦—ASC with 40 zeolite

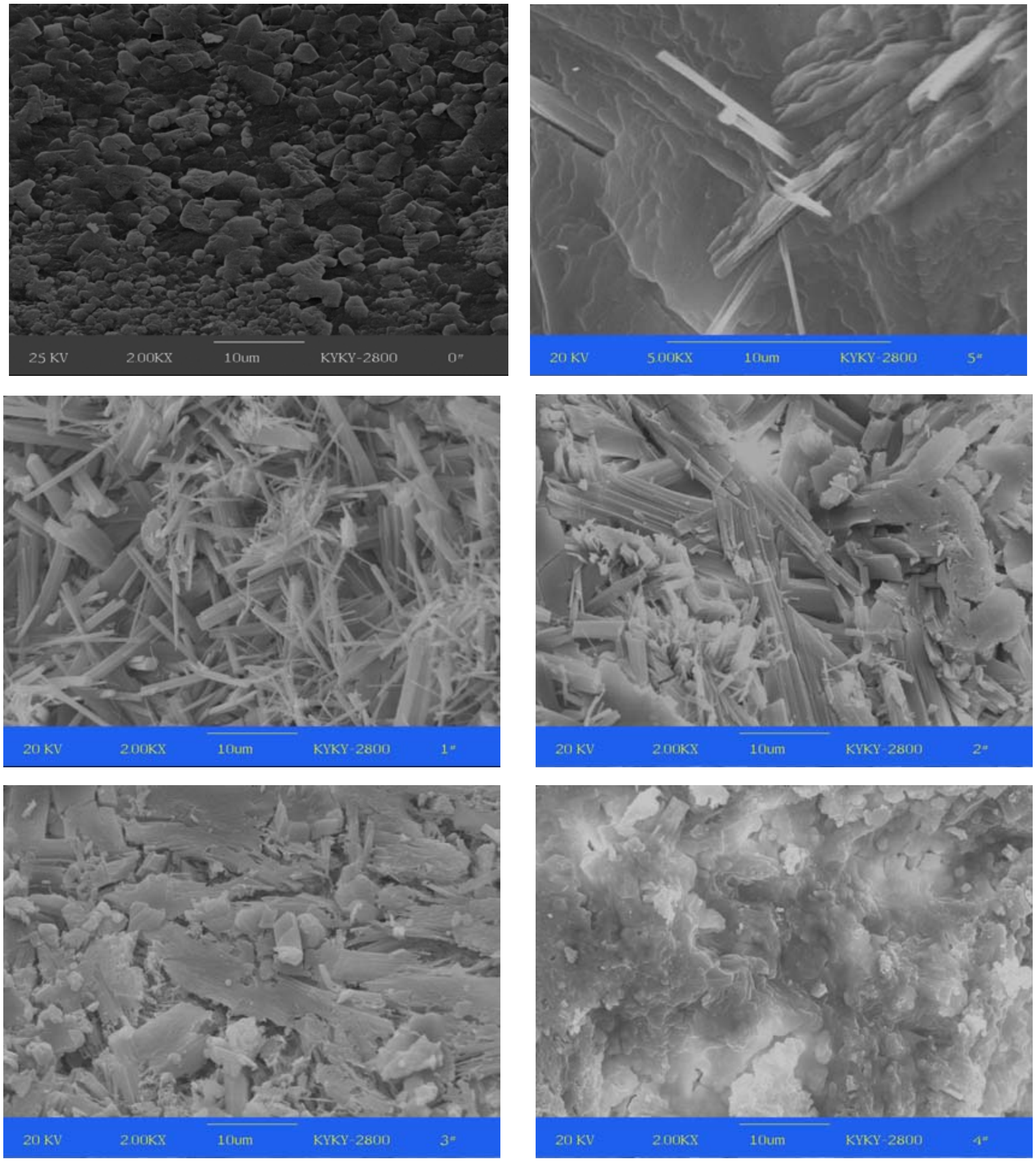

Fig. 3. Impacts of zeolite on microstructure of solidification matrix

1.OPC 2.ASC 3. 10 zeolite 4. 20 zeolite 5. 30 zeolite 6. 40 zeolite

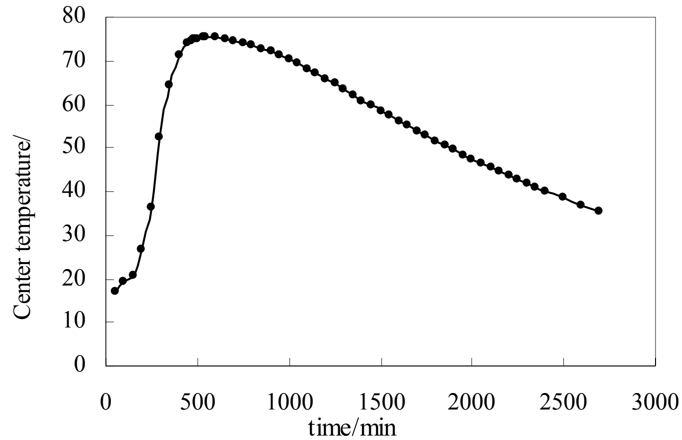

Fig. 4. Center temperatures of ASC cements with 20% zeolite addition in 200L mortar, mass of mortar contained: 120 kg resins, 96kg ASC, 24kg zeolite and 45kg water, in room temperature of 17℃.

REFERENCES

1. M. Natsuda, T. Nishi, Solidification of ion exchange resins using new cementitious material (1) Swelling pressure of ion exchange resin *Journal of Nuclear Science and Technology* 29(1992) 883-889.
2. M. Natsuda, T. Nishi, Solidification of ion exchange resins using new cementitious material (2) Improvement of resin content fiber reinforced cement, *Journal of Nuclear Science and Technology* 29(1992) 1093-1099.
3. L.W. Pan, B.D. Chang, et al., Optimization for solidification of low-level-radioactive resin using Taguchi analysis, *Waste Management* 21(2001)767-772
4. S. Bagosi, L.J. Csetenyi, Immobilization of caesium-loaded ion exchange resins in zeolite-cement blends, *Cement and Concrete Research* 29(1999) 479-485.
5. Y.Z. Zhou, Y.C. Ye, et al., Study on solidification of spent ion exchange resin using ASC cement, *Radiaction protection* 22 (2002) 225-230. (in Chinese)
6. Y.Z. Zhou, G.C. Yun, et al., Solidification of spent ion exchange resin using ASC cement. *Journal of Tsinghua University Science and Technology* 7(2002) 636-640.
7. SEPA, 1986. National standard for long-term leach testing of solidified radioactive waste forms. GB 7023-86.